CRYOspHERic STudies of Atmospheric Trends in stratospherically and radiatively important gases

CRYOSTAT

An RTD Project in the European Commission Fifth Framework Programme EVK2-2001-00116

Final Report
1 January 2002 – 31 December 2005

incorporating the 4th Annual Report for the period 1 January – 31 December 2005

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SECTION 1: MANAGEMENT AND RESOURCE USAGE SUMMARY RELATED TO THE LAST (12 MONTH) REPORTING PERIOD

1.1 Objectives of the reporting period

- Retrograde ice and firn air samples from Law Dome.
- Conduct air extractions on Law Dome ice samples.
- Continue the second year-round field campaign at Halley (Antarctica) including the collection of within-firm air and in situ measurements of CO₂.
- Analysis of firm air and air extracts from ice from Law Dome.
- Analysis of firm air samples from Halley second year-round campaign.
- Finalise all other sample analyses.
- Continue modelling studies with emphasis on atmospheric modelling and radiative forcing.
- Development of models of thermodiffusion in shallow firm with particular reference to measurements from Halley.
- Compile data onto on line database.
- Plan for end-of-project science event with corresponding publication.
- Complete project Final Report.

1.2 Scientific/Technical progress made in different work packages according to the planned time schedule:

- Ice samples retrograded from Law Dome. Air extracted from ice samples and analysed for multiple trace gases by two of the partners. Law Dome firm air also analysed by two partners for an extensive suite of compounds.
- The second year-round campaign at Halley continued in to the spring (austral autumn) of 2005. All samples retrograded at the end of this period, and analyses carried out by several laboratories.
- First measurements in air trapped in ice of CF₄, other related perfluorocarbons, SF₆, CCl₄, and some low molecular weight non-methane hydrocarbons.
- “Joined-up” modelling activities between several participants using atmospheric models to globalise emission inventories to yield hypothetical time trends, which in turn were used as targets for firm modelling allowing comparison with observations in firm air. In some cases this was applied cyclically to derive unknown emission histories for some gases. In other cases it was possible to apply an ‘iterative’ technique to arrive at past atmospheric trends directly by converging assumed trends with actual firm air observations. In both cases radiative transfer modelling was then used to determine the radiative forcing of those gases with significant infrared absorption cross sections.
- Isotope ratios of permanent gases and elemental gas ratios from Halley have been used to test and validate improved thermodiffusion models.
- Isotope ratios of permanent gases from deep firm profiles have been used to investigate the causes of reported fractionation effects at the point of close of firm in impermeable ice, with important implications for our understanding of ice cores records of trace gases isotope ratios. The effect has been found to be dependent on molecular diameter, with a cut-off at about 3.5 Å.
1.3 Milestones and deliverables obtained (cumulative since project began)

- Milestone 1: NGRIP campaign completed.
- Milestone 2: planning activities/meetings completed.
- Milestone 3: NGRIP site specific model and initial data available to consortium.
- Milestone 4: Halley station and permanent firm sampling established.
- Milestone 5: Berkner campaign completed.
- Milestone 6: Berkner site specific firm model and initial measurements available.
- Milestone 7: Berkner ice coring campaign completed.
- Milestone 8: Halley first overwinter campaign completed.
- Milestone 9: Halley first year data available to consortium, but site specific model awaits final laboratory analysis of CO$_2$ in all samples.
- Milestone 10: Berkner Island analyses completed and data available to the consortium.
- Milestone 11: Halley second year-round campaign completed.
- Milestone 12: Law Dome campaign completed.
- Milestone 13/14: Final data from (a) Halley Year 2 and (b) Law Dome available to consortium.
- Milestone 15: Globalised trends of trace gases available to consortium; radiative forcing calculations completed.
- Milestone 16: Final Report is the subject of this Report.

All milestones have been completed.

1.4 Deviations from the work plan or /and time schedule and their impact to the project

As previously detailed, the project has benefited from on a one-year extension to the project granted because of an unavoidable one year delay due to unfavourable sea ice conditions, which caused an entire field season to be cancelled. In the end all of the field campaigns have been successfully completed, exceeding our expectations, including the “optional” additional campaign at Law Dome. This has been no modest accomplishment, and we are deeply indebted to the dedication and professionalism of the field teams and logistical support personnel who made this remarkable achievement possible.

Measurements of carbon monoxide isotopes using continuous-flow mass spectrometry was applied to firm air samples collected at Dome C and at NGRIP. At NGRIP they did not reach the level of precision that we expected, due in part to the fact that SUNYSB, although an official EU CRYOSTAT project partner (AC5), did not obtain the required funding from US national sources, under joint EU-NSF agreements. Excellent results were, however, obtained at other sites by other partners.

Measurements of deuterium of methane in firm air have been successfully made. Measurements of deuterium of methane in ice cores are still in progress, and remain a large technical challenge. In compensation, however, the “new” partner MPIK was able to make comprehensive measurements of the isotopic composition of N$_2$O, including the position-dependent mass-fractionation, not only on firm air as planned, but also on ice core extracts in collaboration with LGGE. The latter was not foreseen in the original Workplan, and represents a major breakthrough in understanding various aspects of past atmospheric chemistry predating the firm record. This is particularly important for N$_2$O as it has a longer history of (evidently human-influenced anthropogenic) change than do the more recent “technological” gases. It marks an outstanding achievement of the project.
The Final Report that follows will attest the wide range of successful activities completed under CRYOSTAT.

1.5 Co-ordination of the information between partners and communication activities

- CRYOSTAT annual meeting in Vienna, Austria April 2005.
- Special Session on firm air and ice cores is being convened for the European Geosciences Union General Assembly in Vienna, Austria, April 2006. Papers from this Session, and others invited, will be used to create a Special Issue on CRYOSTAT science in the journal Atmospheric Chemistry and Physics.
- Frequent bulletins via e-mail distribution list held by the coordinating group, notably with much activity concerning the preparation of this Final Report.
- Data has been submitted to the official CRYOSTAT data archive at http://badc.nerc.ac.uk/data/cryostat/.

1.6 Difficulties encountered at management and co-ordination level and proposed/applied solutions

A frustration has been the exceedingly slow rate of progress in modifying partner status (replacement of OU by MPIK, and the change in status of CSIRO from Subcontractor to Assistant Contractor). This has been due to slow progress in the administration of essentially all institutes involved, including the CEC. The requirement to have all Partners sign revised contracts, rather than allowing executive action by the coordinating body, has added to the delay, although it has not generally been the rate limiting step. In both cases the required contractual alterations did not take place until the very end of the project. A more streamlined system is needed. Although this significantly hampered completion of the project, it ultimately did not prevent a successful outcome.
SECTION 2: EXECUTIVE PUBLISHABLE SUMMARY RELATED TO THE LAST (12 MONTH) REPORTING PERIOD

See Executive Summary for entire project in Section 5.

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<th>Authors</th>
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Planning of future publications:

A number of papers are planned, and in particular are expected to arise from the 2006 Special Session dedicated to CRYOSTAT at the European Geosciences Union General Symposium 2 – 7 April 2006.
SECTION 3: DETAILED REPORT ORGANIZED BY WORK PACKAGES INCLUDING DATA ON INDIVIDUAL CONTRIBUTIONS FROM EACH PARTNER RELATED TO THE LAST (12 MONTH) REPORTING PERIOD

3.1 Workpackage 1: Ice coring/firn extraction campaigns
Participants: AC11 (Law Dome Lead), CR7 (NGRIP Lead), CR8 (Berkner Island Lead), CR4

3.1.1 Objectives (this period)
- Retrograde Berkner Island ice cores (second phase).
- Ship Law Dome firn air to UEA for analysis.

3.1.2. Methodology and scientific achievements related to Work Packages including contribution from partners
- Above objectives completed. (CR4, CR8, AC11)

3.1.3. Socio-economic relevance and policy implication
- Same as overall project (see summary)

3.1.4. Discussion and conclusion
- All CRYOSTAT field campaigns have now been successfully completed.

3.2 Workpackage 2: Year-round Antarctic air and firn campaigns
Participants: CR8 (Halley Lead), CR4 CO1

3.2.1 Objectives (this period)
- Samples from the second over-winter returned to Europe.
- Analyses of samples.
- Analysis of CO₂ and temperature data.

3.2.2. Methodology and scientific achievements related to Work Packages including contribution from partners
- Above objectives completed. (CO1, AC3, CR4, AC6, CR7, CR8)

3.2.3. Socio-economic relevance and policy implication
- Same as overall project (see summary)

3.2.4. Discussion and conclusion
- All CRYOSTAT field campaigns have now been successfully completed.

3.3 Workpackage 3: Ice extraction and measurement of gases in extracted, ambient and firn air
Participants: CO1 (Lead), AC3, CR4, CR7, CR8

3.3.1 Objectives (this period)
- Further develop ice extraction systems and implement on Berkner Island ice.
- Extraction and analysis of Law Dome ice.
- Analysis of Halley year-round samples.

3.3.2. Methodology and scientific achievements related to Work Packages including contribution from partners
- Measurement of firn air samples from Halley Bay continued for δ¹⁵N (N₂), δ¹⁷O, δ¹⁸O (O₂), O₂/N₂, CO₂/N₂, Ar/N₂, ³⁶Ar/⁴⁰Ar, ⁴⁰Ar/O₂, CO₂ (see also WP 4). (CR7)
- Extraction of air from Law Dome ice and analysis for a range of halocarbons, non-methane hydrocarbons and SF₆. (CO1, AC11)
• Groundbreaking measurements of the complete isotopic composition (including position dependent isotopic fractionation) of N₂O (see also WP 5) have been made on ice from Berkner Island and NGRIP. (CR4, AC10)

3.3.3. *Socio-economic relevance and policy implication*

• Same as overall project (see summary)

3.3.4. *Discussion and conclusion*

• Particularly exciting has been the measurements of CF₄ and other PFCs in both firm and ice providing a history from preindustrial times to the present day for these species. This has proved that CF₄ has a natural background concentration, while the majority of fully fluorinated gases are of almost exclusively anthropogenic origin. Also highlighted were variations in CF₄ and C₂F₆ in response to changing industrial practices.

• Other conclusions are covered in WP 4 and 5.

3.4 **Workpackage 4: Within-firm process studies**

Participants: CR7 (Lead), CO1, CR4, AC6, CR8

3.4.1 *Objectives (this period)*

• Incorporate CO₂ measurements into Halley firm model.

• Process studies of gas fractionation near surface and at firm-ice transition and implementation in firm model.

• Affect of advection in near surface firm.

3.4.2. *Methodology and scientific achievements related to Work Packages including contribution from partners*

• Completion of the second year at Halley. (CR8, CO1)

• Analyses of Halley firm air samples has been continued for δ¹⁵N (N₂), δ¹⁷O, δ¹⁸O (O₂), O₂/N₂, CO₂/N₂, Ar/N₂, ³⁶Ar/³⁶Ar, ⁴⁰Ar/⁴⁰Ar, CO₂. (CR7)

• Modelling of Halley firm data with improved high-resolution diffusion model including advection (continued). (CR7)

• Seasonal dependence of near surface convection observed in firm at Halley. (CR7)

3.4.3. *Socio-economic relevance and policy implication*

• Same as overall project (see summary)

3.4.4. *Discussion and conclusion*

• Comprehensive modelling of within-firm processes has been achieved, both for the upper firm and also for the lock-in zone.

3.5 **Workpackage 5: Measurement of isotopic composition of carbon cycle gases and N₂O**

Participants: CR4 (Lead), AC5, CR7, CR9, AC10

3.5.1 *Objectives (this period)*

• Finish sampling work for year-round measurement of key carbon isotopes at Halley, and incorporate data into interpretation.

• Evaluation of strategy to measure δ¹³C and δD of NMHC.

• CO isotopes to be measured on North GRIP and Berkner Island firm air.

• Tests to be carried on pre-industrial ice-core samples (in collaboration with MPIK) for δD of CH₄.

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3.5.2. **Methodology and scientific achievements related to Work Packages including contribution from partners**

- Sampling work finished and measurements. (CO1, CR4, CR8)
- Extracts made for NMHC analysis and tested.
- Groundbreaking measurements of the complete isotopic composition (including position dependent isotopic fractionation) of N₂O (see also WP5) have been made on ice from Berkner Island and NGRIP. (CR4, AC10)
- CO mixing ratio and isotopes on North GRIP firn air have been measured. (AC5)
- Development of δD of CH₄ and measurements on firn air. (AC10)

3.5.3. **Socio-economic relevance and policy implication**

- Same as overall project (see summary)

3.5.4. **Discussion and conclusion**

- N₂O isotopic measurements are largely in agreement with current hypotheses on sources of N₂O and on its stratospheric photochemical degradation (the primary sink).
- CO mixing ratio at NGRIP does not show the large increase with depth previously observed on Devon Island (northern hemisphere) firn air, and is therefore a suitable location for such measurements.

3.6 **Workpackage 6: Data interpretation and modelling studies**

Participants: CR4 (Lead), CO1, AC2, AC3, AC5, AC6, CR7, CR9, AC10

3.6.1 **Objectives (this period)**

- Incorporate measurements from Berkner Island and Law Dome.
- Complete validation of 2D chemistry model globalized trends by:
  - comparing model with measurements and vertical profiles
  - examining inter-calibration of halocarbon data from different groups.
- Provide fully validated globalized trends to CR4 for use in radiative impact calculations.
- If time permits, new halocarbon species of special interest will be incorporated into the 2D chemistry model.

3.6.2. **Methodology and scientific achievements related to Work Packages including contribution from partners**

- Intercalibration studies have been completed. (CO1, AC3, CR4)
- Two approaches to global trend modelling have been employed: (a) iterative modelling of unknown trends towards a match with observed firn profiles, and (b) utilisation of a full chemistry 2-D model (for some species a prescribed OH-field model was used instead) in forward mode (emissions inventories known or assumed) and optimisation mode (emissions calculated by model-observation matching). (CR4, CO1, AC11)
- Radiative transfer modelling has been used to determine the individual radiative forcing effect since preindustrial times of all relevant species individually and collectively. (AC2)
- A number of ‘new’ halocarbon species have been incorporated into the full 2-D model. (CR4)
- The model has been used to investigate the implications of this changing atmospheric composition on stratospheric ozone and temperature. (CR4)
- An interesting spin-off of the modelling effect has been a study showing that for gases with significant stratospheric degradation, their overall atmospheric lifetimes are not constant, but
vary with emission rates. This has important implications for the scientific and regulatory community. (CR4)

- Conceptual model of the production of degradation of alkyl nitrates and their production from NOX and non-methane hydrocarbons has been used to imply rising levels of tropospheric NOX and ozone since the mid-1900’s. (CO1, AC3)

- Investigation of δ15N, δ18O, CO2 etc. on year round samples from Halley using a firm model with variable convection (eddy diffusion) term (see also WP 4). (CR7)

3.6.3. Socio-economic relevance and policy implication

- Same as overall project (see summary)

3.6.4. Discussion and conclusion

- We have achieved an essentially complete history of all major GHGs and ODSs over the 20th century, determined their contribution to radiative forcing, their effect on stratospheric ozone and temperature, and studied aspects of their implications for tropospheric atmospheric chemistry.

3.7 Workpackage 7: Programme management

Participants: CO1 (Lead)

3.7.1 Objectives (this period)

- CRYOSTAT meeting scheduled for 28 April 2005 in Vienna, Austria.
- Plan CRYOSTAT final meeting and "knowledge legacy" from CRYOSTAT activities.

3.7.2. Methodology and scientific achievements related to Work Packages including contribution from partners

- CRYOSTAT meeting held on 28 April 2005 in Vienna, Austria. (All)
- CRYOSTAT Final Report planning meeting held 12 – 13 January 2006 at CEA in Gif-sur-Yvette, France. (All)
- A Special Session dedicated to CRYOSTAT is planned for the European Geosciences Union meeting in Nice on 3 April 2006. This is being convened by two CRYOSTAT PIs (Sturges and Luenberger) and by one international guest convenor (Montzka, US Department of Commerce). (All)
- A Special Issue of papers from CRYOSTAT arising from the above Special Session, together with additional invited and contributed papers, has been approved for publication by the international journal Atmospheric Chemistry and Physics. This will be published towards the end of 2006. (All)
- A public information site and data archive is being maintained at http://badc.nerc.ac.uk/data/cryostat/. (CO1)
- A password-controlled Project “Collaborative Workspace” is being maintained at BADC for the exchange of reports, working documents, preliminary data, etc. (CO1)
- Reporting of cost statements, and this report for the fourth and final project year and Technology Implementation Plan. (All, CO1)

3.7.3. Socio-economic relevance and policy implication

- Same as overall project (see summary)

3.7.4. Discussion and conclusion

- CRYOSTAT has been successfully concluded. Several activities related to scientific dissemination and consolidation of data archives will continue over the next one to two years. Public release of the full data archives will take place on 31st December 2006.
SECTION 4. TECHNOLOGICAL IMPLEMENTATION PLAN (CUMULATIVE)
Please see final electronic version on CORDIS website (e-tip page).

SECTION 5: EXECUTIVE SUMMARY RELATED TO THE OVERALL PROJECT DURATION

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Objectives:
CRYOSTAT was conceived to undertake the first combined measurements of virtually all significant greenhouse gases (GHGs) (other than water vapour), ozone depleting substances (ODSs), and related trace gases in contiguous firm and ice profiles, spanning as much as 200 years, from both the northern and southern polar ice caps. For many gases this would represent the first attempt to measure their complete atmospheric histories from pre-industrial times to the present day. Using inter-linked computer models of both the transfer of gases from the atmosphere to firm and ice, and the atmospheric transport and chemistry of gases, it was aimed to reconstruct the evolution and distribution of these numerous gaseous species in the global atmosphere (hemispheric scale for the shorter-lived gases, inter-hemispheric and tropospheric-stratospheric distributions for the longer-lived gases). Sources and sinks, both natural and anthropogenic, were to be identified and quantified using novel multiple-isotope analyses, and by using trace gas modelling. These reconstructed trends were to be further used to determine the histories of (a) radiative forcing from the measured GHGs, (b) stratospheric ozone, temperature and halogen loading, and (c) tropospheric ozone and related chemical processes.

Scientific achievements:
Three major field campaigns to retrieve firm air and ice spanning 100 - 200 years of atmospheric compositional history were carried out at NGRIP Greenland, and Berkner Island and Law Dome, Antarctica. A continuous two-year experiment to study the transport of gases in to and through firm at Halley, Antarctica was also carried out to improve our ability to reconstruct long-term time trends of the target gases from firm and ice profile.

Analyses of NGRIP firm air showed this to be the most successful Northern Hemispheric (NH) firm air campaign undertaken anywhere to date. NGRIP is less perturbed by in-situ chemical effects than previously reported Arctic firm profiles. More than 90% of all pollutant gases are released in the NH, but conditions for preserving trace gases in firm and ice in the North are usually less suitable than in Antarctica (lesser extent of glacial ice, warmer temperatures, etc.). This unique record from NGRIP is, therefore, highly valuable, especially for shorter-lived gases that are mostly confined to the hemisphere in which they are emitted.

Measurements from Berkner Island and Law Dome have also provided essential information. Comparing trends from both hemispheres, furthermore, has yielded considerable information on the origins and atmospheric lifetimes of the gases studied, and on their global distributions. Long-lived ODSs and GHGs can be studied in both Arctic and Antarctic firm. Firm air records tend to be older and better preserved in the Antarctic. Berkner Island and Law Dome represent very different glacial environments: the former having a relatively low rate of snow deposition and the latter very high. Conformity of reconstructed trends between such different environments provides significant confidence in the reconstructed histories of the gases.

A general and important overall finding of CRYOSTAT has been that our present day atmosphere is chemically entirely different from that of the pre-industrial Earth. Increases – usually large increases - have taken place in the abundance of nearly every gas that we have measured (and we have measured more than sixty), even amongst those that also have natural sources. A few gases have exhibited decreases in the last one or two decades due to changing industrial practices, but still remain above pre-industrial levels. Of the ODSs the only gases with significant pre-industrial concentrations are methyl chloride and methyl bromide, plus a small contribution from chlorofluorocarbons, bromofluoromethane and some other minor halomethanes. Of the GHGs, those with pre-industrial backgrounds are carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O) and carbon tetrafluoride (CF₄). Non-methane hydrocarbons and oxides of nitrogen (as measured by proxy from increased levels of organic nitrates) have also risen substantially since the mid-1950s: likely accounting for what is reported in other studies as a probable doubling or trebling of tropospheric ozone in the NH during the 20th century.

Some specific outcomes include:

- The sum of reactive chlorine in the troposphere and stratosphere from all source gases (CCl₃) has increased almost eight-fold since pre-industrial times, while the sum of reactive bromine (CBr₃) has more than doubled. Effective equivalent stratospheric chlorine (EESC) from a combination of both chlorine and bromine source gases has, likewise, increased during this time by a factor of five.

- Century-long trends of stratospheric ozone and temperature have been derived from the above. The onset of the Antarctic ozone hole in the 1980s has been shown to be accounted for by a model utilising these observed parameters. Ozone loss due to gas-phase reactions reached 40% of pre-industrial values in near-polar areas at about 45 km altitude, although there was evidence for some offset of this damage by "self-
healing" of ozone levels at lower altitudes. Stratospheric temperatures were modelled to have decreased by as much as 7°C by 1998 due to loss of ozone at this altitude.

- The atmospheric lifetimes of many halocarbons are not constant but have varied over time according to their emission histories. In some cases these variations can be pronounced; for example the lifetime of Halon 1301 is calculated to have been 88 years in 1975, but only 58 years in 2002. This has profound implications for the calculation of Ozone Depletion Potentials and Global Warming Potentials.

- The polar trends of halocarbons with lifetimes of less than about a decade are dependent on the location of their principal emissions, as demonstrated by the reconstructed trends of short-lived halon gases. In the case of halons 1211 and 1202 a shift in emissions from North America/Western Europe to China is consistent with observations in the firn air records from Greenland.

- Chloroform has a smaller natural source than previously thought, and has declined in concentration in the last two decades because of changes in paper and pulp manufacture. Other bromine-containing trihalomethanes have previously unrealised anthropogenic sources, possibly from water chlorination.

- The perfluorocarbon "super" greenhouse gases are all almost exclusively of anthropogenic origin, with the notable exception of CF₄. CF₄, however, also has an important source from aluminium smelting, as does C₂F₆. The trends of these two latter gases are, however, changing, as emissions from aluminium smelting decrease while emissions from the electronics industry increase.

- The direct radiative forcing of the halocarbon gases due to their change in concentration from pre-industrial times to 2002 is calculated to be 327 mW m⁻². The amount due to the fluorinated "super" greenhouse gases alone (which are not controlled by the Montreal Protocol) is 17 mW m⁻². That due to CO₂ over the same period is 1460 mW m⁻², for CH₄ 486 mW m⁻², and for N₂O 156 mW m⁻². Radiative forcing due to the super GHGs has, however, been rising at an ever increasing rate, whereas that due to CO₂, CH₄ and N₂O has been rising at a decreasing rate. Furthermore, several of these fluorinated gases have thousand year lifetimes or more, and may become significant in the future in the absence of measures to reduce their emissions.

- Ozone cannot be measured directly in either firn or ice, but increased levels of other gases, non-methane hydrocarbons, and alkyl nitrates, are ‘smoking guns’ of increased tropospheric NO₂ and increased ozone.

