

M. S. Johnson, Research Summary

Atmospheric Chemistry and Climate

Chemistry determines climate

Eleven of the last 12 years (1995 – 2006) rank among the 12 warmest years in the instrumental record of global surface temperature [52]. According to the Intergovernmental Panel on Climate Change it is very likely (meaning > 90% chance) that the observed temperature increase is the result of human activity. The factors driving climate are shown in Table 1. Each has increased, with the exception of stratospheric ozone. Understanding the chemistry of climate at a fundamental level is the unifying theme of my research. This research goal makes extensive use of Physical Chemistry, Atmospheric Chemistry and Spectroscopy.

Factor	Radiative Forcing ^a / W m ²	Relevant papers coauthored by M. S. Johnson
CO ₂ ^b	1.66	[8, 11, 16, 18, 31]
CH ₄	0.48	[28, 