- Novel isotopic measurements of CH₄ and CO have shown that man-induced biomass burning has likely been a significant factor in the observed increased concentrations of these gases. In the case of CO this is the first time that a 20th century trend of this gas has been measured. It is an important player in the atmospheric chemistry that affects the lifetimes of other GHGs and ODSs. For CH₄ there is also clear evidence in its isotope ratios for an enhanced loss process due to oxidation by increased levels of stratospheric chlorine.

- Also entirely novel has been the complete isotopic measurements of N₂O (including position-dependent isotope ratios) pointing to the equal importance of natural and synthetic fertilizers as the prime causes of the observed persistent rise in atmospheric N₂O.

- Process studies have allowed a better quantitative understanding of the manner in which gases move through firn and become encapsulated in ice, thereby significantly improving our ability to interpret ice core records, not only for the time period studied under CRYOSTAT, but of all time scales for which glacial records exist. This is now enabling important questions concerning climate-chemistry feedbacks during climatic cycles to be addressed.

Socio-economic relevance and policy implications:
Climate change and stratospheric ozone depletion are two of the most pressing environmental problems of the day. The anthropogenic causes of these are largely attributable to emissions of gases from industrial processes, power production, refrigeration, biomass burning, agriculture, etc. CRYOSTAT has shown the extent to which human influences have perturbed the natural, pre-industrial composition and chemistry of the atmosphere to produce the atmosphere that we live in today. It has investigated the sources of individual gases, the relative contribution of natural and manmade sources, and has assessed the contributions to stratospheric ozone destruction and/or atmospheric warming of gases individually and in aggregate. It has shown the ameliorating effects of the Montreal Protocol, but illustrates that conditions are as precarious balanced with regard to ozone hole formation as they have ever been. The majority of GHGs, meanwhile, continue to rise including those with lifetimes that span generations. This provides a firm platform from which to judge the efficacy of continued adherence to the Montreal Protocol and the coming implementation of the Kyoto Protocol, and contributes to the scientific underpinning of them both.

Conclusions:
Widespread and dramatic changes in the atmospheric composition of GHGs and ODSs in both hemispheres, and notably the Northern Hemisphere, during the 20th century have been clearly demonstrated by CRYOSTAT measurements.

Keywords: firn, ice, atmosphere, greenhouse gases, ozone depleting substances, climate change, stratospheric ozone, radiative forcing, atmospheric chemistry, Arctic, Antarctic, ozone, O₃, carbon dioxide, CO₂, methane, CH₄, nitrous oxide, N₂O, carbon monoxide, CO, halocarbons, CFCs, HCFCs, HFCs, PFCs, CF₄, Montreal Protocol, Kyoto Protocol
SECTION 6: DETAILED REPORT RELATED TO THE OVERALL PROJECT DURATION

6.1 BACKGROUND

Two of the most pressing environmental problems of the day are human-induced climate change and stratospheric ozone depletion. The latter itself also has profound implications for climate, in addition to the better-known direct impacts on human health and ecosystem vitality. Both are largely the result of the release of numerous gases to the atmosphere from anthropogenic sources. Some such gases are strong infrared absorbers or “greenhouse” gases (GHGs), others are ozone-depleting substances (ODSs). Although the Montreal Protocol, to which the EU is committed, has been successful in cur tailing the release of some ODSs, others continue to rise. Even more intractable is the rise of GHGs, despite the United Nations Framework Convention on Climate Change, to which the EU is a signatory and the proposals to cut emissions under the Kyoto agreement, which all countries of the EU have ratified. Still other gases are precursors of tropospheric ozone, which is itself a powerful GHG, or they may interfere with the natural oxidation cycles responsible for removing many other GHGs and ODSs from the atmosphere. Natural emissions of GHGs and ODSs, and natural processes affecting their distribution, are also an important factor in determining the health of the ozone layer. Yet the degree to which the natural chemistry-climate system has been perturbed by human activity is poorly known. The changing nature of sources, such as soils, wetlands, vegetation, and marine microorganisms, and sinks such as atmospheric oxidation, oceanic and terrestrial uptake, etc. are little understood, yet are themselves sensitive to climate change, past and future. By reconstructing the evolution of the present polluted atmosphere from its “clean” pre-industrial beginnings we hope to better understand how the chemical composition of the Earth’s atmosphere has changed to the presence of mankind on the face of the planet, and hence better predict how it may change in future. CRYOSTAT, therefore, contributes to the scientific underpinning of required to predict the climatic effects due to changing industrial (and natural) emissions, and hence to better plan for the social and economic consequences of such change.

Studies of stratospheric ozone depletion and climate change leading to remedial policies have clear and apparent benefits to European social objectives. The development of an Arctic ozone hole in recent years, and noticeable thinning of mid-latitudinal stratospheric ozone, has lead to increased UV fluxes over Europe. A breakdown in the implementation of the Montreal Protocol process could lead to significantly enhanced UV fluxes over Europe. Such increases would likely result in human health effects, including increased sunburn, excess skin damage and cancers, cataracts, and immune system suppression. Damage would also be suffered by livestock and by commercial crops, as well as by natural fauna and flora. UV penetration in to water bodies has the ability to disrupt food chains, notably by impacts on phytoplankton. Increased UV also results in damage to many exterior construction materials adding maintenance and replacement costs. Higher UV can potentially change the photochemical state of the troposphere, enhancing photochemical smog and ozone production in the lower atmosphere with direct effects on human health (respiratory disease), and indirect effects on climate (ozone and aerosol production).

It is still a controversial issue as to whether deleterious effects have already impacted Europe from stratospheric ozone reductions, but there is no dispute that the global ozone layer “is currently in its most vulnerable state” (Scientific Assessment of Ozone Depletion 1998, WMO, 1999). The occurrence of Arctic ozone holes is influenced by climate, and with stratospheric chlorine-bromine loadings at peak levels, an unusually cold or protracted winter in the Arctic stratosphere could easily trigger a substantial loss of springtime ozone behind the polar front which, both before and after break-up, may affect much of Europe. There is, therefore, a critical need to understand the evolution of stratosphere ozone chemistry from its pre-industrial natural state to its present perturbed state, so that the threat from continued growth of ozone-depleting substances and the efficacy of remedial measures could be assessed.
Table 1. Overview of principal GHGs, ODSs, and related gases measured by CRYOSTAT

<table>
<thead>
<tr>
<th>Gas</th>
<th>ODS/GHG</th>
<th>Man-made and natural sources</th>
<th>Sinks</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>GHG</td>
<td>Fossil fuel combustion, biomass burning, deforestation, oceans, terrestrial biosphere, volcanism, CH₄ and CO oxidation</td>
<td>Uptake by oceans and biosphere</td>
<td>Principal anthropogenic GHG, partitioning uncertain and variable</td>
</tr>
<tr>
<td>CH₄</td>
<td>GHG</td>
<td>Ruminant animals, rice paddies, gas and mining leaks, landfill, biomass burning, anaerobic decomposition</td>
<td>Tropospheric oxidation, stratospheric Cl</td>
<td>Major anthropogenic GHG</td>
</tr>
<tr>
<td>N₂O</td>
<td>ODS</td>
<td>Land cultivation, fertilizer use, oceans, soils, aquifers</td>
<td>Stratospheric oxidation/OD</td>
<td>Major anthropogenic GHG; 'missing' global source(s)</td>
</tr>
<tr>
<td>CO</td>
<td>*1</td>
<td>Fossil fuel burning, biomass burning, CH₄ and hydrocarbon oxidation, oceans</td>
<td>Tropospheric oxidation</td>
<td>Global budget not closed, O₃ precursor</td>
</tr>
<tr>
<td>COS</td>
<td>GHG</td>
<td>Fossil fuel and biomass burning, CH₄ and hydrocarbon oxidation, soils, oceans, oxidation of CS₃ (from wetlands, artificial fibre industry, etc.)</td>
<td>Tropospheric and stratospheric oxidation</td>
<td>Forms aerosols in stratosphere</td>
</tr>
<tr>
<td>CFCs</td>
<td>ODS</td>
<td>Refrigeration and air conditioning, foam blowing, aerosol propellants, electronics industry</td>
<td>Stratospheric photolysis</td>
<td>Direct and indirect effects on radiative balance (changes in stratospheric ozone)</td>
</tr>
<tr>
<td>HCFCs</td>
<td>ODS</td>
<td>Similar to the CFCs which they replace</td>
<td>Stratospheric oxidation, photolysis, tropospheric oxidation</td>
<td></td>
</tr>
<tr>
<td>HFCs</td>
<td>GHG</td>
<td>Similar to CFCs, also chemical industry</td>
<td>Stratospheric, tropospheric oxidation</td>
<td></td>
</tr>
<tr>
<td>Halons</td>
<td>ODS</td>
<td>Fire extinguishers</td>
<td>Stratospheric, tropospheric photolysis</td>
<td>Direct and indirect effects on radiative balance (as CFCs)</td>
</tr>
<tr>
<td>PFCs</td>
<td>GHG</td>
<td>Aluminium smelting, chemical industry, geochemical</td>
<td>Semi-permanent gases</td>
<td>Large global warming potentials (GWP)</td>
</tr>
<tr>
<td>SF₆</td>
<td>SF₆,CF₃</td>
<td>Magnesium smelting, electrical insulation, leak detection, organofluorine production</td>
<td>Very long-lived gases</td>
<td>Very large GWPs</td>
</tr>
<tr>
<td>CHCl</td>
<td>ODS</td>
<td>Fossil fuel combustion and incineration, chemical industry, oceans, biomass burning, terrestrial biosphere</td>
<td>Stratospheric photolysis, tropospheric oxidation</td>
<td>Atmospheric budget poorly constrained</td>
</tr>
<tr>
<td>CCl₃,CH₂Cl,</td>
<td>ODS</td>
<td>Chemical industry, dry cleaning, industrial solvents, fossil fuel combustion, biomass burning, oceans, soils</td>
<td>Stratospheric photolysis, tropospheric oxidation</td>
<td>Atmospheric budgets poorly constrained in many cases</td>
</tr>
<tr>
<td>CH₂Br</td>
<td>ODS</td>
<td>Fumigant, vehicle exhaust, oceans, soils</td>
<td>Tropospheric oxidation, oceans, soils</td>
<td>Atmospheric budget poorly constrained</td>
</tr>
<tr>
<td>RBr/I</td>
<td>Oceans</td>
<td></td>
<td>Tropospheric oxidation and photolysis</td>
<td>Indicators of marine primary productivity</td>
</tr>
<tr>
<td>NMHC</td>
<td>*1</td>
<td>Fossil fuel combustion, biomass burning, gas and mining leaks, agriculture, oceans</td>
<td>Tropospheric oxidation</td>
<td>Tropospheric ozone precursors</td>
</tr>
<tr>
<td>RONO₂</td>
<td>*1</td>
<td>Secondary pollutants from hydrocarbons and NO₂, oceans</td>
<td>Tropospheric thermolysis, oxidation</td>
<td>Indicators of NOx and ozone chemistry</td>
</tr>
</tbody>
</table>

* R refers to an alkyl group; *1. Indirect effects via changes in tropospheric ozone and oxidative lifetimes of key gases.

Likewise there are manifold impacts that may ensue from climate change in Europe (not all necessarily deleterious), again affecting agricultural productivity (changes in rainfall patterns, temperature extremes, migration of pests), human well-being (extreme weather events, flooding, storm surges, avalanches, etc), and economy (construction, aviation and road transport, agriculture, fisheries, coastal defences, etc.). There are also important synergies between stratospheric ozone depletion and climate change. There is a close radiative and chemical coupling between the troposphere and stratosphere such warming of the troposphere has been paralleled by cooling of the stratosphere. This latter effect raises the probability of polar ozone hole development. Likewise, since ozone is itself a radiatively important gas, thinning ozone in the stratosphere, and increased levels at the ground, may both tend to enhance the direct radiative forcing effect.

The seriousness of potential climate change has been underlined by strong statements in the most recent IPCC assessment (Third Assessment Report “Climate Change 2001: The Scientific Basis”, Shanghai, 2001) that climate change over the last 50 years is indeed “likely to have been due to increases in greenhouse gas concentrations”; with predictions of far more pronounced changes to come. It is against this background of concern for the future state of the atmosphere that this study of the impact of industrialisation on the evolution of atmospheric composition, chemistry and climate up to the present day is set.
6.2 SCIENTIFIC/TECHNOLOGICAL AND SOCIO-ECONOMIC OBJECTIVES

CRYOSTAT has employed an holistic approach to deconstruct the identity, both natural and man-made, and changing sources strengths of essentially all significant GHGs (other than water vapour), ODSs, and related trace gases in the atmosphere on time scales that effectively cover the time span over which their emissions have grown as a result of anthropogenic activities. This was achieved by reconstructing their global atmospheric compositional histories from cryospheric records (firm air and ice cores), by determining correlations between hemispheres and between different gases, and by employing atmospheric models to explore source-sink relationships and to reconstruct other non-measured chemical species and parameters. Powerful interpretive tools have arisen from the measurements of stable isotopes of several gases, including some novel isotopic measurements of CH$_4$, N$_2$O, and CO in ice and firm. Isotope ratios can yield information on the various modes of production of the gases (notably between biological and non-biological origins), and on their atmospheric sink processes. Since sources/sinks to and from the atmosphere are often common to a number of gases (e.g. biomass burning, atmospheric oxidation, etc.), this isotopic information also provides a generic interpretive tool.

CRYOSTAT was implemented through a series of combined firm and shallow ice drilling expeditions, providing the first ever such set of comprehensive gas measurements in contiguous firm and ice profiles from both hemispheres (i.e. Greenland and Antarctica). The extraction and measurement of multiple gas species from ice was one of the major innovative aspects and technological challenges of the project. Year-round field studies were also conducted in Antarctica to study the mechanisms controlling transport of atmospheric chemical constituents across the air-snow interface. This allowed us to refine existing firm air transport models, notably to account for thermal diffusion and convection effects in the upper firm, and so ensure accurate conversion of depth profiles into temporal trends. Year round measurements also helped define the seasonal cycle of shorter-lived gases, crucial for the proper interpretation and validation of firm and atmospheric chemistry models.

Combining firm modelling with atmospheric modelling we were then able to convert concentration-depth profiles at single geographic points (i.e. the polar drill sites) first into local time trends, and then into hemispheric/global time-varying latitudinal and altitudinal (troposphere and stratosphere) distributions of species. The reconstructed trends were further used in additional modelling work to explore the impacts of CO$_2$, CH$_4$, N$_2$O, and halocarbon increases on stratospheric Cl$_x$, Br$_x$, ozone, and temperature over the last century or more. Other models were used to examine source-sink relationships for N$_2$O and CH$_4$.

As a final step in this sequence of interpretive studies, the potential impact of these changes on the radiative forcing of climate during the period of 19$^{th}$ and 20$^{th}$ century industrialisation was determined. Radiative forcing due to individual target molecules was assessed using detailed line-by-line and narrow band radiative transfer codes.

The outputs of CRYOSTAT consist of a database (ultimately to become freely and publicly accessible through a central on-line server) of global trends of numerous key atmospheric gases, from pre-industrial times to 2001. It also includes assessments of the consequent impacts of these changes on radiative forcing, on stratospheric composition, chemistry, and temperature, and on the fluxes of certain key gases between environmental compartments. It has produced a set of refined modelling tools of wider utility to the atmospheric chemistry, global climate and glaciological research communities. It has provided various improved techniques for determining gaseous composition from firm and ice cores. Finally, and most significantly, it has improved the state of knowledge on interactions between atmospheric chemistry and climate, which will in turn improve the predictive capability of climate modellers, with important implications for policy-makers.
There are critical economic considerations involved in adopting abatement measures in Europe to counter ozone depletion and climate change. Such measures may be very costly in terms of either emission reduction technology, or development of alternative substances or technologies, although such measures may also create new manufacturing and employment opportunities. A notable issue is the European Union commitment resulting from the Kyoto Agreement to cut CO2 (or equivalent CO2). To cut emissions of CO2 itself will require expensive CO2 emission control devices, energy saving measures with complex economic repercussions both positive and negative, or an increased reliance on non-combustive power generation (nuclear, hydroelectric, and alternative).

A complementary strategy would be to reduce emissions of non-CO2 greenhouse gases such as methane, N2O, tropospheric ozone, HFCs and HCFCs (the latter are already subject to constraints under the Montreal Protocol), and long-lived fluorinated gases such as SF6 and CF4. These may prove to be less costly and more easily realised than reducing CO2 alone, at least in the short term. Conversely, not regulating emissions of such gases may undermine efforts to control climate forcing through CO2 emissions abatement. Again, it is only by understanding the evolution of the anthropogenic greenhouse effects, its links to GHG emissions, and the contributions of natural and anthropogenic sources and sinks, that the cost effectiveness of potential amelioration strategies can be assessed. The various natural and man-made origins of methane, nitrous oxide, and ozone, three of the most important greenhouse gases are, for example, still very poorly understood. Individual source strengths of several halogenated GHGs are incompletely known, whilst CF4 for instance, has controversially been claimed to have natural as well as industrial origins. The long term trend of tropospheric ozone has, to date, largely been a matter of conjecture and deduction.

Similar issues exist with ozone depletors. There has, for example, been much controversy regarding methyl bromide, an agricultural pesticide. Whereas the growth rates of many chlorinated ODSs have begun to decline, bromine in the stratosphere continues to rise almost unabated, and there are concerns regarding illegal production of controlled ODSs, and production of novel ODSs. Global warming could even, indirectly, affect natural sources of ODSs such as methyl chloride, methyl bromide and bromoform. All of these issues lead to uncertainties regarding the time for recovery of the ozone-layer to its ‘natural’ state (or, at least, pre-Antarctic ozone hole conditions), which even optimistic estimates place as being towards the middle of this century.

Certainly there are potentially enormous costs associated with a strategy of inaction. Economic losses from natural disasters increased from $53 billion per year in the 1960’s to $480 billion per year in the 1990’s, of which 80% of the losses were weather-related, and therefore sensitive to climate change. A. Mayer and T. Cooper (Environmental Finance, 1(7), 19-21, 2000) have conjectured that should such trends continue (“business as usual” scenario), global economic losses could exceed Gross Domestic Product (GDP) by the year 2065, at a monetary value of over US$200 trillion at today’s prices. Although these projections are perhaps intentionally provocative, they do serve as a reminder that the understanding and mitigation of global atmospheric change goes to the core of European, and indeed global, prosperity, human well-being, and sustainable growth.
INNOVATIONS IN CRYOSTAT

In the original CRYOSTAT Description of Work we anticipated that a number of novel and significant new measurements, methodologies, discoveries and interpretations would emerge from the project. Here we revisit this list and add further, in some cases unexpected, important findings and developments from CRYOSTAT studies.

- First measurements of multiple trace gases (CFCs, CF₄ and other perfluorocarbons, CCL₄, ethane, alkyl nitrates, etc.) in air occluded in glacial ice.

- First contiguous measurements of trace gases through firm and shallow ice yielding complete histories of these gases from pre-industrial times to the present day.

- Comprehensive measurements of more than sixty trace gases in deep polar firm, demonstrating that whilst a few gases have a natural background, the majority are of man-made origin, and almost all have increased in the atmosphere in the last century.

- First comprehensive measurements of trace gases in firm from the Northern Hemisphere (where more than 90% of pollutants are released) including many for which there was no previous long-term record at all in that hemisphere (e.g. non-methane hydrocarbons, alkyl nitrates, short-lived bromo and chlorocarbons).

- First long term measurements of ‘parent-daughter’ hydrocarbons and nitrated products illustrating that reactive nitrogen levels must have increased in the Northern Hemisphere which would have substantially increased tropospheric ozone (a powerful greenhouse gas in the lower atmosphere) there.

- Assembly of a complete history of reactive chlorine and bromine in the troposphere and stratosphere during the 20th century showing that stratospheric chlorine has increased more than eight-fold since preindustrial times and bromine doubled.

- From the above, century-long trends of stratospheric ozone and temperature have been derived and the onset of the Antarctic ozone hole shown to be accounted for in a model utilising these parameters.

- Model demonstration that for gases with stratospheric sinks, a single value of atmospheric lifetime is not appropriate, but instead it varies with growth rate.

- Derivation of a 20th century history of direct radiative forcing (global warming) due to halogenated trace gases showing the alarming increase in radiative forcing due to very long-lived gases (i.e. those with lifetimes of thousands of years).

- Significant improvements have been made to calculated radiative efficiency factors of several gases including, in some cases, new measurements of their infrared cross sections.

- First measurement of the evolution of δ¹³CH₄ over the last two centuries suggesting an increasing source from biomass burning, and also demonstrating the coupling between methane oxidation and increased chlorine in the stratosphere.

- First comprehensive reconstruction of N₂O isotopic change (nitrogen isotope ratios, oxygen isotope ratios and even position-dependent nitrogen isotope ratios) pointing to the importance of fertilizer use as a prime cause for the upturn in atmospheric N₂O.

- First demonstration, from a novel combination of isotopic signatures and concentration measurements, that the important pollutant carbon monoxide (CO) has increased in the Southern Hemisphere since the early 20th century, most likely due to man-induced biomass burning. CO is an important player in the atmospheric chemistry that regulates many other greenhouse gases and ozone-depleters.

- First comparative measurements of trace gases in ice and firm from low and very high accumulation-rate sites.
- First simultaneous year-round measurements of trace gases in the lower Antarctic atmosphere and upper firm, yielding some of the first ever Antarctic seasonal cycles of some of the gases, and the means to test for conservative transport of gases into the firm record.

- Year-round measurements of isotopic and elemental ratios of permanent gases in firm to allow thermal diffusion effects to be determined and implemented in firm air transport models.

- Studies of fractionation effects at the firm-ice transition, showing these to be highly significant for small atomic/molecular radius gases, but with an upper cut-off at a collision diameter of about 3.6 Å.

- Measurements of multiple isotope ratios are providing important new constraints to the modelling of past (paleo) firm thickness, thereby allowing accurate ice core dating and a far better understanding of synchronicities between atmospheric gases and temperature changes. This has been of significant benefit to paleoclimate science.

- Important improvements in ice extraction and analysis have been developed including novel continuous on-line techniques for water isotopes, and also on-line isotopes of gases: the former of interest in wider field of water analysis (hydrology, medical sciences, etc.).
6.3 APPLIED METHODOLOGY, SCIENTIFIC ACHIEVEMENTS AND MAIN DELIVERABLES

6.3.1 SAMPLE COLLECTION AND MEASUREMENTS METHODOLOGIES

6.3.1.1 Field campaigns

In order to get a complete firm sampling set three sampling sites were chosen: North-GRIP in Greenland (a Northern Hemisphere site that is largely free of interferences from summer melting: a relative rarity in the Northern Hemisphere), and Berkner Island and Law Dome (W-20K) in Antarctica (low and high accumulation sites respectively in Southern Hemisphere). Furthermore it was decided to implement a "permanent" sampling line at the British base of Halley in Antarctica in order to get information on the gas profile evolution in the snow all through the year. Additional samples and studies were incorporated from other sites as appropriate. In particular, several CRYOSTAT studies incorporated data from the study locations of an earlier CEC programme ("FIRETRACC/100": Devon Island in the Northern Hemisphere, and Dronning Maud Land and EPICA Dome C in Antarctica).

The relevant site characteristics are shown in Table 2. The diffusion of air in firm is such that the age of a gas at a given depth is not unique, and the probability for the gas to have a given age is well represented by a log-normal probability law. In the Table are the calculated characteristics of the age distribution of the gas SF₆ at the deepest sampling level for all sites. The age spread indicates the 50% probability that the SF₆ age is within the given limit. This is a suitably representative value but is strictly applicable only to this particular gas. Of interest are the old ages represented by deep firm air at EDC, although the spread of ages if very large and thus the 'dates' assigned at this site are quite uncertain. In contrast the very high snow accumulation rates at LD result in a very narrow age spectrum and a much higher dating accuracy, albeit for younger ages.

Table 2. Firm and ice sampling locations studies considered by CRYOSTAT

<table>
<thead>
<tr>
<th>Site</th>
<th>Lat, Long</th>
<th>Elevation (m)</th>
<th>Mean Annual Temp (°C)</th>
<th>Snow accumulation (cm water y⁻¹)</th>
<th>Lowest sampling depth</th>
<th>Lowest gas (SF₆) sample characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean age</td>
</tr>
<tr>
<td>Dronning Maud Land, Antarctica (DML)*</td>
<td>77°S, 10°W</td>
<td>2176 m</td>
<td>-39°C</td>
<td>7 cm</td>
<td>74 m</td>
<td>59 yrs</td>
</tr>
<tr>
<td>Dome C, Antarctica (EDC)*</td>
<td>75°S, 123°E</td>
<td>3233 m</td>
<td>-53°C</td>
<td>2.6 cm</td>
<td>99 m</td>
<td>175 yrs</td>
</tr>
<tr>
<td>Devon Island, Canada (DI)*</td>
<td>75°N,82°W</td>
<td>1800 m</td>
<td>-23°C</td>
<td>30 cm</td>
<td>59 m</td>
<td>54 yrs</td>
</tr>
<tr>
<td>North Greenland Ice Coring Project (NGRIP)*</td>
<td>75°N,42°W</td>
<td>2975 m</td>
<td>-31°C</td>
<td>17 cm</td>
<td>77 m</td>
<td>62 yrs</td>
</tr>
<tr>
<td>Berkner Island, Antarctica (BI)*</td>
<td>79°S,45°W</td>
<td>900</td>
<td>-26°C</td>
<td>13 cm</td>
<td>63 m</td>
<td>156 yrs</td>
</tr>
<tr>
<td>W-20K Law Dome, Antarctica (LD)*</td>
<td>66°S,112°E</td>
<td>1390 m</td>
<td>-19°C</td>
<td>15 cm</td>
<td>51 m</td>
<td>67 yrs</td>
</tr>
<tr>
<td><strong>Year-round studies:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Halley, Antarctica†</td>
<td>75°S,26°W</td>
<td>20</td>
<td>-19°C</td>
<td>50</td>
<td>21 m</td>
<td></td>
</tr>
</tbody>
</table>

*FIRETRACC project; †CRYOSTAT project; ‡intentionally drilled only in to the upper firm
NGRIP

The firm air sampling at NGRIP was performed in June 2001 during the deep-drilling project at NGRIP. The firm hole was drilled with a Danish shallow drill, but most of the air sampling equipment, except the bladder, was provided by this project. The firm core was been drilled, logged and packed, and density determined by NGRIP personnel to whom we are extremely grateful.

The location for the firm air sampling has been chosen in order to avoid contamination from the main camp (generator and vehicles) by going upwind of the most frequent wind direction and at a reasonable distance to the main camp. A good compromise was found at about 2 km WNW from the main camp.

In order to have an undisturbed surface for the first sampling levels, the first 7.5 m of firm were drilled with a hand auger producing the same diameter core and hole as the main drill. The firm hole was been drilled to 100 m depth in 11 days between 25 May and 4 June 2001. An extra 12 m hole was drilled by hand on 3 June 2001 in order to get an accurate temperature profile of the first 10 meters.

The sampling procedure was similar to that used during previous projects: The hole was drilled to a certain depth level. The exact depth was determined using a measuring tape. Immediately afterwards, the bladder was lowered and inflated to seal the bottom of the hole and the firm air extraction pumps then started. The CO₂ mixing ratio was continuously monitored with a LICOR CO₂ analyzer to check the quality of the air pumped from the firm. Filling of flasks was started only after the CO₂ mixing ratio had stabilised at a constant low level (i.e. lower than present day and lower than that in the overlying firm layers). CO₂ and temperature data are shown in Figure 1.

A total of 172 (+3 recycled) samples were taken at 20 different depth levels. One to three levels could be sampled in one day. Except for the last two levels, the pumping time was between one and two hours depending on the number of flasks to be filled. Atmospheric samples were taken on several occasions during the sampling period for quality control and present-day reference purposes. The two last firm levels were special. At 76.7 m the flow rate through the sample tube was only 1 to 1.5 litre/min (instead of 4 l/min), indicating near impermeable conditions. The last level was drilled to 79.48 m. No air could be withdrawn from that depth. The sample flasks were shipped back to 8 different laboratories involved (University of Bern, UEA Norwich, LGGE Grenoble, LSCE Gif-sur-Yvette, IMAU Utrecht, MPI Mainz, NCAR Boulder, INSTAAR Boulder).

The NGRIP ice core collected for CRYOSTAT had a total depth of 100.1 m and was 76 mm in diameter. The core was split in half with one half shipped to the University of Copenhagen and the other to the University Heidelberg from whence the bags below 50 m were shipped to Bern, and then Grenoble.
Berkner Island

At Berkner, (Antarctica), the firn air sampling was performed in January 2003, during the first year of a 950 m French-British deep drilling. The sampling procedure was very similar to the one used for the NGRIP campaign. The drilling has been done with a shallow drill developed by the British Antarctic Survey. 154 samples have been recovered from 25 different depths down to the close off depth (65 m). Unfortunately a small leak developed in the sampling train during pumping of some of the bottommost samples and the data for those samples had to be discarded. The Berkner CRYOSTAT core, retrieved in January 2003, had a total depth of 82m, and a diameter of 106 mm. The full core below 20 m depth was shipped to Cambridge.

Law Dome

The expedition to Law Dome in October-November 2004 collected 55 firn air samples at 17 levels from the surface to a depth of 55 metres at the DSSW 19K location (19 km west of DSS deep drill site near Law Dome summit). The age at the bottom of the firn layer ranges from 49 to 59 years (depending on the diffusivity D of the trace gas of interest) and the age spread is very narrow, about 5 years spectral width [Trudinger et al., 2002]. The mean age and age distributions for the selected samples are shown in Figure 2. Large samples (100s of litres STP) of air from the key depths are stored at CSIRO Marine and Atmospheric Research in Aspendale, Victoria, and sub samples of these and of the earlier DSSW 20K firn samples have been collected in 1 litre Silcocans at 40 psig and held at the University of East Anglia.
Ice core samples retrieved to access the firm layer are kept at the Australian Antarctic Division ice core storage in Hobart, Tasmania. Air samples were also collected from the firm surface at DSSW19K for studies of possible photochemical production of compounds such as CO. Ice core air samples from the existing DE08 and DE08-2 ice cores held at CSIRO were extracted to extend the firm air record back to pre-industrial times.

**Halley**

To survey the evolution of different gas profiles in firm through different seasons, a semi-permanent air sampling system was established at the British Antarctic base of Halley in 2003 (see schematic in Figure 3). Uniquely the hole was backfilled with high-purity quartz sand of lower permeability than the surrounding firm to effectively seal the hole from ingress of surface air. The pumping system consisted of a set of 6 “Dekabon” tubing connected to a manifold in order to pump firm from different depths. Each Dekabon line was fitted with a quartz-fibre plug at the bottom end to prevent either snow or sand being drawn up the tube. In the field a LiCor CO₂ analyser was used to control the quality of the sampling and to make *in situ* measurements for later interpretation. A thermistor string allowed measurements of temperature to be made at 10 different levels. Figure 3 shows the layout of the tubes within the hole.

Figure 2. The mean age at the bottom of the firm at DSSW19K as a function of the diffusivity coefficient (left) and the modelled age distributions for CO₂ at the deepest sampling depths (right).
Figure 3. Schematic of the permanent air sampling system of Halley. The left side shows a schematic of the full 21 m firm hole, while the right side is a close up of surface level tubing A.

First, a core was drilled and 2049.5cm measured and collected, then the longest Dekabon tube and thermistor string forming the central cable was lowered down the bottom of the hole. Each subsequent length of Dekabon was attached to this central cable, at a horizontal distance from the cable (using wire spacers), so that the sand used to back-fill the hole could run freely between all the tubing. Finally sand was 'misted' down the centre of the hole while the tubing was periodically checked for suction. The hole was filled with sand until approximately 40 cm below the surface at which point it was filled with snow taken from the surface to avoid the dark sand absorbing sunlight and warming up that region. The Dekabon line ran back 100 m to the Clean Air Sector Laboratory (CASLAB), itself located 1.5 km upwind from the main operations base. The air line switching gear, pumps, CO₂ instrument, and bottle filling equipment were all located within CASLAB.

6.3.1.2 Development of new laboratory methodologies

We discuss here only recent methodologies that were developed under the auspices of the CRYOSTAT project. Other methodologies have been discussed either in the open literature or in the Final Report of the earlier FIRETRACC project.
NMHC extraction from large air samples (pilot study)

Isotopic analysis of atmospheric non-methane hydrocarbons (NMHCs) and, in particular, the analysis of the deuterium/hydrogen (D/H) ratio would be a highly valuable measurement. This is because the dominant self-cleansing property of the troposphere is based on H-atom abstraction by the OH radical, which in turn induces large kinetic isotopic fractionation effects. The major obstacle in applying D/H isotope analysis to atmospheric NMHCs is not only the low abundance of D itself but, in particular, the low concentrations of NMHCs (in the parts per trillion range). Such a methodology represents a huge technical challenge that has as yet never been successfully overcome. We have now performed the first stages of this process by quantitatively separating C₂-C₅ NMHCs from 300 L air samples, together with CO₂ as the carrier gas matrix, by using ultra-high efficiency ("Russian Doll") cryogenic traps. After diluting the extracted NMHC mixtures with hydrocarbon free air, and determining the mixing ratios, good agreement with original whole air sample analysis has been demonstrated for alkanes and several halocarbons. Furthermore, the mixture of NMHCs in the CO₂ matrix has proven to remain unchanged over several years when conveniently stored in glass ampoules. These 'extracts' or 'concentrates' of condensables extracted from the larger air samples remain stored and will soon enable the D/H isotope analysis of trace gases to be performed (continuing work in progress).

¹⁷O correction for CO₂ mass spectrometric isotopic analysis

A study was mounted to investigate the reason for the dependence of δ¹³C(CO₂) on the CO₂ oxygen isotope composition and for the δ¹³C discrepancy among existing data-correction algorithms. The possible discrepancy is in some cases as much as 0.1 %o: much larger than the current accuracy of CO₂ isotope analysis (~0.02%o) and the target accuracy of 0.01%o. We made a re-calibration of the ¹⁷O absolute abundance in the international standards VSMOW and VPDB-CO₂. This has fundamentally improved the accuracy of CO₂ mass-spectrometric analyses and has eliminated the dependence of δ¹³C(CO₂) on the CO₂ oxygen isotope composition. This is an important advance not only for this project but also for that part of the scientific community engaged in studying the origins of atmospheric CO₂ in the atmosphere.

A new device for extracting gases from ice cores for analysis of the isotopic ratio of trace gases

A new extraction line has been developed under CRYOSTAT for the specific application of measuring the stable isotopic ratios of carbon monoxide and nitrous oxide (Figure 4). The principle is as follows. An ice sample of about 1 kg is sealed in a glass container, put under vacuum, and then slowly melted. The air released during melting is continuously transferred through water traps into a small gas trap held at liquid helium temperature. Thus all condensable gases except water vapour are stored in a small volume which can then be connected to the analytical instruments for stable isotopic determination. This procedure provides quantitative extraction of the gases and saves time compared with the previously-used method where the sample was refrozen after melting.
Tests of this system were carried on for carbon monoxide and nitrous oxide. Measurements of CO are particularly challenging because of the low concentrations and reactivity of CO and the difficulty in avoiding contamination and artefact formation. The extraction was tested with an artificial bubble-free ice sample into which a standard gas of known composition (including isotopic ratios) was added. Tests were also performed without ice but only with a transfer of the standard gas from the glass container into the gas trap, using the same protocol. Overall, the system proved to be free of significant artefacts on the different isotopic ratios. It has been successfully used for reconstructing N₂O stable isotopic ratios during pre-industrial times [Bernard et al., 2006, see Section 6.3.3].

![Diagram of extraction device](image)

**Figure 4.** Schematic of the extraction device for isolating gases from 1 kg of ice and trapping them in a small volume held at liquid helium temperature

**Validation of a large volume dry cruser for analysis of ultra-trace gases in ice**

The CSIRO large volume (>1 kg) 'cheese-grater' design of dry ice crusher has been previously described with reference to the analysis of carbon cycle gases and their isotopic ratios [Trudinger et al., 1999]. Within CRYOSTAT the system was optimised (with respect to cryogenic drying temperatures, sealing materials, decontamination procedures, etc.) and tested for the analysis of gases comprising just a few tens of parts per trillion. This proved successful for a number of gases, yielding some of their first systematic measurements in ice cores (see Section 6.4).

**Continuous on-line extraction techniques**

An important new development has been continuous on-line techniques for water and air extracted from ice cores developed by CR7 [Huber and Leuenberger, 2002, 2003, 2004, 2005; Huber et al., 2003]. Water isotope ratio determination of any of the water phases (water vapour, water, ice) is of great relevance in different research fields, such as climate and paleoclimate studies, geological surveys and hydrological studies. Conventional techniques for water isotopes are available in different configurations but all of them are rather time-consuming. In the frame of CRYOSTAT we developed new fast on-line techniques that process water as well as ice samples. The analysis time is only ~5 minutes per sample which includes equilibration and processing. Measurement precision and accuracy are better than 0.1‰ and 1‰ for δ¹⁸O and δD, respectively, comparable to
conventional techniques. The new on-line techniques are able to analyze a wide range of aqueous samples. This allows, for the first time, to make continuous isotope measurements on ice cores. Similarly, continuous and fast analysis of aqueous samples can be of great value for hydrological, geological and perhaps medical applications [Huber and Leuenberger, 2005].

Furthermore a new technique for the on-line analysis of air isotopes extracted from ice cores has been developed [Huber and Leuenberger, 2004]. This technique allows rapid analyses with high resolution of the main air components nitrogen, oxygen and argon. Measurement precision is comparable to precisions obtained by conventional techniques. It is now possible to measure $\delta^{15}$N and $\delta^{18}$O over entire ice cores, so helping to synchronize chronologies, to assess gas age-ice age differences, and to calibrate paleothermometry for detection of rapid temperature changes. This new on-line air extraction and analysis technique complements the water methods in an ideal way, since it separates the air from the melt-water of an ice sample. The remaining water waste flux can directly be analyzed by complimentary water analysis methods [Huber and Leuenberger, 2005].

Other ice extraction devices

Other devices developed under CRYOSTAT include a small centrifugal ‘cheese-grater’ device, a melting/helium sparging device, and a static melting/vacuum device developed by CO1. Large air samples for isotope analysis of N$_2$O and D/H of CH$_4$ used two techniques: melting-refreezing and continuous evacuation during melting.

6.3.1.3 Models used in CRYOSTAT

The principal models employed in CRYOSTAT are listed in Table 3. FIRN refers to physical models of transport of gases through firm, CHEM refers to chemical transport models; and RAD refers to a radiative transfer model. The models already existed but all were significantly updated, improved and validated for CRYOSTAT purposes. In some cases this has resulted in major advances in modelling capabilities both within the scientific area of interest of CRYOSTAT and beyond.
Table 3. Principal models employed in CRYOSTAT

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIRN1</td>
<td>'Inverse' firn model of molecular diffusion and gravitation of gases in firn, involving simultaneous solution of four conservation equations for ice accumulation, air in open pores, trace gases in open pores, and air in closed pores. Primarily used to determine site-specific effective diffusivity profiles required by 'direct' firn models by inversion of well-known atmospheric trace gas histories (e.g. CO₂, CH₄, SF₆, etc.). Based on Rommelaere at al. [1997] and tortuosity calculation of Fabre et al. [2000].</td>
</tr>
<tr>
<td>FIRN2</td>
<td>'Direct' firn diffusion model based on similar principals to FIRN1 but used to convert known or hypothetical time trends into firn depth profiles for comparison with measurements. This is the 'workhorse' platform-independent model made available to all CRYOSTAT participants. A further development, partly achieved under CRYOSTAT has been the implementation of an iterative/Bayesian synthesis technique [Trudinger et al. 2002].</td>
</tr>
<tr>
<td>FIRN3</td>
<td>Firn diffusion model of molecular diffusion and gravitation (different solution scheme to FIRN1/2) that also incorporates a term for thermal diffusion. Used specifically to study isotopic fractionation effects, and will feed into refinement of FIRN2.</td>
</tr>
<tr>
<td>CHEM1</td>
<td>2-D zonally-averaged atmospheric chemistry model containing 18 equal area (sine weighted) latitudinal bands, six 2.5 km atmospheric layers to the tropopause, a single 'sink' through the upper boundary to simulate stratospheric loss, prescribed OH field, seasonally varying advective and diffusive transport, and (in one version) ocean-atmosphere feedback. It is suited to fast exploratory studies and multiple runs, and gases with significant air-sea exchange. It does not simulate changing transport, nor stratospheric chemistry.</td>
</tr>
<tr>
<td>CHEM2</td>
<td>2-D zonally averaged atmospheric chemistry-transport model [Brasseur et al, 1990; Martinier et al., 1995] containing 5° latitude bands, and 1 km atmospheric layers to 85 km. Radiation, transport and chemistry of the middle atmosphere are fully coupled. Mean monthly climatological dynamics and temperatures [Randel, 1987] are imposed in the troposphere. Photolysis rates are calculated on-line with the TUV3.9 model [Madronich, 1993; Madronich, personal communication, 1998]. Chemistry includes HOₓ, NOₓ, CH₄, CO, PAN, Clₓ, and Brₓ, represented by 55 long and 28 short lived species. Further halocarbon species, and ¹³C of methane and its oxidation products, have also been added. A 15 day time-step over 100 yr requires about 6 hours of CPU time on a recent PC. The chemical and photochemical reaction rates were updated to take into account recent evaluations [Atkinson et al., 1997b; Sander et al., 2003]. The model ability to simulate large scale meridional gradients and long term trends was tested using ¹³Kr.</td>
</tr>
<tr>
<td>CHEM3</td>
<td>8-box global Eulerian transport model calibrated against SF₆, allowing simulation of long-term trends of CH₄ mixing ratios and isotopic composition (¹³C/¹²C and D/H). Yearly emission strengths of CH₄ sources in each box are tuned until the difference the model and measurements data is minimized. It is particularly well suited for non-equilibrium situations such as the anthropogenic increase of CH₄.</td>
</tr>
<tr>
<td>CHEM4</td>
<td>3-D general circulation chemistry-transport model at 2.8° latitude/longitude resolution and altitude to 0.01 hPa. The tropospheric chemistry scheme includes a comprehensive treatment of NMHCs. The model runs in either climatological mode for long term trends, or uses assimilated European Centre for Medium-range Weather Forecasting (ECMWF) data (40-year re-analysis if available) to represent actual meteorological conditions. An emissions database of gaseous precursors to ozone and acids over the 20th century is available to impose additional constraints/validation.</td>
</tr>
<tr>
<td>RAD1</td>
<td>Radiative forcing due to individual target molecules using detailed line-by-line and narrow band radiative transfer codes, used in conjunction with climatologies of temperature, humidity, ozone, cloud amount, and the reconstructed trends. Use of modelled latitudinal/vertical distributions improve the accuracy of the calculations for shorter-lived gases. A database of infrared absorption lines and cross-sections exists for most gases; additional cross-sections have been determined as part of CRYOSTAT where required.</td>
</tr>
</tbody>
</table>
6.3.2 PROCESS STUDIES OF GAS TRANSPORT IN FIRN AIR AND ENTRAPMENT IN ICE CORES

6.3.2.1 Motivation for firn process studies

The transport of gases through firn is dictated by a number of physical and chemical processes. Most present day models of such transport account only for gravitational effects and free-air diffusion. Other processes can be significant, notably thermodiffusion, convection/ventilation (both of which act predominantly in the upper few metres of firn), and chemical interactions between gases and the ice matrix. These processes are very poorly understood and are, for the most part, have hitherto been inadequately represented in firn models. CRYOSTAT studies aimed to study these effects by modelling observations in the Halley firn column.

In addition to firn and shallow ice studies, deep polar ice cores provide invaluable information on past climate and environmental changes. They offer a unique direct archive of past atmospheric composition trapped in the air bubbles or air hydrates preserved inside the ice matrix. The ice isotopic composition itself is commonly used to quantify past local temperature changes. Due to the common archiving of both past temperature changes and past greenhouse gas composition, ice cores provide a unique framework within which to study the phase relationships between past changes in climate and past changes in atmospheric radiative forcing. However, several key uncertainties limit our ability to fully exploit the ice core information:

(i) Gas age/ice age differences exist – and can be very large - because of the firn entrapment processes. Firn air becomes isolated from exchange with the atmosphere at a depth of between ~50 to 100 m, corresponding to an age of the surrounding snow that can range in age anywhere between decades and millennia depending on the accumulation rates and temperatures. The assessment of the phase relationships between past temperatures (commonly derived from the stable water isotopes of the ice phase) and past atmospheric composition (analysed from the gas phase) requires the modelling of this age difference. This in turn requires accurate modelling of the densification and close-off processes over time. The firn air sampling and analyses conducted with CRYOSTAT has provided key datasets for the assessment of existing models, and their improvement, over a wide range of surface characteristics [Landais et al., 2006].

(ii) Quantification of past temperature changes. The classical use of ice isotopic composition ($\delta^{18}O$, $\deltaD$) based on the observed present-day spatial linear relationship with temperature has been recently challenged. Past changes in moisture origin, precipitation intermittency, and condensation conditions were suggested to have significantly altered the consistency of the spatial isotope-temperature slope with time [Jouzel et al., 1997; Jouzel et al., 2003]. In Greenland, both borehole temperature reconstructions at the scale of glacial-interglacial changes [Dahl-Jensen et al., 1998], and a recently developed alternative paleothermometry method, based on firn $\delta^{15}N$ and $\delta^{40}$Ar thermal and gravitational diffusion [Severinghaus et al., 1998], have revealed a discrepancy of up to 200% in past temperature estimates in Greenland. In order to improve past temperature reconstructions from Greenland deep ice cores, the gas fractionation method requires an improved knowledge on firn air convection, gas diffusion processes (including the estimation of the thermal fractionation coefficients), heat diffusion in the firn, and close-off processes. Therefore, CRYOSTAT firn air sampling aimed, in addition to the reconstruction of atmospheric composition history, to apply a variety of methods in order to improve the understanding of $\delta^{15}N$ and $\delta^{40}$Ar fractionation inside a variety of present-day firns.

(iii) Elemental fractionation. Gases with small atomic diameters are able to permeate through the ice or along grain boundaries or micro-cracks. There are two occasions where this effect plays a role: (1) such gases may escape during storage of the ice cores; and (2) gas fractionation may occur at the firn-ice transition. For the interpretation of ice core records of the past atmospheric composition it is very important to quantify such effects. An application of oxygen loss at the firn-ice transition for dating old ice has recently been proposed by Bender [2002].
CRYOSTAT studies have addressed all of the above issues with utility not only to CRYOSTAT science (i.e. firm air and shallow ice from the last two hundred years), but also the wider glaciology and paleoclimate science community.

6.3.2.2 Influence of seasonal variations in surface convection on the diffusive column length

During the 2003/04 firm air samples were collected at Halley, Antarctica from the semi-permanent 21 m firm hole (see Section 6.3.1.1). A year around set of firm air samples were analyzed for various isotopes (δ^{15}N, δ^{18}O, δ^{38}Ar), element ratios (δO2/N2, δAr/N2, δAr/O2) and elements (CO2) by mass spectrometry (Finnigan MAT Delta Plus XL IRMS). From the firm air profiles a strong attenuation of the seasonal temperature induced variations was observed and could be attributed to ventilation of the uppermost layers of the firm column (down to approximately 0.4 m depth). The convective zone was simulated by an approach of Severinghaus et al. [2001], where vertical mixing of air is enhanced by eddy diffusion. With this method it was possible to derive a seasonal cycle in the ventilation strength with maximum values occurring in autumn and spring. This asymmetric seasonality alters the levels of concentration and isotope ratios at the firm-ice transition (close-off depth). This effect is especially important for δ^{15}N, which is taken as a measure for the diffusive column height in order to estimate the age difference between gas and surrounding ice for the interpretation of deep ice cores [Schwander et al., 1997].

One-dimensional diffusion model

Air movement in the porous firm can be described with a one-dimensional diffusion equation [extended model of Schwander et al., 1993]:

\[
\frac{\partial c}{\partial t} = \frac{1}{s} \frac{\partial}{\partial z} \left[ s \cdot D(z,T) \left( \frac{\partial c}{\partial z} - \frac{\Delta mc}{kT} + \frac{\alpha c}{T} \frac{\partial T}{\partial z} \right) \right]
\]

where \(c\) is the concentration, \(t\) the time, \(z\) the firm depth, \(\Delta m\) the mass difference of a gas to the mass of air, \(g\) the gravitational acceleration, \(k\) the Boltzmann constant \((k = 1.38066 \times 10^{-23} \text{J} \text{K}^{-1})\), \(T\) the temperature, \(s\) the porosity and \(D\) the diffusion coefficient. The model considers ordinary molecular diffusion driven by the concentration gradient \(\partial c/\partial t\), gravitational enrichment \(\Delta mc/kT\) of heavier species compared to the lighter ones with increasing depth [Craig and Wiens, 1996; Schwander, 1989] and the thermal diffusion effect \(\alpha c/T \cdot \partial T/\partial z\). The latter process describes the tendency of heavier species to move towards the colder regions within the firm and is thus, driven by the temperature gradient within the firm column.

Simulation of the convective zone

Convection in the firm was simulated by adding to the ordinary diffusion an eddy diffusion term \(D_{eddy}\) [according to Severinghaus et al., 2001]:

\[
\frac{\partial c}{\partial t}_{eddy} = s \cdot D_{eddy}(z) \left( \frac{\partial^2 c}{\partial z^2} \right)
\]

where

\[
D_{eddy} = D_0 \cdot \exp \left( -\frac{z}{z_p} \right)
\]

With this formulation the simulation of the convective zone has two free parameters, which are the surface diffusivity \(D_0\) and the penetration depth \(z_p\) controlling the vertical decay of the process. \(D_0\) is on the order of magnitude of the molecular diffusion coefficient, and \(z_p\) is less than one meter for Halley Station.
Seasonal cycle of ventilation strength

Figure 5 shows measured and modelled δ¹⁵N profiles for six different sampling dates ranging from spring to winter of the year 2003. The development of the profiles with increasing depth is characterized by the gravitational enrichment of the heavier ¹⁵N¹⁴N (mass 29) compared to the lighter ¹⁴N₂ (mass 28) and the temperature induced bell-shaped deformation. As expected from the seasonal temperature amplitude in the firn, δ¹⁵N is enriched on the surface in Austral winter and depleted in summer.

In Figure 5(a) model runs are based on the diffusion model without consideration of surface convection. Comparison of data and model shows that the seasonal amplitude is not reproduced properly by the model especially for the samples taken within the first half of the year (19.02.03 – 27.06.03). Thus, another process must play a role in Halley firn, which is surface convection, i.e. a vertical displacement of air superimposing the air mixing driven by diffusion. Convection in the upper firn layers reduces the effect of thermal diffusion.

![Figure 5](image)

**Figure 5.** Measured (symbols) and modelled (lines) firn air profiles from Halley for (a) the diffusion model without convection and (b) with an implemented eddy term.

The model with the eddy term was fitted to the data by adjusting the two free parameters of surface diffusivity D₀ and penetration depth z₀ (Figure 5(b)). As it turned out the convection process has a seasonal cycle with maximum values in autumn and winter, i.e. within the first half of the year (Figure 6), where the penetration depth is up to 0.4 m and the surface diffusivity on the order of magnitude of the molecular diffusion Dₘ. This implies that the temperature induced seasonal variations in the firm air profiles are no longer balancing each other, i.e. a shift in the isotope ratio will remain down to the close off depth, and hence also appear in the air bubbles within the ice.

Implications for ice core records

δ¹⁵N has been used as a measure for the past evolution of the diffusive column heights (DCH), taking into account the influence of gravitation and thermal diffusion. A parameterisation of the convection term could be implemented in the model for future studies. This could provide additional clues for some observations that are not fully understood to date (see sections below).
6.3.2.3 Fractionation at the firm-ice transition

The elemental and isotopic ratios of noble gases (He, Ne, Ar, Kr, and Xe), oxygen and nitrogen measured in firm air from two sites demonstrated very evidently a fractionation of gases with small atomic diameters. The first set of samples was taken in 1998 at DI (FIRETRACC project). The second set was taken in 2001 at NGRIP (CRYOSTAT). He and Ne were strongly enriched relative to Ar with respect to the atmosphere in the air near the close-off depth at around 50 – 70 m. The enrichment increases with depth and reaches the maximum value in the deepest samples just above the zone of impermeable ice, where no free air could be extracted anymore. Similarly, elemental ratios of O$_2$/N$_2$, O$_2$/Ar and Ar/N$_2$ increased with depth. In contrast, but in line with expectations, isotopic ratios of $^{15}$N/$^{14}$N, $^{18}$O/$^{16}$O, and $^{36}$Ar/$^{38}$Ar showed no significant enrichment near the close-off depth. The observed isotopic ratios in the firm air column can be explained within the uncertainty ranges by the well-known processes of gravitational enrichment and thermal diffusion. To explain the elemental ratios, however, an additional fractionation process during bubble inclusion has to be considered. We implemented this additional process into our firm air model [Huber et al., 2006] where we followed the approach used by Spahni et al. [2003]. In every time step a fraction of air was added to the closed pore space by removing it from the open pores at this depth. In addition to Spahni et al. we assumed a constant fractionation factor for each gas species during bubble inclusion. The fractionation factors were found by fitting model profiles to the data (Figure 7). We found very similar close-off fractionation behaviour for the different molecules at both sites. For smaller gas species (mainly He and Ne) the fractionation factors are linearly correlated to the molecule size, whereas for diameters greater than about 3.6 Å the fractionation seems to be significantly smaller or even negligible (Figure 8).
Figure 7. Noble gas ratio measurements from NGRIP. The solid lines are the diffusion model results with adjusted close-off fractionation factors whereas the dashed lines represent model results without the close-off fractionation.

Figure 8. Close-off fractionation factors from the model fits of NGRIP (triangles) and Devon Island (circles), plotted against their diameter. Close-off fractionation factors are significantly below one for small molecules, and are approaching one with increasing size. Close-off fractionation for molecules larger than the critical size of about 3.6±0.1 Å were not distinguishable from unity within the uncertainty range.

Different diffusion processes have been discussed in prior literature (Poiseuille diffusion, molecular diffusion, effusion, Knudsen diffusion, steric diffusion, etc. [Bender et al., 1995; Craig et al., 1988]), but none of them can explain the detected size dependent behaviour properly. The mass of the molecule is not important, since the effect on isotope ratios is very low. The fractionation seems to be only size dependent with a critical size of about 3.6 Å. A possible explanation for this could be the diffusion of molecules through channels in the ice lattice. From our findings we
believe that the effect of close-off fractionation is nonexistent or at least very small for isotope ratios and for large molecules like Xe, Kr, N₂, CO₂, CH₄, and N₂O. This is an important confirmation for the integrity of polar ice cores as a climate archive of the ancient atmospheric composition of these gases.

The findings also help to improve firn gas models because the observed fractionation is very sensitive on fluctuation of the permeability and thus diffusivity within and above the bubble close-off zone. Variations in the diffusivity profile, like quasi-impermeable layers, can be better assessed and implemented in the models.

6.3.2.4 The δ¹⁵N problem

Firm models simulate the firn densification (sintering) based on more or less empirical densification laws. Then they compute the mixing of the air in the pore space of the firn layer. It is assumed that the near surface layer is at least partly mixed by airflow (convection, wind pumping). Below is a zone with stagnant air where mixing is predominantly made by molecular diffusion. At the firn-ice transition air is occluded into bubbles. In the transition zone there is still open pore space, but below a certain depth there exist impermeable layers or layers with near-zero diffusivity, which prevent practically any further vertical gas exchange. This depth is termed lock-in depth (LID). The gravitational settling of heavier isotopes (¹⁵N, ⁴₀Ar) stops at the LID and the isotopic ratios level out to a constant value below this depth. Accordingly the zone between LID and the final close-off depth is termed the non-diffusive zone [Sowers 1992].

The LID can thus be estimated from firmification models or from the air isotopic composition (δ¹⁵N and δ⁴₀Ar). Both methods give consistent results for Greenland and Antarctica at present climatic conditions. This confirms that firmification models correctly reproduce the present LID over a large range of surface conditions. However, a systematic mismatch is observed for the Last Glacial Maximum (LGM) at many Antarctic sites. This problem creates some discomfort, because obviously the present understanding misses something. Landais et al. [2006] have reviewed several hypotheses that have been proposed to explain the discrepancy. These hypotheses include:

(a) varying thickness of the convective and/or non-diffusive zone

(b) extrapolation of firm models to LGM conditions is inappropriate

(c) thermal fractionation not taken into account

(d) inaccuracy of palaeo-temperature and/or palaeo-accumulation estimates.

New δ¹⁵N measurements from two coastal Antarctic sites (Kohnen Station and Law Dome) provide depth estimates different from firmification model calculations (Figure 9). Hypotheses (a) to (c) can only explain a minor part of the discrepancy for those sites with glacial conditions in the range of polar climatic conditions presently observed. The discrepancy can, however, be resolved by revising the estimate of past accumulation rates. δ¹⁵N measurements can, therefore, help to constrain past accumulation rate and improve ice core dating. But at low accumulation sites on the Antarctic plateau neither of the hypotheses or a combination of them could fully explain the observed isotopic ratios in the air from LGM.
Figure 9. $\delta^{15}$N measurements on the EDML ice core (grey). $\delta^{15}$N evolution from the Arnaud et al. [2000] model forced by surface conditions (accumulation rate and temperature) assumed to be modern levels for Early Holocene (EH) and deduced from the water isotopes for LGM (black line). As we used the steady-state model by Arnaud et al. [2000], we simulate only one mean value for $\delta^{15}$N for the LGM and one for the EH. The modelled $\delta^{15}$N signal between LGM and EH should therefore not be considered with high confidence.

6.3.2.5 Thermal gradients in the firm column

Temperature gradients in the firm lead to gas fractionation by thermal diffusion. Moreover such gradients affect firm densification, which is strongly temperature dependent. Thermal gradients are induced in the upper firm layers by seasonal temperature variations and in the whole firm column by abrupt temperature shifts (Dansgaard-Oeschger events). At sites with very low accumulation rates a thermal gradient is observed through the whole ice sheet. This gradient is caused by the geothermal heat flux in connection with the low vertical heat advection.

Goujon et al. [2003] have, as part of CRYOSTAT, developed a new firm-model that includes a thermal model of the whole ice sheet. The model improves the estimate of variations of close-off characteristics (density, close-off depth, delta age) in relation with past climate parameters (temperature and accumulation rates). In addition, the model allows a reconstruction of the evolution of gravitational and thermal isotopic fractionations in firm. Under present-day conditions, the modelled profiles are in good agreement with the available temperature measurements in firm. The comparison of the modelled $\delta^{15}$N results to measurements allows to better constrain the $\delta^{18}$O-temperature relationship, used to infer the surface temperature history, and the model can help to validate the long-term borehole-based temperature.

The model reproduces well the evolution of $\delta^{15}$N at high accumulation sites (e.g. Greenland as shown in Figure 10), but there are difficulties to model low accumulation sites during glacial time, as discussed in the previous section.
6.3.2.6 Is there natural convection in firn?

During winter the surface of the polar ice sheets is about 20 to 25 K colder than the mean firm temperature. Potentially this could cause instability in the stratification of the firm air. We have investigated the possibility whether the surface layers could be mixed by such convection (Bénard type convection). The criterion for onset of Bénard convection is given by the Rayleigh-Darcy number Ra:

$$Ra = \frac{\rho_f g \beta_f k \Delta T r}{\mu D_m}$$

Typical values of parameters for polar sites are: $\rho_f$ (fluid density) = 1 kg m$^{-3}$; $g$ (acceleration due to gravity) = 9.81 m s$^{-2}$; $\beta_f$ (fluid volume expansion coefficient) = 0.004 K$^{-1}$; $k$ (permeability) = 4×10$^{-9}$ m$^2$; $h$ (layer thickness) = 10 m; $\Delta T$ (temperature difference) = 25 K; $r = (\Delta c)_f/(\Delta c)_m$ (volume heat capacity ratio fluid/porous medium) = 1.5×10$^3$; $\mu$ (dynamic viscosity) = 1.6×10$^{-5}$ Pa s; $D_m$ (thermal diffusivity of porous medium) = 7×10$^{-7}$ m$^2$ s$^{-1}$. This results in a numerical value of Ra = 5.2. Empirical critical values Ra, for the onset of convection are between 3 and 40.

Wintertime conditions on polar ice sheets are thus just in the critical range. Using a 3-D finite element convection model (Fefs Flow) we could simulate Bénard type convection, when using slightly higher temperature gradients. However the time required to build up convection cells in the model was on the order of several years, i.e. typical polar conditions are too close to the critical Raleigh-Darcy number to start up convection during the winter months. But the model has also shown that uneven temperature distribution on the surface can create substantial air flow in the near surface layers. Such uneven temperature field could result from wind-pumping or shadowing by topographic features (e.g. sastrugis).

6.3.2.7 Seasonal cycle of trace gases at Halley

Throughout 2003 and 2004 ambient and 1 m subsurface samples were collected first monthly (2003) and then weekly (2004) at Halley, Antarctica using a novel in situ firm air sampling system. The data from 2004 is still being quality controlled. From the samples collecting during 2003 the seasonal cycles of CH$_3$I, CHCl$_3$, CHBrCl$_2$, CHBr$_2$Cl, CHBr$_3$, CH$_2$Br$_2$ and CH$_2$BrCl are now already determined for the first time in Antarctica. The seasonal amplitudes for the brominated species (winter:summer) were consistent with the reported literature for a variety of polar sites in both hemispheres (mostly in the Arctic) [Butler et al., 2004; Cicerone et al., 1988; Rasmussen and Khalil, 1984; Sturges et al., 2001; Yokouchi et al., 1996]. For example, the phase and amplitude of
the seasonal cycle of CHCl₃ was consistent with that reported for Cape Grim, Tasmania [O’Doherty et al., 2001; Prinn et al., 2000], although a lower annual average was observed (Figure 11 (a)). The phase (winter maximum, summer minimum) of the seasonal cycles for CHBr₃ and CHBr₂Cl were observed to be in direct anti-phase to the reported cycles for the Arctic [Cicerone et al., 1988; Yokouchi et al., 1996] as expected due to seasonal variations in the OH and photolysis sinks. However, the phase of CHCl₃, CHBrCl₂ and the dihalomethanes (CH₂BrCl and CH₂Br₂) showed a −3 month inter-hemispheric shift. This would suggest that for these species there is likely to be either a significant influence of interhemispheric transport affecting the Southern Hemisphere seasonal cycle or a strong seasonal cycle in the southern hemisphere sources or more likely a combination of both.

At Halley, there was evidence, from comparisons of the ambient and 1m subsurface samples, for elevated concentrations of CH₃I, C₂H₅I, CHBr₃, CHBr₂Cl, CHBrCl₂, C₂H₅Br and CH₂BrCl within the snow pack relative to the overlying atmosphere (Figure 11 (b); shown for CH₃I only). The timing of these elevated concentrations was after the austral polar sunrise, and then through austral summer, which suggested a possible photochemical production mechanism within the shallow snow similar to that reported for CH₃I and C₂H₅I at Summit, Greenland [Swanson et al., 2004]. This indicates that deep firm profile measurements of these gases may be biased by summertime in situ production, and may not truly represent atmospheric composition for these particular species. Conversely, it gives us confidence that the reconstructed trends of gases such as CHCl₃ are indeed representative of trends in the overlying atmosphere.

Further work on processing the data from the deeper firm layers at Halley is still in progress.

![Figure 11](image.png)

**Figure 11.** Measurements of monthly ambient and 1m Halley firm air for 2003 of (a) CHCl₃ (with superimposed seasonal cycle from Cape Grim, Tasmania [O’Doherty et al., 2001]); and (b) CH₃I in the same samples (with seasonal cycle fitted to ambient data and plot of solar irradiance).

### 6.3.3 TRENDS AND BUDGETS OF CARBON CYCLE GASES AND N₂O

#### 6.3.3.1 Introduction

The CO₂, CH₄ and (to a lesser extent) N₂O trends since pre-industrial times are very well-known. This results both from atmospheric monitoring network set up over the last decades, and from previous cryospheric studies where both ice core and firm air samples were collected and analysed for these trace-gas mixing ratios.

In the frame of CRYOSTAT, it was important to determine the mixing ratio profiles of CO₂ and CH₄ in firm air. Indeed CO₂ and CH₄ firm air profiles represent the primary measurements required for parameterising the firm air diffusion models (see Section 1 “sample collection and methodologies”).

But our main focus was to progress in the attribution of sources and sinks in the evolving budget of carbon cycle gases and N₂O, through a comprehensive study of their stable isotopic ratios and trends. Numerous questions remain unanswered regarding the causes of their recent increase,
and the evolution of the stable isotopic ratios provides a unique means to reduce the range of scenarios able to explain this increase.

6.3.3.2 CO₂, CH₄ and N₂O trends

CO₂ and CH₄ mixing ratios were measured on NGRIP and Berkner firm air samples by CR4, using gas chromatography and calibration against international standard prepared by CSIRO (Australia). Compared with trends obtained from monitoring networks, the Cape Grim air archive and the ice core measurements from Law Dome (Antarctica), these data have been the cornerstone of the firm air diffusion model. They allowed us to produce the primary diffusivity profiles on which other trace compounds have been scaled, according to their relative diffusivity in air with respect to CO₂ or CH₄.

N₂O mixing ratios were measured on NGRIP and Berkner firm air samples by AC10, in parallel with stable isotopic measurements, using a dedicated system coupling a gas chromatograph and an isotopic-ratio mass spectrometer. The resulting profiles were used to check the suitability of the firm air samples for N₂O investigations, by comparing these measured profiles with the modelled ones (Figure 12).

![Figure 12. N₂O mixing ratio as a function of depth in NGRIP and Berkner Island firm air (squares) and ice (rhombus). The horizontal error bars are 1σ uncertainty. The continuous lines correspond to the output of the firm air diffusion model fed with the atmospheric N₂O trend reconstructed from ice core and atmospheric monitoring measurements (Bernard et al., 2006). Measurements and model outputs show an excellent agreement.](image)

6.3.3.3 CO₂ isotopes

The temporal evolution of the $^{13}$C/$^{12}$C ratio of atmospheric CO₂ has already been carefully determined by our Australian colleagues from CSIRO, using the Law Dome (Antarctica) ice cores and firm air samples, the Cape Grim air archive and atmospheric measurements at monitoring stations [Franck et al., 1999].

In the frame of CRYOSTAT, we performed measurements of both $^{13}$C/$^{12}$C and $^{18}$O/$^{16}$O of CO₂ in Dronning Maud Land, Dome C and Berkner firm air. A complicating factor in such studies is the potential reaction between gases and the firm/ice matrix. CRYOSTAT measurements have shown that CO₂ oxygen isotope exchange may operate on short time scales with a clear correlation to firm temperature. We suggest the CO₂ exchange rates (expressed as a half-life, T½) be used as a new characteristic of firm sites, giving a measure of hydration activity in firm, and possibly an index of firm metamorphism near close-off depth [Assonov et al., 2005]. The change in the isotopic composition of CO₂ at depth is shown in Figure 13(a) for the three sites in Antarctica. We have used the firm air diffusion model of Rommelaere et al. (1997), with the effective CO₂ diffusivity profile adjusted according to Fabre et al. (2000) to date the profile, and hence determine exchange times. The strong dependence of T½ with temperature is shown in Figure 13(b).
Figure 13. $^{13}$C and $^{18}$O variations (also $^{14}$C) in CO$_2$ from firn air at the given depths (a); and the logarithm of the derived exchange rate constant versus the inverse of firn at the three sites (b).

6.3.3.4 CH$_4$ isotopes

In the frame of our former EC project FIRETRACC/100, we had been able to reconstruct the temporal trend of both the $^{13}$C/$^{12}$C and the D/H ratios of methane, over the last 50 years. Within CRYOSTAT, the reconstruction of the $^9$CH$_4$ of CH$_4$ has been extended back to the pre-industrial time, by a combination of firn air and ice core measurements. This work constitutes a "first" from CRYOSTAT: although a few ice core measurements had been performed in the late 1980s by Harmon Craig and his colleagues at Scripps (USA), no reconstruction was available covering the full anthropogenic CH$_4$ increase.

Our approach relied on an on-going collaboration with Dr. Todd Sowers at PennState University (USA). With NSF support, he has been able to collect firn air samples at South Pole station, during two expeditions held in 1995 and 2001. The South Pole firn air samples provide the oldest firn air ever extracted from polar ice caps, dating back to the early 1900s for CH$_4$. The two sets of firn air tanks have been measured by CR4, using a custom pre-concentration line coupled with a gas chromatograph and an isotopic-ratio mass spectrometer.

As the same protocol and calibration gas were used on the 1995 and 2001 firn air batches, it allowed us to calculate that $^9$CH$_4$ has increased by an average of 0.06 ± 0.02‰ per year over the 6 years between samplings [Sowers et al., 2005].

Combining the firn air measurements made by CR4 and the ice core measurements performed by T. Sowers at PennState University (on Antarctic Siple Dome ice), we show that the $^9$CH$_4$ of atmospheric CH$_4$ has increased by 1.8 ± 0.2‰ between 1820 A.D. and 2001 AD (Figure 14, Sowers et al., 2005). The $^{13}$CH$_4$ changes in both data sets are the result of an increase in the relative proportion of CH$_4$ sources with elevated $^{13}$C/$^{12}$C isotope ratios. In collaboration with T. Mark at the University of Heidelberg (Germany), we used an eight-box model of the atmosphere to test scenarios of CH$_4$ sources since pre-industrial, against our atmospheric reconstruction. One conclusion of our work is that the observed trend could have involved a 16 Tg/yr increase in CH$_4$ emissions associated with biomass burning over the past two centuries.

We also measured $^{13}$CH$_4$ in Berkner and NGRIP firn air. Due to the reduced age of the gas at close-off depth compared to South Pole, these measurements did not allow to improve the trend deduced from the latter site. On the other hand, NGRIP allowed us to constrain the trend for the most recent period, in the northern NH. It suggests that $^{13}$CH$_4$ increased by 0.35 ‰ since the 1950s, i.e. with an average of 0.007 ‰ per year, significantly smaller than over Antarctica.

In addition to the experimental work, CR4 conducted a sensitivity study of the tropospheric $^{13}$C/$^{12}$C ratio of CH$_4$ to changes in the chlorine load in the stratosphere (Figure 15). The approach relied on a two-dimensional photochemical model including the strong isotopic fractionation associated with the oxidation of CH$_4$ by Cl.
It suggests that this factor could be responsible for an increase of the $^{13}$C/$^{12}$C ratio of CH$_4$ by about 0.3‰ since the 1970s (Figure 15), i.e., a significant part of the overall enrichment of CH$_4$ observed from firm air and ice core reconstructions since pre-industrial time.

**Figure 14.** Upper graph: depth profile of the CH$_4$ mixing ratio (left), $^{13}$CH$_4$ (middle) and $^{13}$CH$_4$ difference between the 1995 and 2001 sampling, as a function of depth in South Pole firm. Note the inversion of the $^{13}$CH$_4$ trend in the deepest section of the firm. Being observed for the first time in firm due to the unusually old age of the gas in the close-off range of South Pole, this feature results from the difference of diffusion coefficient between the two isotopologues of CH$_4$.

Lower graph: temporal evolution of the CH$_4$ mixing ratio and the $^{13}$CH$_4$ over the last 150 to 200 years. The rainbow lines correspond to the envelope of atmospheric scenarios agreeing with the firm air measurements, when used as input to the firm air diffusion model. The blue squares are results obtained on Siple Dome ice samples. The black, green and red lines correspond to the $^{13}$CH$_4$ atmospheric signature in the southern box of the BOSCAGE box model, when considering an anthropogenic contribution to biomass burning of respectively 20%, 30% and 70%.

The comparison between the BOSCAGE model output and the firm air and ice core reconstruction suggests that the biomass burning component of the CH$_4$ budget could have increased by 16 Tg/yr since pre-industrial times [Sowers et al., 2005].
Additional information on the global methane budget may be derived from measurements of the deuterium content, but very few measurements exist to date. Figure 16 shows depth profiles of CH$_4$ and δD derived from the NGRIP air samples. The decrease in CH$_4$ concentration with depth is accompanied by a decrease in δD as expected, but surprisingly δD shows a minimum near the bottom of the firm core. Further work is continuing on these novel analyses and their interpretation.

**Figure 16. CH$_4$ and δD of CH$_4$ in NGRIP firm air**

### 6.3.3.5 N$_2$O isotopes

The greenhouse warming potential of N$_2$O is about 300 times greater than for CO$_2$. With a current rate of increase of 0.25% per year, there is a strong need to better characterize its budget and the origin of the anthropogenic perturbation of this budget.

A first attempt to determine the evolution of the $^{15}$N/$^{14}$N and $^{18}$O/$^{16}$O isotopic ratios of N$_2$O since pre-industrial time was carried on by Sowers and colleagues, based on the Greenland GISP2 ice core and South Pole firm air (Sowers et al., 2002). For both isotopic ratios, they found heavier values around 1800 A.D. than today, the δ$^{18}$O change being larger than the δ$^{15}$N one. This suggested that the industrial increase of N$_2$O did not involve a single source with a constant isotopic ratio signature. Sowers et al. proposed that their isotopic trend reflected a progressive shift from tropical sources to more temperate sources of N$_2$O, impacting the δ$^{18}$O signature through the meteoric water isotopic gradient with latitude.

In the frame of CRYOSTAT, CR4 and AC10 joined their expertise to provide the first-ever comprehensive isotopic investigation of N$_2$O since pre-industrial time: $^{15}$N/$^{14}$N and $^{18}$O/$^{16}$O isotopic ratios were determined, but also the position-dependent $^{15}$N/$^{14}$N ratio (on the central and terminal N atoms). For that purpose, a new methodology was developed to extract the gas from ~1
kg ice samples (see section 1). Measurements were carried on NGRIP and Berkner firm air and on a few ice samples dating from the 18th and 19th century (Figure 17). We used the LGGE firm air diffusion model in direct mode to determine the atmospheric scenarios able to reproduce the firm air profiles and ice core values. More than 1000 scenarios were tested based on exponential or polynomial functions representing possible atmospheric trends for each isotopic ratio. The envelopes of suitable scenarios are shown in Figure 18. The temporal trends for all isotopic ratios are negative; the difference between pre-industrial and present-day ratios amounts to 2.8 ‰, 2.4 ‰, 3.2 ‰ and 1.6 ‰ for $\delta^{15}$N$_2$O, $\delta^{14}$N-14N-O, $^{14}$N-$\delta^{15}$N-O and $\delta$N$_2$O$^{18}$O respectively [Bernard et al., 2006].

Figure 17. From left to right: profiles of N$_2$O mixing ratio, $\delta^{15}$N$_2$O, $\delta^{14}$N-14N-O, $^{14}$N-$\delta^{15}$N-O and $\delta$N$_2$O$^{18}$O as a function of depth in NGRIP (upper panels) and Berkner Island (lower panels) firm air (squares) and ice core samples (rhombus). Error bars are 1σ uncertainty. The continuous lines correspond to the best atmospheric scenario compatible with these profiles. The dashed lines represent the envelope of scenarios satisfying the statistical criteria [Bernard et al., 2006].
Our measurements thus conclude to a smaller depletion of $\delta N_2^{18}O$ than $\delta^{15}N_2O$, in contradiction to the findings of Sowers et al. [2002]. But in our case, the trends deduced from firn air and from ice core measurements are consistent, whereas they were significantly different in the case of Sowers et al. [2002]. Our observations are also more consistent with the fact that stratospheric fractionation of $N_2O$ imprints a larger shift on $^{15}N$ than on $^{18}O$.

The amplitude of the $\delta^{15}N_2O$ change since 1700 A.D. appears compatible with a scenario where half of the $N_2O$ increase comes from the use of natural fertilizers whereas the other half is related with synthetic fertilizers [Bernard et al., 2006]. Unfortunately the precision obtained on the intramolecular nitrogen isotopic signature does not yet allow us to make full use of this additional constraint; this will require additional analytical work.

6.3.3.6 CO mixing ratio and its isotopes

CO is the main scavenger of OH in the atmosphere today. As such, it can indirectly affect the methane budget, through changes of the OH levels and thus the main sink of CH$_4$ in the atmosphere today. Its budget is far from well quantified, and there is even an important debate going on about its temporal trend over the last decades to centuries. Very few ice core measurements are available so far (mainly performed by CR4) and atmospheric measurements cover a very limited spatial and temporal scale. In addition, harmonization of the CO calibration scales between laboratories is a complicated task making more difficult the observation of significant trends when combining different datasets. Firn air can help to constrain the recent history of this critical gas for atmospheric chemistry, and can provide additional constraints by tracing the causes of possible mixing ratio changes through isotopic measurements ($^{13}C/^{12}C$, $^{16}O/^{18}O$ and the $^{14}C$ content).

Figure 18. From top to bottom: temporal evolution of the $\delta^{15}N_2O$, $\delta N_2^{18}O$, $\delta^{14}N$-$^{14}N$-$^{15}O$, $^{14}N$-$\delta^{15}N$-$^{15}O$ of atmospheric $N_2O$ since 1700 A.D. based on firn air and ice core measurements performed on NGRIP (left panels) and Berkner Island (right panels) samples. The rainbow lines represent the best scenario (central line) and the envelope of atmospheric scenarios able to reproduce the firn air and ice core depth profiles. The green symbol and error bars (1σ uncertainty) correspond to the ice core measurements [Bernard et al., 2006].
In the frame of CRYOSTAT, CR9 conducted a comprehensive CO investigation on firn air collected at Dome C, DML and Berkner Island (Figure 19). In addition CR4 measured the CO mixing ratio on Dome C and DML samples, and its $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ isotopic ratios on Dome C samples (with support from AC5). Among the three sites, Berkner Island appears the only one where artefacts related with the collection of the samples did not jeopardize the production of a reliable atmospheric history. Still, $^{14}\text{CO}$ measurements indicated that in-situ production of this compound by cosmic radiation in the firn matrix precluded the attainment of any reliable temporal record.

Using the firn air diffusion model in direct mode, we conclude from the Berkner dataset that the atmospheric CO mixing ratio over Antarctica increased from ~38 ppbv in 1900 A.D. to a level of 52.5 ppbv in the time period 1990s-2000 (Figure 20; Assonov et al., 2006). This positive trend would have been accompanied by a slightly negative trend of $^{13}\text{CO}$, pointing toward an important role played by the increasing CH$_4$ mixing ratio on the southern CO sources. But the reconstructed trend of the CO mixing ratio requires that an additional contribution to the increase came from other sources of CO. Biomass burning is the likely candidate.

**Figure 19.** From left to right: CO mixing ratio, $^{13}\text{CO}$ and $^{18}\text{O}_{\text{CO}}$ as a function of depth, at the three Antarctic sites investigated in the frame of CRYOSTAT (Dome C, Dronning Maud Land and Berkner Island). Only the Berkner Island series appear free of sampling artefacts.

**Figure 20.** CO mixing ratio reconstructions based on CH$_4$ (red line) and CH$_3$Cl (blue line) trends, compared with the measured CO values in Berkner Island firn (black dots). The curve in the lower part shows the age distribution for the sample at 58.88 m, on an arbitrary scale.

In the Northern Hemisphere, our CO investigations performed on firn air collected at Devon Island (in the frame of FIRETRACC/100) showed that its mixing ratio is probably affected by a mechanism of in-situ production in the deeper part of the firn [Henderson et al., 2006]. AC5, in collaboration with CR4, performed CO measurements on NGRIP firn: no significant CO mixing
ratio increase is observed in the deepest samples compared to shallower ones. Although the scattering of the measurements does not allow yet to reconstruct any significant temporal trend, it indicates that there is hope to get access to such temporal trend from firn air collected at the coldest sites of the Greenland ice cap.

6.3.3.7 Conclusion

The unique combination of analytical expertise from different CRYOSTAT partners on the determination of carbon cycle trace gas and N₂O mixing and isotopic ratios from firn air and ice core samples has proved to be much successful. These new data now constitute cornerstones against which global models including the biogeochemical cycles of greenhouse gases and trace gases affecting atmospheric chemistry will be tested in the future. They already point out that biomass burning has been an important player responsible for part of the atmospheric trend of CH₄ and CO mixing ratios, and that the N₂O evolution probably results from the main action of increased use of natural and synthetic fertilizers in agriculture.

6.3.4 TRENDS AND BUDGETS OF HALOGENATED TRACE GASES

6.3.4.1 Summary of halocarbon measurements in the deep firn profiles

A summary of the halocarbon trace gas concentration profiles from Berkner Island and NGRIP made as part of CRYOSTAT are shown in Annex 1. Profiles are shown as mole fractions (i.e. concentrations in parts per trillion (ppt)) versus depth. The samples from greatest depth represent the oldest air, but this “age” is not a single figure but rather a probability distribution (Green Function) of ages. The age is different for different gases; i.e. it depends on the diffusion coefficient of the gas in question, its concentration gradients in the firn, molecular weight, etc. An identical atmospheric trend for the same gas will, furthermore, give rise to different depth profiles at different locations, due to differences in firn properties (temperature, accumulation rate, permeability, etc.).

The figures in Annex 1 give a qualitative impression of changing concentrations with time, and allow the measurements to be readily surveyed. It should be noted that the depth ordinate is not linear with age, but rather the time scale becomes increasingly compressed with age. As a general rule the mid-point of the profile is roughly representative of the 1980s, and the lowest depth air with average ages around the 1950s. Air in the top few metres (the ‘convective zone’) is well mixed and of about the same age as the surface air at the time of coring.

Some gases with very large seasonal variations (e.g. methyl iodide, bromoform, etc.) exhibit a pattern of changing annual concentrations in the upper ten or twenty metres. This manifests as steeply rising concentrations with depth in the upper firn, since firn coring is normally conducted in the summer when atmospheric concentrations of short-lived gases are at a minimum (due to loss by photolysis and reaction with hydroxyl radical). The larger subsurface concentrations are thus representative of the higher atmospheric concentrations during the preceding winter. Below this zone, diffusive effects obliterate any seasonal signals, and the concentrations observed in the firn are then equivalent to deseasonalised annual or multi-annual averages. The need to have prior knowledge of the annual cycle of short-lived gases to properly model the observed firn profiles is obvious from these profiles of the short-lived gases, and was part of the motivation of the in situ firm measurements at Halley (Section 6.3.2.7).

To reconstruct an accurate long term chronology for any gas requires the use of firn diffusion models as has been described in earlier sections. For the modelling to be successful either the likely atmospheric trend must be known (e.g. from emissions inventories), or a trial-and-error method employed (formalised in the case of the Monte Carlo deconvolutions used for the CH₄ isotope study described in 6.3.3.4). For gases which have relatively monotonic increases with time, i.e. which neither level off nor reverse in trend, then an iterative procedure can be used in which pseudo-dates are assigned to concentrations. This technique was partly developed under CRYOSTAT [Trudinger et al., 2002]. In this latter case an arbitrary atmospheric trend is taken as the initial input (e.g. a
linear trend from some notional preindustrial value, increasing to the known contemporary value at the time the firn was drilled). One or other of these various methods have been used for most of the gases measured, and these results are discussed in the following subsections. Trends for a few minor gases have not been reconstructed where their trends turn over.

Some general observations can be made from the depth profiles. Most halocarbons have risen very significantly since the 1950's; the only explanation for which can be as a result of industrial activity. The 'strong' greenhouse gases such as SF$_6$ and C$_2$F$_6$ have no preindustrial concentrations and are thus of entirely man-made origin. Some, such as some of the HFC gases (e.g. HFC-134a, HFC-143a, etc.) have risen over a very short time frame (e.g. mostly in the last twenty years), and are still rising very steeply. For shorter-lived gases, and those that are rising steeply, differences in absolute concentrations are clearly observed between the trends in the NH and SH. This is partly due to a lag in concentrations between north and south of about 1.5 years, so that for compounds emitted exclusively in the north (true for most man-made pollutants) it takes this time for SH concentrations to reach those in the north, even in the absence of any chemical loss. For gases with atmospheric lifetimes that are similar to this mixing time, then the effect of destruction in the troposphere during transport from the NH to SH is also readily apparent. Hence the absolute concentrations for HFC-134a, HFC-125, etc. are lower in the SH, whereas the similar concentrations of SF$_6$, CF$_4$, etc. in both hemispheres reflect their very long lifetimes in the atmosphere such that they are uniformly mixed throughout the global atmosphere.

Of the ozone depleting gases the majority have zero or near-zero concentrations at the bottom of the firn; i.e. they are associated with industrial emissions since the 1950s and have no natural sources. Some of the HCFCs (HCFC-141b) have increased the most in recent years. HCFC-22, on the other hand, has a longer time history. The CFCs have largely turned over and are no longer increasing in the atmosphere due to their control under the Montreal Protocol. One Protocol gas, CH$_3$CCl$_3$, has actually decreased significantly due to its short atmospheric lifetime (about 4 years).

Some ODSs do not drop to zero in the lower firn. Notable examples are CH$_3$Cl and CH$_3$Br. It is clear, therefore, that these gases have natural as well as industrial sources. These are important gases, as they are the largest natural sources of chlorine and bromine respectively to the stratosphere, and are thus two of the major controlling factors of the unperturbed stratosphere. CH$_3$Cl has risen a small but significant amount in the fifty year or more history represented by the firn profiles. The reason for this rise is unknown. CH$_3$Br also evidently has a natural background overlain by anthropogenic emissions. Both of these will be discussed further below, as will CHCl$_3$ which likewise appears to have a natural background. CCl$_4$ does not reach zero concentrations in the lowermost firn, but our ice core studies have show that it does decline to near zero in older air. CCl$_4$ is one of the earliest halogenated halocarbons to have been used on an industrial scale, with emissions predating the earliest firn air.

6.3.4.2 Modelling of long-lived Montreal Protocol gases

The CHEM2 model was used primarily to assess the trends and budgets of species for which emission flux data are available, the simulations were started at the beginning of the production of these anthropogenic compounds (1908 for CCl$_4$). As this model represents explicitly stratospheric chemistry, the destruction rates and lifetimes of CFCs, Halons and CCl$_4$ were calculated explicitly. A number of compounds destroyed in the troposphere were also simulated (CH$_3$CCl$_3$, HCFCs and HFCs). Only halocarbon concentrations were allowed to vary with time, thus the OH field was kept constant in order to detect deviations from measurements of halocarbon concentrations which could indicate a change in OH. This model study also allowed for deriving the spatial structure of halocarbon atmospheric concentrations for use as input for Global Warming Potential calculations. SF$_6$ and CF$_4$ were modelled for this purpose, although their destruction is too long to be significant in 100 years (3200 years and virtually infinite lifetimes respectively). In order to compare CHEM2 model results with CRYOSTAT firn measurements, modelled trends were used as input to the
FIRN1 firn diffusion model [Rommelaere et al., 1997; Fabre et al., 2000]. The model interlinkages are shown in Figure 21.

![Diagram of model interlinkages](image)

**Figure 21.** Joint use of CHEM2, FIRN1, and emission/concentration data in order to derive trends and budgets of halocarbon species.

The CHEM2 model was constrained with emissions reported to AFEAS [2004] (CFC-11, CFC-12, CFC-113, CFC-114, CFC-115, HCFC-22, HFC-134a, HCFC-141b, HCFC-142b). Recent estimates of non-reported emissions were used where available (CFC-11: McCulloch et al., 2001; CFC-12, CFC-113, HCFC-22, and HFC-134a: McCulloch et al., 2003). For CCl4, emission data from Simmonds et al. [1998] were used until 1995, and extrapolated using the same methodology of scaling to CFC production. McCulloch [1992] and Butler et al. [1998] were used for H-1211 and H-1302. CH3CCl3 emissions were taken from McCulloch and Midgley [2001] and SF6 emissions from Maiss and Brenninkmeijer [1998, 2000]. When required, extrapolation to 2002 was performed using AFEAS [2004] and UNEP [2002a] sales data and the same methodology as in earlier data sets for sales to emission conversion. This gives more reliable results than a simple linear extrapolation of emission data. During this project, the chemical and photochemical reaction rates were updated to take into account recent recommendations [Sander et al., 2003]. This implied a major change in lifetimes of several halocarbon compounds (see also section 6.3.4.3), thus the results obtained with both JPL 1997 [DeMore et al., 2003] and JPL 2003 [Sander et al., 2003] data are compared to provide a rough indication of uncertainties in trends and budgets due to atmospheric chemical losses.

The trends calculated with CHEM2 were used as input to FIRN1 model and compared to the five FIRETRACC and CRYOSTAT firm air measurement sites (see Figure 22 for an example and the complete results in Annex 2). Using sites with different drill dates, and from both hemispheres, allows for evaluating more accurately halocarbon trends and budgets. When a systematic shift between model results and firm air measurements was observed, a constant correction factor was applied to the emission flux. Such a model adjustment to CRYOSTAT generally allows for fitting correctly the experimental data at all five sites. The factors used mostly fall within known uncertainties as reported in UNEP [2002b], and Table 4. Model results were compared to available atmospheric trends and vertical transport was validated using comparison of CFC-12 with stratospheric balloon [Engel et al., 1998] and total column [Zander et al., 2000; NDSC/NCEP, 2005] measurements.
Figure 22. Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for CFC-12. Stars: UEA measurements with PLOT column, triangles: UEA measurements with DB5 column, green dashed line: CHEM2+FIRN1 results with JPL 1997 violet dashed line: kinetic constants, CHEM2+FIRN1 results with JPL 2003 kinetic constants, Black continuous line: CHEM2+FIRN1 results adjusted to firm data.

CFC-12 results are shown as an example (Figures 22 and 23). Similar results for other compounds are reported in Annex 2 which shows firm modelling output compared with measured depth profiles (Figures A2.1 – A2.19); and Annex 3 which shows a comparison with available existing direct atmospheric observations (Figures A3.1 – A3.3). In all cases the final "best guess" trends at CRYOSTAT sites for all species, including those for which emission estimates do not exist, are shown in Annex 4 (Figures A4.1 – A4.3). For CFC-12, the differences between model results and experimental data fall within the uncertainty limit (5-10%) reported in UNEP (2002b) (see Table 4). The comparison with atmospheric trends (CMDL and AGAGE networks) shows consistent slopes for recent years, but increased model-data differences between 1995 and 1990 suggest that CFC-12 emissions may have slowed down earlier than expected. A similar behaviour is observed for CFC-11 (Table 4). The best model-data agreement with both firm measurements and atmospheric record is obtained for CFC-113. However, the emission scenario overestimates its recent decrease (after 1998). By contrast, large uncertainties in the CCl₄ budget are related to an oceanic sink of uncertain magnitude [UNEP, 2002b]. No published atmospheric trends are available for CFCs 114 and 115. Only one firm air record was published for these compounds [Sturrock et al., 2002]. The use of a chemistry model constrained with emission data allowed for a first estimate of their source/sink equilibrium.
Table 4. Summary of uncertainty indicators and CRYOSTAT main conclusions for the species modelled with CHEM2. Column 2 indicates the systematic shifts between raw model results (CHEM2 with JPL 2003) and CRYOSTAT data; indications in italics (second line) show model-data differences reported by UNEP (2002). Columns 3 and 4 indicate lifetime and concentration differences between model runs using JPL 1997 and JPL 2003 photochemical data. Column 5 compares inter-calibration differences between UEA and NCAR measurements in CRYOSTAT with those reported in UNEP (2002) in italics.

<table>
<thead>
<tr>
<th>Species</th>
<th>Adjust factor</th>
<th>Δlifetime JPL 03/97</th>
<th>Δconc. JPL 03/97</th>
<th>Calibr. UEA-NCAR</th>
<th>CRYOSTAT findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFC-11</td>
<td>3% (5-10%)</td>
<td>-5.9%</td>
<td>-1.7%</td>
<td>1.0% (&lt;2%)</td>
<td>Slow down of emissions may be earlier than expected. Confirms a well constrained budget.</td>
</tr>
<tr>
<td>CFC-12</td>
<td>8% (5-10%)</td>
<td>-7.1%</td>
<td>-1.0%</td>
<td>1.5% (&lt;2%)</td>
<td>Slow down of emissions may be earlier than expected.</td>
</tr>
<tr>
<td>CFC-113</td>
<td>-3% (small)</td>
<td>-5.5%</td>
<td>-0.8%</td>
<td>1% (&lt;2%)</td>
<td>Recent emission decrease may be overestimated. Confirms a well constrained budget.</td>
</tr>
<tr>
<td>CFC-114</td>
<td>15%</td>
<td>-3.4%</td>
<td>-0.3%</td>
<td>20% (few data)</td>
<td>Lifetime smaller than previous estimates. First budget estimate.</td>
</tr>
<tr>
<td>CFC-115</td>
<td>5%</td>
<td>-13%</td>
<td>-0.25%</td>
<td>20.3% (few data)</td>
<td>Lifetime smaller than previous estimates. First budget estimate.</td>
</tr>
<tr>
<td>CCl₄</td>
<td>8% (fact 1.5-2)</td>
<td>2.5%</td>
<td>-2.8%</td>
<td>6% (3-4%)</td>
<td>Deepest firn samples consistent with insignificant natural source.</td>
</tr>
<tr>
<td>H-1211</td>
<td>0 (uncertain emiss.)</td>
<td>-69%</td>
<td>-41%</td>
<td>15.8% (10-15%)</td>
<td>Lifetime smaller than previous estimates. Uncertain emissions and calibration.</td>
</tr>
<tr>
<td>H-1301</td>
<td>0 (uncertain emiss.)</td>
<td>-5.2%</td>
<td>-0.8%</td>
<td>-19.8% (30%)</td>
<td>Uncertain emissions and calibration.</td>
</tr>
<tr>
<td>H-2402</td>
<td>-</td>
<td>-23%</td>
<td>-9.3%</td>
<td>-1.5%</td>
<td>New budget estimate.</td>
</tr>
<tr>
<td>SF₆</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>1.6%</td>
<td>Confirms a well constrained budget.</td>
</tr>
<tr>
<td>CF₄</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>First trend estimate.</td>
</tr>
<tr>
<td>CH₃CCl₃</td>
<td>0 (≤3%)</td>
<td>-4.6%</td>
<td>-8.8%</td>
<td>1.6% (3%)</td>
<td>Deepest firn samples suggest insignificant natural source. Small OH change over the last 40-50 years.</td>
</tr>
<tr>
<td>HCFC-22</td>
<td>8% (slightly&lt;0)</td>
<td>-7.6%</td>
<td>-5.7%</td>
<td>1.8% (&lt;5%)</td>
<td>Confirms emissions/sinks unbalance suggested by McCulloch et al., 2003.</td>
</tr>
<tr>
<td>HCFC-21</td>
<td>-</td>
<td>-22%</td>
<td>-22.5%</td>
<td>0</td>
<td>First trend and emission estimate.</td>
</tr>
<tr>
<td>HCFC-123</td>
<td>-</td>
<td>-7.6%</td>
<td>-14%</td>
<td>0</td>
<td>First trend and emission estimate.</td>
</tr>
<tr>
<td>HFC-134a</td>
<td>8%</td>
<td>-10.5%</td>
<td>-2.4%</td>
<td>0 (&lt;5%)</td>
<td>Emissions/sinks unbalance similar to HCFC-22.</td>
</tr>
<tr>
<td>HCFC-141b</td>
<td>35% (slightly&gt;0)</td>
<td>-24%</td>
<td>-6.9%</td>
<td>12.2% (&lt;5%)</td>
<td>Emissions/sinks unbalanced.</td>
</tr>
<tr>
<td>HCFC-142b</td>
<td>20% (slightly&gt;0)</td>
<td>-12.5%</td>
<td>-4.7%</td>
<td>-5.4% (&lt;5%)</td>
<td>Emissions/sinks unbalanced.</td>
</tr>
<tr>
<td>HFC-152a</td>
<td>-</td>
<td>-7.7%</td>
<td>-8.9%</td>
<td>0</td>
<td>First trend and emission estimate.</td>
</tr>
</tbody>
</table>
Figure 23. Comparison of CHEM2 model results (lines) for CFC-12 with atmospheric data (plus signs). Upper curves: trends at ground level at different latitudes (colours), lower left: stratospheric balloon measurements, lower right: infrared spectroscopic measurements of total column.

No model adjustment was necessary to obtain a very good agreement with data for CH$_3$CCl$_3$ atmospheric trends from the AGAGE network. As no change in OH occurs in our simulations, our results suggest that changes in OH remained very limited over the last forty to fifty years. As previously observed [McCulloch et al., 2003], the agreement is less satisfactory for HCFC-22. Our results suggest that a similar increase of emissions (8%) is necessary to equilibrate the HCF-134a budget. New source estimates [AFEAS, 2004] improved the results for HCFCs 141b and 142b but important adjustments remain necessary. Our results suggest that the budgets of HCFCs and HFCs are still less well understood than those of major CFCs and CH$_3$CCl$_3$.

As an alternative to historical emission data, the CHEM2 model can also be constrained with surface concentration data as a boundary condition. This approach was used for compounds with no available emission estimates (H-2402, HCFC-21, HCFC-123, HFC-152a). The trends and inter-hemispheric differences were estimated by trial-and-error using the FIRN1 diffusion model and comparison with CRYOSTAT data. As the model explicitly calculates the atmospheric sink of these compounds, this approach allows for estimating the emissions necessary to close their budgets and maintain the imposed surface concentration. Furthermore, re-imposing the calculated annual average flux as a CHEM2 boundary condition allows to simulate seasonal variations of concentrations due to photochemistry, which are important for HCFC-21, HCFC-123, HFC-152a. The reconstructed trends and emissions are provided in Annex 4.

6.3.4.3 Halocarbon lifetime modelling

The CHEM2 model extends up to 85 km altitude and thus allows calculation of lifetimes of long-lived halocarbon species. Chemical lifetimes are often considered as constants, but are in fact the inverse of globally averaged destruction rates, and may undergo temporal variations due, for example, to variations in oxidant concentrations. Another source of lifetime variations is
atmospheric transport. A pollutant emitted at the Earth's surface and destroyed only in the stratosphere (such as CFCs and Halons) has no chemical loss in the troposphere, therefore its lifetime is virtually infinite at the beginning of its emission, since its transport to the stratosphere requires several years before chemical destruction can begin. In the CRYOSTAT project, the amplitude and impact on calculated trends of such lifetime variations were quantified.

Even for very long lived compound (several hundred years), the equilibrium lifetime can be calculated within a few years because in the destruction region, the local lifetime is short. As atmospheric density is very small at high altitudes, this short local lifetime is still consistent with a long global lifetime. The model is initialized with very small concentrations, which are kept constant at the ground and an equilibrium concentration field is rapidly obtained. Calculations were performed with two widely used sets of chemical and photochemical reaction rates: JPL 1997 [DeMore et al., 1997] and JPL 2003 [Sander et al., 2003]. For most halocarbons, the most recent evaluation (JPL 2003) introduced absorption cross sections data at longer wavelengths and a temperature dependence for these cross sections. Reaction rates of halocarbons destroyed in the troposphere with OH were also re-evaluated. Our results are generally consistent with the latest global ozone assessment (Table 5). The lifetimes of CFC-114, CFC-115 and Halon-1211, however, appear to be significantly lower than previously thought. Other differences are commented in the comments to Tables 4 and 5.

Modelled yearly average lifetimes for 1975 and 2002 (Table 5) illustrate the time variations observed between the first emission peak of major CFCs and the recent period of concentration decline. The absence of time variations in lifetimes of halocarbons destroyed in the troposphere confirms the strong role of troposphere-to-stratosphere transport on transient lifetimes of halocarbons destroyed in the middle atmosphere, as well as causing the lifetime peak at the beginning of emissions (Figure 24, left panel). Time trends of all modelled halocarbon lifetimes are provided in Annex 5 (Figure A5.1 – A5.3).
Table 5. Photochemical lifetimes of halocarbons computed with CHEM2 model. Notes: (1) The oceanic sink is not taken into account in the CHEM2 lifetimes. (2) As lifetimes of compounds destroyed in the troposphere reported in UNEP, 2002b are scaled with respect to CH$_3$CCl$_3$, the new evaluation of CH$_3$CCl$_3$ reaction rate with OH (JPL 2003) induces an increased difference between CHEM2 with JPL 2003 and UNEP, 2002b for all halocarbons destroyed in the troposphere.

<table>
<thead>
<tr>
<th>Species</th>
<th>Equilibrium lifetimes</th>
<th>Transient lifetimes</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFC-11</td>
<td>45</td>
<td>46</td>
</tr>
<tr>
<td>CFC-12</td>
<td>100</td>
<td>93</td>
</tr>
<tr>
<td>CFC-113</td>
<td>85</td>
<td>76</td>
</tr>
<tr>
<td>CFC-114</td>
<td>300</td>
<td>178</td>
</tr>
<tr>
<td>CFC-115</td>
<td>1700</td>
<td>560</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>26</td>
<td>39</td>
</tr>
<tr>
<td>H-1211</td>
<td>16</td>
<td>32</td>
</tr>
<tr>
<td>H-1301</td>
<td>65</td>
<td>61</td>
</tr>
<tr>
<td>H-2402</td>
<td>20</td>
<td>33</td>
</tr>
<tr>
<td>CH$_3$CCl$_3$</td>
<td>5</td>
<td>4.4</td>
</tr>
<tr>
<td>HCFC-22</td>
<td>12</td>
<td>11</td>
</tr>
<tr>
<td>HCFC-21</td>
<td>1.7</td>
<td>1.8</td>
</tr>
<tr>
<td>HCFC-123</td>
<td>1.3</td>
<td>1.2</td>
</tr>
<tr>
<td>HFC-134a</td>
<td>14</td>
<td>12.5</td>
</tr>
<tr>
<td>HCFC-141b</td>
<td>9.3</td>
<td>8.0</td>
</tr>
<tr>
<td>HCFC-142b</td>
<td>17.9</td>
<td>16</td>
</tr>
<tr>
<td>HFC-152a</td>
<td>1.4</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Figure 24. Amplitude and impact of temporal variations in CFC-11 lifetime. Left: CFC-11 lifetime (full line) and emission flux (dashed line) between 1940 and 2002. Right: modifications of the CFC-11 trend when imposing a homogeneous CFC-11 sink in the whole atmosphere: the inverse of the equilibrium lifetime (long dashed line) and when imposing the equilibrium lifetime as a scaling factor to the calculated CFC-11 sink (short dashed line); the reference simulation is plotted as full line.

The trends and budgets of halocarbons destroyed in the stratosphere are often calculated using tropospheric-only models. In such cases, the chemical sinks are not calculated but a constant and homogeneous sink (the inverse of the equilibrium lifetime) is imposed in the whole atmosphere. We compared the results obtained this way (Figure 24 right, long dashed line) to our reference simulation (full line), and obtained a significant bias on the CFC-11 trend (about 8%). Similar tests carried out with other halocarbons destroyed in the stratosphere (Annex 6; Figures A6.1) showed that the strongest biases are observed for species having a relatively small lifetime and emitted over a long time period: the effect of the chemical sink on the trend is maximized in this case.

The above test does not allow for discriminating between the effects of a spatially homogeneous lifetime, and a time-independent lifetime. This is why a second test was performed (short dashed line in Figure 24 right). The chemical sink was calculated normally and then scaled with the inverse of the equilibrium lifetime. This suppresses the time variations in the chemical sink while keeping its normal spatial structure. The impact on the halocarbon trends is much smaller than with the previous test. This is consistent with the fact that the largest temporal variations of the lifetime occur at the very beginning of emissions, when these emissions are still small.

6.3.4.4 Modelling the effect of variation in spatial patterns of emissions: halon gas case study

In modelling the global abundance of trace gases to match the long term trends reconstructed from firn measurements, some latitudinal distribution of emission flux strengths is applied and is normally held constant. The actual geographic distribution of emissions is usually unknown, and instead some surrogate is used (often it is based on population, GDP, electricity generation capacity, or some similar metric). In truth the actual distribution makes little difference for gases with lifetimes that are long compared to mixing times in respective hemispheres. The same is not true of shorter lived gases where, for instance, some significant loss due to tropospheric chemistry may occur between the emission regions and the polar locations where the firn and ice core samples are collected. A remarkable illustration of this came to light during a CRYOSTAT study of the four known brominated "halon" gases (these are used as fire suppressants/extinguishers and are controlled under the Montreal Protocol). One of these gases, H-1202, is significantly shorter-lived (c. 3 yr) than the other three halons, but was observed to exhibit concentrations in firn air in the Arctic and Antarctic profiles that were more similar than would be expected for this lifetime.

In this example, the CHEM1 model was instead employed in conjunction with FIRN1 to study the effect of changing the global distribution of emissions [Reeves et al, 2005]. Different weightings
were applied to the 18 equal area latitudinal bands. Figure 25 shows the effect of modelling different latitudinal distributions (labelled A to H) for the location of NGRIP for each of the four halons. The distributions tested are shown in Figure 26. Distribution A is the “standard” distribution previously used to model a range of CFCs, HCFCs and HFCs with this model [e.g. Fraser et al., 1999] and is based on a number of industrial indices. The global emissions were first tuned to fit the observations at Dome C in the SH (not shown). At NGRIP (Figure 25) the two long-lived halons H-1301 and H-2402 show, as expected, essentially invariant modelled concentrations irrespective of which distribution of emissions is used (not all runs shown for clarity). In contrast the modelled trend for H-1202 at NGRIP is highly dependent on the latitudinal distribution assumed as is, to a lesser extent, H-1211. The best fit is when the ‘standard’ distribution if followed up until 1986 and then switches to distribution F where the emissions are from more southerly latitudes. This is consistent with the known shift in production and use of H-1211 from N. America, W. Europe and Japan before this date, to China afterwards. H-1202 is not known to be manufactured directly, but is believed to arise as a fugitive emission from the inefficient manufacture of H-1211.

Figure 25. Measured and model derived depth profiles of the four halons at NGRIP.
Figure 26. The latitudinal emissions distributions for model runs A to H. The percentage of the total emissions is plotted as a function of the central latitude of the model boxes.

6.3.4.5 Short-lived ODS modelling

There is a growing appreciation that short-lived halocarbons can, in fact, contribute to stratospheric ozone depletion since fast transport through the tropical tropopause by fast tropical convection is now known to be a primary route of injection for halocarbons in to the stratosphere, as discussed in the 2002 WMO/UNEP Scientific Assessment of Ozone Depletion (see Chapter 2; Ko et al., 2003). Little is known, however, regarding the sources of such short and very short-lived substances (VSLS), and even less about their long term atmospheric trends. The NGRIP firm profile has provided the first reliable long-term measurements of such gases in the NH.

Chloroform

CHCl$_3$ was measured in firm air from NGRIP, Dome C, DML and Devon Island. Figure 27 shows the CHCl$_3$ measurements plotted versus CFC-12 as a time ordinate instead of depth (see above). The samples collected in the convective zones (i.e., effectively surface air) are not included in the comparison plots (above 10m for NGRIP and Dome C, and above 3 and 5m for DI and DML, respectively) since these vary on a short time frame dependant on changing air mass, whereas the concentrations in the firm below this depth represent longer term average values. There is excellent agreement between the two Arctic sites (NGRIP and DI) and between the two Antarctic sites (DML and Dome C). The plot suggests that in the NH the atmospheric concentration of CHCl$_3$ has increased by almost a factor of 2, from 7 to 14 ppt, before declining in more recent times to around 10 ppt. CHCl$_3$ in the SH has also increased but only by about 2 ppt.

The CHEM1 model was employed to investigate the temporal evolution of CHCl$_3$ burden over the 20th Century and the anthropogenic contribution to the global budget. In order to match the observed firm air measurements at NGRIP the anthropogenic contribution to the total global CHCl$_3$ budget has been shown, with the aid of the 2D model, to have been close to 40% at the peak in atmospheric CHCl$_3$ in 1990 declining to ~19% in 2002. The 2D modelling shows that the atmospheric concentration of CHCl$_3$ has increased in both hemispheres from ~5 ppt to ~14 and ~10 ppt in the northern and southern hemispheres, respectively (Figure 28). The recent decline, during the 1990's, in atmospheric CHCl$_3$ concentrations was likely to be the result of changing working practices in the pulp and paper industry with a move away from elemental chlorine use to other bleaching technologies such as chlorine dioxide, which are understood to produce less chlorinated by-products, e.g., dioxins. The long term trend in source strengths that give rise to the best fit to the firm air measurements is shown as a global average in Figure 29. The best fit required that CHCl$_3$ from global paper and pulp production decline at the same rate as documented for the US, and that
emissions from drinking water level out after 1990, in accordance with moves in the US and Europe to reduce the amount of contact between disinfectant chlorine and organics in water (which gives rise to trihalomethanes and other chlorinated toxic organics).

![Graph showing CHCl₃ versus CFC-12](image)

**Figure 27.** Firn air measurements of CHCl₃ versus CFC-12 at NGRIP and DI in the Arctic and DML and Dome C in the Antarctic.

![Graph showing CHCl₃ in Northern and Southern Hemispheres](image)

**Figure 28.** Modelled atmospheric evolution of CHCl₃ during the 20th Century in both hemispheres.

![Graph showing trends in individual emissions of CHCl₃](image)

**Figure 29.** Trends in individual emissions from the major sources of CHCl₃ to the atmosphere: P+P = paper and pulp production, WC = water chlorination, OI = other industrial used to modelled the atmosphere evolution shown in Figure 27.
Other trihalomethanes (THMs) and dihalomethanes (DHMs)

The NH atmospheric concentrations of CHBr$_3$, CHBr$_2$Cl and CHBrCl$_2$ were observed to have increased during the 20$^{th}$ Century by $\sim$20% from measurements of NGRIP firn air (Figure 30). These increases equate to estimated anthropogenic fluxes of $20 \pm 6$, $0.78 \pm 0.17$ and $0.71 \pm 0.1$ Gg yr$^{-1}$ for CHBr$_3$, CHBr$_2$Cl and CHBrCl$_2$, respectively. CHBr$_3$ has been reported to contribute $\sim$95% [Allonier et al., 1999; Jenner et al., 1997] to the total THM's measured in coastal power plant effluent such that this is reported to be the dominant source of anthropogenic CHBr$_3$ [Quack and Wallace, 2003]. As a result the contribution of the other brominated THMs (CHBr$_2$Cl and CHBrCl$_2$) are much smaller and this difference may account for the much smaller estimated fluxes of these species relative to CHBr$_3$. This is in agreement with the observations of CHBr$_2$Cl and CHBrCl$_2$ being present at concentrations approximately 4 – 7% of CHBr$_3$ in a variety of coastal power plant effluents [Allonier et al., 1999; Jenner et al., 1997]. Interestingly, the estimated fluxes of CHBr$_2$Cl and CHBrCl$_2$ are $\sim$4% of the CHBr$_3$ flux, which would support the source of these species being the result of seawater chlorination.

Our results show that, in the case of bromoform at least, seawater chlorination far outweighs freshwater as an anthropogenic source of bromoform, and the small apparent atmospheric fluxes of the bromochloromethanes, which are believed to exceed emissions of bromoform in freshwater chlorination [Lepine and Archambault, 1992], also argues against a significant impact of freshwater chlorination on observed atmospheric THM concentrations. The estimated 20 Gg Br yr$^{-1}$ anthropogenic flux of CHBr$_3$ from the observed increase in the firn at NGRIP was comparable, within the likely uncertainties, with the $\sim$26 Gg Br yr$^{-1}$ estimated emission of CHBr$_3$ from water chlorination [Quack and Wallace, 2003]. The estimated anthropogenic fluxes for all three brominated THM's when compared to the estimated global fluxes [Ko et al., 2003] suggests that seawater chlorination could be a significant source ($\sim$10%) of these species to the atmosphere.

The 20$^{th}$ century history of CH$_2$Br$_2$ showed no change in concentration consistent with it being entirely natural in origin, in agreement with previous Antarctic firn air measurements [Sturges et al., 2001].

![Figure 30. Gravity corrected firn air measurements of CHBr$_3$, CHBr$_2$Cl and CHBrCl$_2$ versus CFC-12 at NGRIP.](image)

6.3.4.6 Perfluorocarbons

CF$_4$ and C$_2$F$_6$ are the two most abundant fully fluorinated gases in the contemporary atmosphere and are potent greenhouse gases (global warming potentials 6500 and 9200 times larger than carbon dioxide, respectively) as a result of both their very long lifetimes (>10000 years) and intense infrared adsorption situated near the “atmospheric window” region of the terrestrial radiation spectrum. CF$_4$ has previously been shown [Harnisch et al., 1996] to have a significant
natural background of approximately 50% of contemporary concentrations. Through the analysis of firn air from both hemispheres (NGRIP, Greenland and Berkner Island, Antarctica) and air recovered from Antarctic ice cores (Law Dome) the atmospheric concentrations of tetrafluoromethane (CF₄) and hexafluoroethane (C₂F₆) have been observed to have grown rapidly in the atmosphere post 1950 (Figure 31). These results also confirm a natural background of 36 ± 1.5 pptv for CF₄ whilst showing that C₂F₆ is entirely anthropogenic in origin with undetectable concentrations (<0.005 ppt) observed prior to ~1930.

CF₄ and C₂F₆ have known anthropogenic sources, mainly from the aluminium and semiconductor industries. Industrial aluminium production began in the 1880's and due to improvements in the Hall-Herault electrolytic process production increased dramatically during the 20th Century (www.aluminium-world.org). The relationship between CF₄ and C₂F₆ has been observed to change during the 1990's (Figure 32) as a result of reduced emissions of both CF₄ and C₂F₆ from the aluminium industry (~60%; www.aluminium-world.org) coupled with growing emissions of C₂F₆ from its increased use in the semiconductor industry (www.epa.gov). CF₄ and C₂F₆ contribute more than 55% of the radiative forcing of the fully fluorinated species (Figure 33) and these results have implications for radiative forcing calculations. The combined radiative forcing from CF₄ and C₂F₆ has been calculated to be 4.94 mW m⁻² in 2002.

Figure 31. CF₄ and C₂F₆ measurements in polar firn and ice from NGRIP, Berkner Island, Dome C (firn) and Law dome (ice).

Figure 32. The changing relationship between CF₄ and C₂F₆ as observed in NGRIP and Berkner Island firn air (right) associated with changes in emissions from aluminium smelting and semiconductor manufacture (left).
6.3.5 IMPLICATIONS FOR ATMOSPHERIC CHEMISTRY, COMPOSITION AND CLIMATE

6.3.5.1 Atmospheric chlorine trend

CRYOSTAT has measured essentially all of the source gases that provide the chlorine observed in the stratosphere. The amount of chlorine present in the troposphere from these gases is known as CCl\textsubscript{4}. Using the reconstructed time trends it is possible to plot a history of tropospheric CCl\textsubscript{4}, as is shown in Figure 34. This clearly shows the enormous increase in chlorine loading in the atmosphere from organic gases. In the NH total CCl\textsubscript{4} has increased by more than a factor of seven since preindustrial times (480 to 3690 ppt Cl). Total CCl\textsubscript{4} has been decreasing in the NH since 1993 and in the SH since 1995 (because of the transport time delay between the NH and SH). The decline, however, has been small (by about 7% in the NH and 5% in the SH). CCl\textsubscript{4} abundance is only slightly smaller in the SH than the NH because the majority of source gases are long-lived in the atmosphere compared to global transport and mixing times. This is the first time that such a complete inventory of chlorinated gases has been assembled for the entire 20\textsuperscript{th} century and, moreover, for both hemispheres.

Figure 35 shows a breakdown of the major classes of source gases contributing to CCl\textsubscript{4}(tot). The term VSLS refers to "Very Short-Lived Substances" (defined by Ko, et al., 2003 as having lifetimes of about half a year or less) and here comprises the sum of CHCl\textsubscript{3}, CH\textsubscript{2}Cl\textsubscript{2} and C\textsubscript{2}Cl\textsubscript{4} (several other VSLS were measured but were found to contribute only about a ppt or less each in the firm air measurements). The CFCs include minor CFCs such as CFC-114 and CFC-115, and also include H-1211 as the only chlorine-containing halon. From Figure 35 it can be seen that in preindustrial times CCl\textsubscript{4}(tot) was derived almost exclusively from CH\textsubscript{3}Cl with a very minor contribution from VSLS (exclusively CHCl\textsubscript{3}). More than 90% of the increase in CCl\textsubscript{4} in both hemispheres has been due to the CFCs together with CCl\textsubscript{3} and CH\textsubscript{2}Cl\textsubscript{2}. The chlorine loading from the CFCs plus CCl\textsubscript{4} alone has levelled out and is now decreasing slowly; slowly because although emissions of these gases have almost altogether ceased due to the Montreal Protocol, they are very long-lived and will decline slowly with time. Most of the decrease in CCl\textsubscript{4}(tot) has been due to the decline in CH\textsubscript{3}CCl\textsubscript{3} due to its short lifetime. It, alone amongst the organic chlorinated gases, has almost returned to pre-industrial (zero) levels. At this point the rate of decline of CCl\textsubscript{4}(tot) will slow down since further reductions will in future be dictated by the rate of destruction of the CFCs. In fact CCl\textsubscript{4}(tot) may even temporarily grow slightly because of increasing contributions from the HCFCs (although these are themselves regulated under the Montreal Protocol, but on a longer time frame than the CFCs). The three VSLS gases are all declining due to changing industrial practices (see above), and CCl\textsubscript{4} from VSLS should soon return to a pre-industrial level comprising only a background concentration of CHCl\textsubscript{3}.
Figure 34. Sum of chlorine (CCl3(tot)) from all significant chlorine-containing organic gases in both hemispheres.

Figure 35. Contribution of different halocarbons or groups of halocarbons to CCl3(tot) in (a) the Northern Hemisphere and (b) the Southern Hemisphere.

The tropospheric trend of CCl3 can be converted into a quantity termed Effective Equivalent Chlorine (EECl). This applies a factor for “relative fractional (halogen) release” (FR) for each constituent species where FR represents the amount of chlorine released in the mid-stratosphere relative to the amount of chlorine released by the same amount of CFC-11. FR factors were taken from Table 1.4 of Montzka et al. [2003] using the best estimate WMO numbers where available, or the values from Schaufler et al. [2003] in the same Table where not. Where neither are given then the value from the halocarbon with nearest atmospheric lifetime is used. An absolute fractional release factor of 0.8 for CFC-11 is used to correct all of the FR values, in common with Montzka et al. [2003]. For the VSLS species an FR of 1.2 was assumed (i.e. all of the gases reaching the stratosphere are assumed to fully degrade) but they were instead corrected for tropospheric loss using the ratios in the upper troposphere to marine boundary layer given in Table 2.10 of Ko et al. [2003]. EECI so calculated can also be readily converted to Effective Equivalent Stratospheric Chlorine (EESC) simply by adjusting the years for an approximate 3.5 yr time lag for transport of gases from the surface to the mid-stratosphere. The calculated trend for both EECl and EESC are
shown in Figure 36. They are qualitatively in agreement with Montzka et al. [2003] who showed measured and modelled EECI for 1910 to 2010, but our calculated peak EECI concentrations are about 7% higher than those of Montzka et al. [2003].

![Total Cl from Halocarbons](image)

**Figure 36.** Calculated Effective Equivalent Chlorine (EECl; solid line) due to all chlorinated source gases, and the same lagged by 3.5 years to give Effective Equivalent Stratospheric Chlorine (EECI).

### 6.3.5.2 Atmospheric bromine trend

A similar approach to that outlined above has been followed for organic bromine source gases, to derive an analogous quantity CBr$_y$. In this case the principal contributors are the halon gases, methyl bromide, and VSLS' bromine species (namely CHBr$_3$, CH$_2$Br$_2$, CH$_3$BrCl, CHBrCl$_2$ and CHBr$_2$Cl). The resulting trends are shown for both hemispheres in Figure 37 and, broken down by category, in Figure 38. Although bromine is less abundant than chlorine in the atmosphere, it's catalytic cycles in the stratosphere are such that it is far more effective at removing ozone from the stratosphere than chlorine. The efficiency of this removal relative to chlorine (expressed as the "alpha factor" $\alpha$) varies depending on location in the stratosphere. It is commonly taken as 45 in conformity with the 2002 WMO/UNEP Ozone Assessment (WMO, 2003). Figure 37 shows that atmospheric bromine from these source gases has doubled since pre-industrial times to a peak of about 24 ppt (global average) and is now declining.
Figure 37. Sum of bromine (CBr_3(tot)) from all significant bromine-containing organic gases in both hemispheres.

Figure 38. Contribution of different halocarbons or groups of halocarbons to CBr_3(tot) in (a) the Northern Hemisphere and (b) the Southern Hemisphere.

Figure 38 shows that the recent decline in CBr_3(tot) is largely due to declining CH_3Br in the NH arising from its control under the Montreal Protocol. This gas does, however, have a significant natural background and it is unlikely that it will decrease to below what is evidently a pre-industrial background of about 5 ppt. The contribution from the halons to halogen loading has occurred more recently than from the CFCs. Their concentrations are still rising but the rate of growth has slowed considerably in recent years. Most of the halons are quite long-lived and will decline slowly with time even after emissions have ceased. There is a significant background level of bromine from VSLS species. This amount is difficult to assess since the very short lifetimes of the gases (notably in the case of bromoform) implies that their concentrations could be spatially variable both horizontally and vertically. Surface values of bromoform, for example, varied by a factor of two at the different drill sites. The values are representative of the polar regions, and may be quite different in the tropics where most VSLS are injected in to the stratosphere. Nevertheless it can be stated that VSLS bromine has changed little on a global basis, with only small increases in the trihalogenated bromine species (see above).
The bromine trends can also be used to calculate EECI and EESC by using an efficiency factor to convert bromine to an amount of chlorine that would remove an equivalent amount of ozone in the stratosphere. Fractional release factors were taken from the same literature source as described above for the chlorinated gases, and an alpha factor of 45 was assumed. The combined EECI and EESC from the sum of both chlorinated and brominated species is shown in Figure 39. The fact that total equivalent chlorine from all relevant halogenated species has peaked and is now declining implies that, all other things being equal, ozone levels should now begin to recover, but the fact that equivalent chlorine remains at only just below record high levels means that the stratosphere is still at its most vulnerable to ozone loss, and the polar ozone hole will remain a persistent problem for some time in to the future.

![Figure 39. Calculated Effective Equivalent Chlorine (EECI; solid line) due to the sum of all chlorinated and brominated source gases, and the same lagged by 3.5 years to give Effective Equivalent Stratospheric Chlorine (ECCI).](image)

6.3.5.3 Trends in stratospheric ozone and temperature

The CHEM2 model [Brasseur et al., 1990; Martinerie et al., 1995] was used to assess the impact of changes in halocarbon concentrations on stratospheric temperature and ozone. The heterogeneous chemistry leading to the ozone hole (around 15-20 km altitude) is difficult to simulate with 2D models because the formation of polar stratospheric clouds is related to zonal transport. Thus the CRYOSTAT program did not guarantee to provide such results. The existing parameterization of heterogeneous stratospheric chemistry in the model [Granier and Brasseur, 1992] was tested for century time scale simulations and was found to be unstable. We then did not have time to develop a new scheme.

However, the impact of halocarbons through homogeneous chemistry was examined as planned. This mechanism destroys ozone most efficiently around 45 km altitude where $O_3$ concentration was reduced by more than 40% near polar regions in 1998 (Figure 40). This reduction induces a slight increase in $O_3$ concentrations in the lower stratosphere through a “self-healing” effect: lower ozone at high altitudes implies UV radiation reaching lower layers and hence an increased ozone production in this region. As ozone is a major source of heat in the middle atmosphere, less $O_3$ implies lower temperatures. The cooling reaches 7°C at mid-latitudes around 45 km altitude.
Figure 40. Change in (left panel) stratospheric ozone (%) and (right panel) temperature (Kelvin) between the beginning of 20th century and 1998 due to halocarbon concentration changes through homogeneous chemistry. The X-axis shows latitudes (degrees), the Y-axis indicates altitudes in km.

These results are consistent with earlier steady-state simulations (4.5 years long) around 1850 and 1990 [Martinerie et al., 1995]. The continuous simulations over the last century performed within CRYOSTAT allowed us to define the timing of this change (Figures A7.1 and A7.2 in Annex 7). Significant changes in ozone and temperature started to occur in the 1970s and peaked around 1998, then the impact of halocarbon emission reduction related to the Montreal protocol became visible, and ozone started to increase again and induce a warming of the upper stratosphere. The long transport time between the Earth surface and 45 km altitude is responsible for a 9 years time shift between emission reduction and the start of ozone recovery.

In a separate study using CHEM4 [Steil et al., 2003] a transient simulation for the time period 1960 to 2000 was carried out. The boundary conditions for emissions and the surface concentrations of halocarbon and greenhouse gases have been prescribed based on observations, and are broadly consistent with firm and ice core measurements from CRYOSTAT. The model in general reproduces the observed mean state and inter-annual variability of temperature, ozone and water vapour in the stratosphere, including the polar regions (Figure 41).

The simulation included forcings by observed sea surface temperature (SST), major volcanoes and the solar cycle. The 11-year solar cycle effects on ozone and dynamics were investigated by comparing time-slice simulations with solar maximum and solar minimum radiative boundary conditions at the top, and showed similar patterns of wind changes in stratosphere and troposphere. The Quasi-Biennial Oscillation (QBO) of the zonal wind in the lower tropical stratosphere was assimilated from observations. The El Niño/La Niña signal in SST has a clear impact on stratospheric water vapour and ozone via tropical tropopause temperature, in agreement with observations. Volcanoes enhance stratospheric water vapour via heating of the “cold point”, causing more ozone destruction in the gas phase.

The chlorine increase resulting from anthropogenic CFC and HCFC emissions caused the development of the Antarctic ozone hole in the early 1980s, and ozone depletion in the Arctic lower stratosphere, as can be seen in Figure 41. Simulated transport from the stratosphere to the troposphere has been tested using cosmogenic $^{14}$CO as a diagnostic tracer [Jöckel et al., 2002]. and confirms that stratosphere-troposphere exchange is generally strongest in the Northern Hemisphere.
The general conclusions from this latter study are that:

- For increased chlorine concentrations additional cooling of the upper stratosphere by gas phase ozone depletion causes enhanced heating by descent in the lower stratosphere, reducing the polar stratospheric clouds (PSC) abundance and heterogeneous ozone depletion in this region.
- The QBO strongly influences transport of tracers into the stratosphere.
- Lower stratospheric ozone and water vapour show a clear signal of El Niño/La Niña.
- The 11 year solar cycle modulates ozone in the upper stratosphere and the mesosphere.
- Transport from the stratosphere to the troposphere in the model seems to be overestimated for Southern Hemisphere winter/spring (from $^{14}$CO diagnostics).

6.3.5.4 Implications for tropospheric chemistry

Non-methane hydrocarbons, alkyl nitrates and $NO_x$

Firm air samples from NGRIP were analysed for a range of alkyl nitrates ($C_1-C_5$) together with selected alkanes (ethane, propane, n-butane, i-butane, n-pentane) by CO1 and AC3. All the non methane hydrocarbons (NMHC) studied increased substantially from the beginning of the record to the early 1990s, and have since declined, consistent with declining emissions in Europe and North America in the last decade. For example, the atmospheric abundance of the butanes has approximately doubled between 1950 and 1990 (Figure 42(a)). However, they have not as yet declined to the concentrations present in the 1950s. The $C_1$ – $C_2$ alkyl nitrates both appear to have been affected by chemical production in the lower firm, but isopropyl nitrate, isobutyl nitrate and the pentyl nitrates all indicate plausible atmospheric histories in the firm (Figure 42(b)). Similar to the NMHCs the alkyl nitrates show increasing abundances since the 1950s, reaching a plateau in the early 1990s. In contrast to the alkanes, however, they increased several-fold during this period (factors of five or six), and in the last decade have declined more slowly, or in some cases have remained constant.

Assuming that the route to formation of alkyl nitrates is via the degradation of alkanes by hydroxyl radical, and subsequent reaction of the peroxy radicals with NO, then an increase in the abundance of $NO_x$ in the Northern Hemisphere (NH) can be deduced ($NO_x$ being the sum of the
reactive nitrogen species NO and NO₂). There are understood to be additional sources of the <C₅ peroxy radicals, mainly <C₄, which are thought to arise from the decomposition of larger alkoxy radicals [Atkinson, 1997; Flocke et al., 1994]. These additional sources have been suggested to be the cause of deviations from the ideal behaviour predicted by kinetics for the pure hydrocarbon-alkyl nitrate system [Bertman et al., 1995; Roberts et al., 1998]. As a result, it has been suggested that the shorter chain alkyl nitrates (<C₅) cannot be simply related to their parent hydrocarbons [Flocke et al., 1998]. Therefore, only the 2-pentyl nitrate/n-pentane and 3-pentyl nitrate/n-pentane measured ratios were used with a simple kinetic method, involving a simplified steady state approach in order to investigate the 20th century atmospheric NOₓ trend [Worton, 2005]. The results of this simplified approach suggest that in the background NH high latitude atmosphere the concentrations of NOₓ have increased by a factor of ~5 over the latter half of the last century (Figure 43(a)). This is in reasonable agreement with the estimated emissions of NOₓ published as part of the Emission Database for Global Atmospheric Research (EDGAR) database, the development of which has also been a CRYOSTAT activity [van Aardenne et al., 2001]. The EDGAR database estimates an increase in NOₓ emissions from 4 to 16 Tg N yr⁻¹ between 1950 and 1990 (Figure 43(b)).

Figure 42. NGRIP firm air measurements of (a) i,n-butanes; and (b) 2-butyl nitrates (2C₅ONO₂), 2-pentyl nitrate (2C₅ONO₂) and 3-pentyl nitrates (3C₅ONO₂) versus CFC-12 as a pseudo-date ordinate.

Figure 43. Estimated NH NO increase from simplified kinetic approach (a), compared with reported increasing NH emissions of NOₓ from the EDGAR database (b).

The results shown in this work indicate evidence that an increasing trend in the tropospheric ozone abundance is likely. This is supported by recent work reported by Lamarque et al. [2005] using a global chemistry transport model and the estimates of anthropogenic precursor emissions from van Aardenne et al. [2001] to evaluate the tropospheric ozone evolution between 1890 and 1990. Lamarque et al. [2005] estimate that the tropospheric ozone burden has increased ~30% over this timeframe from the best estimates of ozone precursor emissions. They also shown that the ozone
lifetime has decreased by ~30% over the same timeframe and that although the abundance of tropospheric ozone has increased the ozone production efficiency in the troposphere has decreased resulting in a less NOx limited troposphere. Lamarque et al. [2005] suggest this indicates that the use of single parameter relating increase tropospheric ozone burden to NOx emissions would be a rather crude approximation. It is apparent that a more sophisticated interpretation is required to interpolate the observed trends in the alkyl nitrates and the parent hydrocarbons to indicate the likely variation in tropospheric ozone over the latter half of the last century.

As noted above, the CHEM2 modelling (Section 6.3.4.2) was entirely consistent with a tropospheric OH field that was invariant over at least the later half of the 20th century. This contributes to the present debate on whether global OH has changed in response to changing atmospheric composition, and to what extent it is robust to such chemical forcings. The evidence here is that it is robust.

6.3.5.5 Halocarbon radiative forcings

*Integrated absorption cross sections*

The halocarbons integrated absorption cross sections (IXS) were taken from absorption cross section data measured at the Ford Motor Company and compiled at Reading. The gases for which no measurements were made by the Ford Motor Company, the absorption cross sections were taken from HITRAN 2004 database (i.e. CCl4; Rothman et al. [2005]) or the Pacific Northwest National Laboratory (PNNL) Spectral Database (i.e. SF6) provided by the Virtual Planetary Laboratory at the Jet Propulsion Laboratory. For gases for which no absorption cross sectional spectral data was freely available, values from studies reported in the IPCC [2001] were used (CFC113, CFC114 and CFC115). The IXS differ slightly from previously published values from the AC2 group (Sihra et al. [2001]) due to updates made by Ford Motor Company since that study. These updates were mostly extending the infrared spectral range over which the measurements were made and hence the inclusion of minor bands. In certain cases (e.g. CF3) a more detailed and accurate measurement of the infrared spectrum was made to avoid the possibility of saturation of the absorption bands of the halocarbon (Hurley et al. [2005]). The integrated absorption cross sections were compared to other values in the literature to ensure that there were no obvious discrepancies with recent studies. In all cases the spread in values of the integrated absorption cross sections were within 15% of the most recent studies.

*Radiative efficiencies*

The radiative efficiencies were calculated from the absorption cross sections for halocarbons with updated values. Two radiative transfer codes were used to calculate the radiative efficiencies following the method outlined in Hurley et al. [2005]. For the rest of the gases whose IXS sections had not significantly changed, the radiative efficiencies from Sihra et al. [2001] were used. The radiative efficiencies also include a lifetime adjustment (Sihra et al. [2001]) which takes into account the variation with height of the concentration of gas, and is important for the shorter lived gases. For the halocarbons whose IXS we did not have, the radiative efficiencies were taken from IPCC [2001]. The radiative efficiency of CFC-114a was assumed to be the same as for CFC-114, with the expectation of a small percentage error in the value.

*Radiative Forcings*

One of the aims of the CRYOSTAT project was to compile a time history of the halocarbon radiative forcing. The radiative forcing was calculated using an estimate of the global annual mean surface abundance of each gas for each time step. The surface mixing ratios were obtained from the 2-D chemistry transport model for the majority of halocarbons but for seven halocarbons abundances which were taken from trends specific to the firm sites derived using the iterative trend
reconstruction technique described earlier (i.e. for HFC-23, CFC-114a, HFC-143a, HFC-125, C$_2$F$_6$, C$_3$F$_8$, c-C$_4$F$_8$ and SF$_5$CF$_3$).

**Comparison of 1998 radiative forcings with previous determinations**

The halocarbon radiative forcing for 1998 calculated by CRYOSTAT is estimated to be 318 mWm$^{-2}$ which is 5\% lower than the estimate given in the Third Assessment Report (TAR; IPCC (2001)) of 335mWm$^{-2}$. The CRYOSTAT estimate includes ten halocarbons which were not included in the TAR estimate. However these ten halocarbons all have small contributions e.g. HCFC-21 which contributes 0.04 mWm$^{-2}$. The difference in estimates between CRYOSTAT and TAR arise from two main contributions. One contribution is from the differences in the 1998 abundances of the gases measured by CRYOSTAT and that given in TAR. The second is from the differences in the radiative efficiencies used in CRYOSTAT and that of values from a variety of studies used in TAR. The difference in the estimates for CFC-12 and CFC-11 are the most significant. These arise from the radiative efficiencies used in CRYOSTAT (0.295 Wm$^{-2}$ ppb$^{-1}$ for CFC-12 and 0.242Wm$^{-2}$ ppb$^{-1}$ for CFC-11) being lower than the radiative efficiencies quoted in TAR (0.32 Wm$^{-2}$ ppb$^{-1}$ for CFC-12 and 0.25Wm$^{-2}$ ppb$^{-1}$ for CFC-11). However the differences are within 8\% from the TAR estimates.

**Time histories of halocarbon radiative forcing**

The time history of the halocarbon radiative forcing is given as that arising from a change in concentration from 1750 (taken as pre-industrial) to various dates: 1958, 1968, 1978, 1988, 1998, 2000 and 2002. In all cases only the direct radiative forcing effect is taken into account. The indirect effect due to destruction of stratospheric ozone (a negative forcing) by chlorinated and brominated gases is not included. There is a large increase from 1958 to 1988 in the halocarbon radiative forcing mainly from CFC-12 and CFC-11. From 1988 to 1998 the increase is less and the contributions from the CFC-12 and CFC-11 are seen to be levelling off. The contribution from the hydrochlorofluorocarbons and hydrofluorocarbons increased from 1988 onwards (Figure 44).

![Figure 44](image.png)

**Figure 44.** Global annual mean radiative forcing of halocarbons measured by CRYOSTAT due to their concentration changes from the year 1750 (preindustrial)

Since the direct radiative forcing due to chlorinated and brominated species is at least partly offset by negative indirect forcing, it is also pertinent to consider the forcing due to species which are only fluorinated. This is also relevant because these gases are not controlled by the Montreal
Protocol, since they are not ODSs. They presently do not have any specific controls, but they are referred to in the Kyoto Protocol. The radiative forcing due to this "basket" of HFCs, perfluorocarbons and fluorosulphur compounds is shown in Figure 45. In this instance the radiative forcing is dominated by four compounds: SF₆, CF₃, HFC-23, and HFC-134a. The first two gases are of particular concern as they have atmospheric lifetimes of thousands of years (essentially infinite in the case of CF₃). The aggregate radiative forcing from these gases is small in comparison to CO₂ (1.46 W m⁻² over the same time frame; IPCC [2001]); i.e. for the gases shown in Figure 45 this amounts to less than 1% of the forcing due to the increase in CO₂ between 1750 and 1998. The equivalent radiative forcings due CH₄ and N₂O between 1750 and 1998 equate to 486 and 156 mW m⁻² respectively. The total direct forcing due to halocarbons therefore lies between that due to N₂O and CH₄. The forcing due to fluorine-only containing gases is about 4% and 11% of that due to CH₄ and N₂O, respectively. The rate of growth in radiative forcing due to the fluorine-only containing gases is, however, increasing rapidly, whereas that due to CO₂ is decreasing (due to saturation of the CO₂ IR absorption bands), that due to N₂O is essentially zero, and that due to CH₄ is negative. The radiative forcing from CH₄ and N₂O due to changes in their concentration between 1750 and dates from 1850 to 2004 is shown in Figure 46.

![Graph showing radiative forcing and concentration changes](image)

**Figure 45.** Global annual mean radiative forcing of HFCs, perfluorocarbons, and fluorosulphur compounds measured by CRYOSTAT due to their concentration changes from the year 1750 (preindustrial).

![Graph showing CH₄ and N₂O concentration and radiative forcing](image)

**Figure 46.** Global annual mean concentration, and radiative forcing due to concentration changes since the year 1750 (pre-industrial), for (a) CH₄ and (b) N₂O.
6.3.6 RESEARCH OUTCOME BENEFITS TO RELATED SCIENTIFIC COMMUNITIES

The outcomes of CRYOSTAT project have permitted significant progress in the understanding of air trapping processes in the firm for a variety of surface conditions, both in Greenland and Antarctica. In parallel with the CRYOSTAT project, several new deep ice cores have recently been recovered owing to a strong support of European Commission, European Science Foundation and many European nations.

In Greenland, the NGRIP deep drilling was achieved in 2004, offering a 3085 m deep ice core and providing the first undisturbed Northern Hemisphere ice core record covering the full past climatic cycle back to the end of the penultimate interglacial. Three CRYOSTAT partners have been involved in high resolution analysis of air trapped in NGRIP ice core and have used the CRYOSTAT outcomes to improve past temperature reconstructions over series of abrupt events. It was already revealed that these abrupt climate changes are associated with temperature rises reaching 8 to 16°C within a few decades to centuries. These analyses, combined with methane measurements, have also been used to assess the phase relationships between changes in Greenland temperature and changes in atmospheric methane concentrations, and place bipolar ice cores into a common chronological framework. The CRYOSTAT firm air sampling at NGRIP was particularly fruitful and relevant for the best use of the ice core records.

The European Project for Ice Coring in Antarctica (EPICA) was designed to recover to complementary deep ice cores, one at the site of Dome C (a CRYOSTAT site) and the second at Kohnen Station, in the Dronning Maud Land area. The Dome C drilling was completed in 2005, leading to 3301 meters of ice and offering the longest paleoclimate record available from ice cores, back to 800 000 years (twice longer than the Vostok record), while the Kohnen Station drilling is still in progress. CRYOSTAT Dome C and BAS station firm air studies are being incorporated to improve firm modelling and reduce the uncertainties on the differences between ice and gas ages at these sites. The outcomes will be significant both on the very dating of the ice cores, and the assessment of phase relationships between past temperature changes and past atmospheric composition changes. An intercomparison of firm models and CRYOSTAT results has already permitted an assessment of firm model capabilities and suggested that the discrepancies between glacial-interglacial changes in ice core δ15N and firm model results can be used to refine the modelling of past accumulation changes. The most recent Dome C results point to dramatic changes in the intensity and pacing of climatic cycles prior to 400 000 years ago [EPICA-community-memories, 2004] [Steenlethaler, et al., 2005] [Stahn, et al., 2005]. Detailed further studies of past changes in local temperatures and greenhouse gases planned with the EC EPICA-MIS project will benefit from CRYOSTAT outcomes.

In the near future, new deep ice cores are planned with the International Partnership for Ice Core Science (IPICS), both in Greenland and Antarctica. The construction of an array of ice cores will require an intensive use of gas records to provide a common chronology, pointing out to the long term outcomes of firm air studies. Local firm air studies should be planned, following the CRYOSTAT protocols and providing an extended knowledge of the behaviour of polar firm processes under a larger range of surface characteristics. Within the International Polar Year (2007-2009), it is in particular planned to search for the oldest possible firm air from Antarctica.

Beyond the ice core community, an improved use of deep ice cores permits new reconstructions of past polar temperature changes, and a better precision on the phase relationships between past temperature changes and past atmospheric composition changes. These results are critical for the assessment of the capabilities of coupled climate – biogeochemical cycles models to capture several aspects of past climate changes, including a correct representation of the sequence of events during rapid changes and climate transitions. In this sense, process studies conducted within CRYOSTAT have relevance for the understanding of past climate changes and the test of climate models, one of the key directions endorsed by the international PAGES program.
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6.3.7 FOLLOW-ON ACTIVITIES PRESENT AND FORESEEN

An activity that has already taken place as direct result of CRYOSTAT is an expedition to collect firn air and ice from Dronning Maud Land by Partner CR7. This firn air is currently under study by a number of CRYOSTAT partners.

An illustration of the importance of continuing firn air studies is shown in Figure 47. This shows how firn profiles can change radically even over a small number of years, due to changing atmospheric growth rates. Meanwhile, due to the inescapable compression of firn air as more snow accumulates, every year that passes is a year irrevocably ‘lost’ from the firn air record at any given site. These considerations have prompted the CRYOSTAT community and others to propose that a project called the ‘Search for the Oldest Firn Interstitial Air’ (SOFIA) is required to find the optimum location for the oldest possible firn air to be extracted and measured (and additional amounts archived for future analyses as techniques improve or previously unrecognised gaseous species are discovered).

SOFIA has been included as a subproject under the umbrella of the International Partnerships in Ice Core Science (IPICS) which is a proposal for an International Polar Year (IPY) Initiative. This proposal has been endorsed by the International Polar Year Committee, although this as such carries no promise of funding. The modelling work required to pinpoint the most likely locations for exploratory firn drilling has been approved both as a national IPY project, and has already secured funding from the Netherlands government. Other glaciological activities in planning could be used as potential logistical platforms for SOFIA activities. These might include:

- the International IPY-approved project TASTE-IDEA which includes an Antarctic traverse that might intercept promising firn drilling sites
- a project based at the new and near-complete French-Italian Dome C station and which could include a ‘permanent’ firn air installation similar to that installed at Halley
- a proposed French-Chinese expedition to study gas enclosure and firm structure in the very cold, old, low accumulation rate firm at Dome A

Other more unusual structures might be examined for older firm air. These include "megadunes" which occur in some parts of the Antarctic; and layered firm such as might exist on the warmer seaward side of Law Dome. Very old firm air has indeed been reported by US scientists from megadunes; but in both of these cases the reconstruction of trends is difficult because conventional firm diffusion models cannot be applied to such conditions.

It is the earnest wish of the CRYOSTAT PIs that efforts also go into another Greenland firm drilling, such was the success of the NGRIP campaign. There is still much to be learnt about NH trends of trace gases, and it is hoped that a Greenland site with yet older dates, or perhaps even less post-depositional chemical effects, may be found. Planned activities at NGRIP and Summit under the IPY-endorsed NEEM project may perhaps provide the logistic springboard for such a campaign.

Figure 47. Modelled depth profiles for two trace gases (CH₃CCl₃ and CFC-11) at a NH (NGRIP) and SH (Dome C) firm sampling site in each of three years: 1993 (solid line), 1998 (short dash) and 2003 (long dash).
6.4 CONCLUSIONS INCLUDING SOCIO-ECONOMIC RELEVANCE, STRATEGIC ASPECTS AND POLICY IMPLICATIONS

CRYOSTAT has shown that the chemical composition of the atmosphere is far removed from its natural pre-industrial state and that, in the last hundred years or so, this has resulted in a dramatic change in stratospheric ozone, the absorption of terrestrial radiation by atmospheric gases, and in the chemical makeup and cycling of reactive gases in the troposphere.

We have shown much that was not previously well known regarding the sources of many important gases. We now know that CH₄ and CO have risen over time at least in part because of an increase in deliberate biomass burning. We know that the upswing in N₂O can be largely attributed to natural and synthetic fertilizer use. We have shown that very few chlorinated source gases existed before industrialisation and less than half of brominated gases are from natural sources. Even for those gases that do have natural sources, almost every one has also been found to also have an industrial source, and to have increased in the atmosphere in the last century. We can reconstruct what these changes will have meant to stratospheric ozone levels, and these reconstructions show the onset of the Antarctic ozone hole, and indicate that the stratosphere is colder now because of this loss of ozone. We can also determine by how much the increase in multiple radiative gases will have directly warmed the atmosphere. We note in particular the rapid rise in “super” greenhouse gases of which all but one are of exclusively manmade origin, and several of which have lifetimes which are for all relevant purposes infinite. We also know that human activities have entirely changed the gas-phase chemistry of even the remote lower atmosphere (troposphere). Non-methane hydrocarbons, CO, and NOₓ have all increased substantially in fifty years, and will have changed both the chemical loss rates of other ODSs and GHGs, and will have almost certainly increased background levels of ozone (which acts as a powerful GHG in the lower atmosphere).

Internationally, and within the EU, the issues to which CRYOSTAT is relevant are being addressed by participation in the Montreal Protocol process to ban or limit ozone-depleting substances, and by participation in the United Nations Framework Convention on Climate Change - most recently in the form of the Kyoto Agreement. The European Union has been at the forefront of these efforts to control pollution emission, both by drawing up legislation to limit European emissions, but also by promoting research which feeds in to international assessments, such as those established by the United Nations Environment Programme (UNEP) and World Meteorological Organisation (WMO). These assessments include the “Scientific Assessments of Ozone Depletion” of which the European Commission is a headline sponsor, and the Intergovernmental Panel on Climate Change (IPCC).

The EU and its member states have signed and ratified both the UN Framework Convention on Climate Change and, most recently, the revised Protocol from the Kyoto Summit. The EU has stated that: "Climate change is one of the most challenging environmental problems for the next decades. Work on common and co-ordinated policies and measures within the Community should be intensified with a view to domestic action providing the main means of meeting the Kyoto commitments" (European Council Meeting Vienna, 1998). The EU has ambitious plans relative to the climate change negotiations, with a target of 8% reduction in greenhouse gas emissions in the commitment period 2008-2012 compared to 1990 levels, and to be geared towards further reductions after 2012. It recognises that the EU politicians “will face difficult decisions which may affect our economy and society”. It is the purpose of this project to contribute to the information on which those decisions can be made.

CRYOSTAT has provided a direct input of data and knowledge to the UNEP/WMO and IPCC international scientific assessments, both of which are a major influence on the international agreements in which European member states participate, and to which European Union policy is directed. Several of the principal investigators in CRYOSTAT are lead authors, co-authors or contributors to the series of UNEP/WMO and IPCC assessments. The historical trends of pollutants derived from air archives and cryospheric records feature prominently in these assessments, and in
many cases are based on research by some of the members of this consortium. Indeed scientific findings arising from CRYOSTAT are already being incorporated in to the 2006 WMO/UNEP Scientific Assessment of Ozone Depletion, of which the CRYOSTAT Scientific Coordinator is a principal author.

This work cannot be carried out without inter-European and international collaboration. Retrieval of firm and ice is a difficult and costly activity, and commonly involves collaboration between countries to maximise manpower, expertise, logistic support, and scientific output. This situation is amplified in this project with the requirement to undertake three drilling campaigns and a two year continuous Antarctic experiment, all in a short time period, and with significant time overlaps (particularly allowing for the long shipping times). This schedule is entirely beyond the capabilities of a single national research group. CRYOSTAT has, in fact, utilised the combined resources of the majority of principal national ice drilling teams within Europe and Australia.

In the process of carrying out the research we have also trained a number of PhD students, producing the next phalanx of Earth scientists for Europe and beyond. This training has led to other training activities by the Partners, including the Marie Curie Early Stage Training scheme “Fellowships in Antarctic Air-Sea-Ice Science” (FAASIS) which is presently training eight PhD students and which arose from the collaboration between Partners CO1 and CR8.

6.5 DISSEMINATION AND EXPLOITATION OF THE RESULTS

The core of data dissemination from CRYOSTAT is data archive held by the British Antarctic Data Centre (BADC). This is reached via an informative set of web pages at http://badc.nerc.ac.uk/data/cryostat/. The data is presently password protected whilst the Partners exploit their intellectual property rights in the process of writing papers on CRYOSTAT findings. By January 2007, however, we expect the database to have been opened to free public access. The database if in NASA-Ames format, a widely use standard formatting protocol. It can be automatically downloaded in this format, or can be downloaded as an Microsoft Excel spreadsheet. An intuitive interface also allow the data to be readily plotted on the screen without downloading; useful for a quick look at the data available. Also accessible from BADC for the exclusive benefit of the Partners is the CRYOSTAT Collaborative Workspace where working and final drafts of papers, reports, data sets, etc., can be exchanged between Partners.

Dissemination is also via the science papers that have been written and are in the process of being so (listed elsewhere in this Report). During the lifetime of CRYOSTAT we have held two Special Sessions dedicate to CRYOSTAT science at the Annual General Assemblies of the European Geosciences Union, in Nice, France; first in 2002 and then in 2004.

The CRYOSTAT Scientific Coordinator and another CRYOSTAT principal investigator, together with a ‘guest’ convenor from the USA, have been organising a final Special Session on firm and ice core studies at the EGU General Assembly in Vienna in April 2006. This time they have also arranged with the journal “Atmospheric Chemistry and Physics” published by EGU to also produce a Special Issue of the journal containing papers arising from the meeting, and other papers from CRYOSTAT investigators and invitees working in the same field. This will serve as a lasting legacy from the project.

6.6 MAIN LITERATURE PRODUCED

A list of CRYOSTAT literature is complied in Section 2 of this Report.
REFERENCES


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ANNEXES TO SECTION 6

ANNEX 1: DEPTH PROFILES OF HALOCARBON GASES MEASURED AT BERKNER ISLAND AND NGRI P

In this Annex are presented the depth profiles of halocarbon gases measured at Berkner Island (the left hand column) and NGRIP (the right hand column). Each row is for a separate gas.

No Data
No Data
No Data
No Data
No Data

No Data
No Data
ANNEX 2: DETAILED TRENDS OF MONTREAL PROTOCOL GASES, HFC-134a, HFC-152a, SF₆ AND CF₄

The halocarbon trends calculated with the CHEM2 atmospheric chemistry model were used as input to the FIRN1 model of gas diffusion in firn in order to compare concentration-depth profiles with FIRETRACC and CRYOSTAT data. Detailed results are shown on the following figures.

Measurements:
- Stars: UEA measurements with PLOT column
- Triangles: UEA measurements with DB5 column
- Circles: NCAR measurements
- Crosses: MPI measurements

The inter-calibration differences between UEA and NCAR measurements were carefully examined on samples measured at the same sites and depths. In the NCAR measurements were corrected for inter-calibration differences with UEA using the factors presented in the main text (Table 4.1). For H-1211, the NCAR calibration scale was adopted because it better fits the CMDL atmospheric measurements, and UEA measurements were corrected. The analytical precision varies from one species to another. In particular, species with very low concentrations show less precision (HCFC-21, HCFC-123 and HFC-152a). The two deepest samples at Berkner should not be trusted too much as they show some contamination for many chemical species.

Model results:
- Green dashed line: CHEM2+FIRN1 results with JPL, 1997 photochemical reaction rates.
- Violet dashed line: CHEM2+FIRN1 results with JPL, 2003 photochemical reaction rates.
- Black continuous line: CHEM2+FIRN1 results adjusted to firn data using a constant scaling factor on halocarbon emissions (and JPL, 2003 photochemical reaction rates).
- Black dashed line (Devon Island only): results obtained with a different diffusivity profile in FIRN1, and CHEM2 results adjusted to firn data.

Differences between the first three curves illustrate uncertainties in CHEM2 model results due to uncertainties on lifetimes and historical emissions. One major source of uncertainty on FIRN1 model results is related to the site-specific depth-diffusivity profile. At Devon Island, the effect of ice layers due to occasional melting enhance the uncertainties on the diffusivity profile. An adjusted diffusivity profile was used (Black dashed line), which allows to correct systematic deviations between model and measurements for all species.

An originality of this study is to use constraints from different drill sites, as well as atmospheric trends and historical emissions to provide best constraints on the reconstructed trends. The 5 years difference between firn measurements at different sites also provides a constraint on recent trends.

Comments:

Model results generally fit all data very well, although the depth profiles at the different sites have very different shapes. Species with "bell shape" trends (increase, then strong decrease in concentrations over recent years) such as CCl₄ and CH₃CCl₃ appear more difficult to model (more sensitive to uncertainties on firn diffusivity). A time shift in calibration scales was detected for HFC-134a, this explains why a single model run could no fit the data from all sites.
Figure A2.1: Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for CFC-11
Figure A2.2: Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for CFC-12
Figure A2.3: Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for CFC-113
Figure A2.4: Comparison of CHEM2+FIRN model results to CRYOSTAT data for CFC-114
Figure A2.5: Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for CFC-115
Figure A2.6: Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for CCl₄

Figure A2.7: Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for Halon-1301
Figure A2.8: Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for Halon-1211
Figure A2.9: Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for Halon-2402

Figure A2.10: Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for CF₄
Figure A2.11: Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for SF$_6$. 
Figure A2.12: Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for CH$_3$CCl$_3$
Figure A2.13: Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for HCFC-22

Figure A2.14: Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for HCFC-21
Figure A2.15: Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for HCFC-123

Figure A2.16: Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for HFC-134a
Figure A2.17: Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for HCFC-141b

Figure A2.18: Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for HCFC-142b
Figure A2.19: Comparison of CHEM2+FIRN1 model results to CRYOSTAT data for HFC-152a
ANNEX 3: COMPARISON OF CHEM2 MODEL RESULTS WITH ATMOSPHERIC TRENDS

The CHEM2 atmospheric chemistry modelled trends were compared with atmospheric trends at different latitudes from the ALE/GAGE/AGAGE and CMDL networks.

Atmospheric data:

As the monthly values available in the databases would completely cover model results and prevent detailed comparisons, yearly average values were plotted (plus signs). The different colours represent different measurement sites:

ALE/GAGE/AGAGE data (http://cdiac.ornl.gov/ftp/ale_gage_Agage)
- Violet plus signs: Adrigole (52°N) and Mace Head (53°N)
- Black plus signs: Oregon (45°N) and Trinidad Head (41°N)
- Turquoise plus signs: Barbados (13°N)
- Green plus signs: Samoa (14.3°S)
- Pink plus signs: Cape Grim (40.7°S)

CMDL data (http://www.cmdl.noaa.gov/hats)
- Black plus signs: Alert (82.5°N)
- Violet plus signs: Pt. Barrow (71.3°N)
- Orange plus signs: Niwot Ridge (40.1°N)
- Turquoise plus signs: Mauna Loa, Hawaii (19.5°N)
- Blue plus signs: Cape Kumukahi, Hawaii (19.5°N)
- Green plus signs: Samoa (14.3°S)
- Pink plus signs: Cape Grim (40.7°S)
- Yellow plus signs: South Pole (90°S)

Model results (lines):

The different colours represent results corresponding to the same latitudes as the measurement sites. As the model meridian resolution is only 5 degrees, linear interpolations were made between the grid points North and South of the measurement sites. The simulation represented is the one adjusted to firm data using a constant scaling factor on halocarbon emissions, and JPL, 2003 photochemical reaction rates.

Comments:

Model results for the sites represented in turquoise and blue (Barbados (13°N), Mauna Loa, Hawaii (19.5°N), and Cape Kumukahi, Hawaii (19.5°N)) show a high seasonal variability because the inter-tropical convergence zone (the transport barrier between the two hemispheres) shifts seasonally North and South of these sites. Monthly mean experimental data (not plotted here) show similarly increased seasonal variations. The CHEM2 model results generally fit better the ALE/GAGE/AGAGE data than the CMDL data. As the same model results are used in both cases, this can only be due to differences between ALE/GAGE/AGAGE and CMDL calibration scales. Note that as model results are adjusted to UEA CRYOSTAT data, the better fit to ALE/GAGE/AGAGE mostly means that UEA calibration scale is closer to ALE/GAGE/AGAGE than CMDL. However, no model adjustments were made for CH3CCl3, H-1211 and H-1301. As there is no available emission data set for H-2402, the modelled trend for this species is less precise and only shows a rough shape that fits the FIRETRACC/CYOSTAT data.

The model adjustment factors used are constants that shift the trends up or down without modifying their shape. Thus the model appears successful at simulating the trend shapes (constrained by historical emissions) as well as the latitudinal gradients.
Figure A3.1. Comparison of CHEM2 model results with atmospheric trends: CFC-11, CFC-12, CFC-113
Figure A3.2. Comparison of CHEM2 model results with atmospheric trends: CCl₄, CH₃CCl₃, HCFC-22
Figure A3.3. Comparison of CHEM2 model results with atmospheric trends: HFC-134a, HCFC-141b, HCFC-142b, Halon-1211, Halon-1301, Halon-2402
ANNEX 4: BEST GUESS TRENDS AT THE CRYOSTAT SITES FOR HALOCARBONS MODELLED WITH CHEM2

Comment: As there are no available emission data sets for H-2402, HCFC-21, HCFC-123 and HFC-152a, the modelled trends for these species is less precise and only shows a rough shape that fits the FIRETRACC/CRYOSTAT data. However the explicit modelling of their chemical sinks allows us to evaluate the seasonal variations due to atmospheric chemistry. Such variations are important for HCFC-21, HCFC-123 and HFC-152a.

Figure A4.1. Best guess trends for halocarbons modelled with CHEM2+FIRN1 at the CRYOSTAT drilling sites: North GRIP (continuous line) and Berkner (dashed line): CFC-11, CFC-12, CFC-113, CCl4, CH3CCl3, HCFC-22
**Figure A4.2.** Best guess trends for halocarbons modelled with CHEM2+FIRN1 at the CRYOSTAT drilling sites: North GRIP (continuous line) and Berkner (dashed line): H-1211, H-1301, H-2402, HFC-134a, HCFC-141b, HCFC-142b
Figure A4.3. Best guess trends for halocarbons modelled with CHEM2-FIRN1 at the CRYOSTAT drilling sites: North GRIP (continuous line) and Berkner (dashed line): CFC-114, CFC-115, SF₆, HCFC-21, HCFC-123, HFC-152a
ANNEX 5: TEMPORAL VARIATIONS IN HALOCARBON LIFETIMES AND EMISSION FLUXES

Figure A5.1. Temporal variations in halocarbon lifetimes (full lines) and emission fluxes (dashed lines): CFC-11, CFC-12, CFC-113, CFC-114, CFC-115, H-1211.
Figure A5.2. Temporal variations in halocarbon lifetimes (full lines) and emission fluxes (dashed lines): H-1301, H-2402, ccl4, CH3CCl3, HCFC-22, HFC-134a.
Figure A5.3. Temporal variations in halocarbon lifetimes (full lines) and emission fluxes (dashed lines): HCFC-141b, HCFC-142b, HCFC-21, HCFC-123, HFC-152a.
ANNEX 6: IMPACT OF TEMPORAL VARIATIONS IN STRATOSPHERIC HALOCARBON LIFETIMES ON CONCENTRATION TRENDS

Figure A6.1. Impact of temporal variations in stratospheric halocarbon lifetimes on their concentration trend. Full line: reference simulation. Long dashed line: simulation with homogeneous halocarbon sinks in the whole atmosphere (the inverse of the equilibrium lifetime). Short dashed line: simulation with halocarbon sinks scaled with the equilibrium lifetime.
ANNEX 7: CHANGE IN STRATOSPHERIC OZONE SINCE THE BEGINNING OF 20TH CENTURY

Modelled changes arising from changing halocarbon concentrations and their effect on homogenous gas phase chemistry.
Figure 7.1. Change in stratospheric ozone (%) between the beginning of 20\textsuperscript{th} century and 1958, 1968, 1978, 1988, 1990, 1992 due to halocarbon concentration changes through homogeneous chemistry. The X axis shows latitudes (degrees), the Y axis indicates altitudes in km.
Figure 7.2. Change in stratospheric ozone (%) between the beginning of 20th century and 1994, 1996, 1997, 1998, 1999, 2002 due to halocarbon concentration changes through homogeneous chemistry. The X axis shows latitudes (degrees), the Y axis indicates altitudes in km.
ANNEX 8: CHANGE IN STRATOSPHERIC TEMPERATURE SINCE THE BEGINNING OF 20th CENTURY

Modelled changes arising from changing halocarbon concentrations and their effect on homogenous gas phase chemistry.
Figure 8.1. Change in stratospheric temperature (Kelvin) between the beginning of 20th century and 1958, 1968, 1978, 1988, 1990, 1992 due to halocarbon concentration changes through homogeneous chemistry. The X axis shows latitudes (degrees), the Y axis indicates altitudes in km.
Figure 8.2. Change in stratospheric temperature (Kelvin) between the beginning of 20th century and 1994, 1996, 1997, 1998, 1999, 2002 due to halocarbon concentration changes through homogeneous chemistry. The X axis shows latitudes (degrees), the Y axis indicates altitudes in km.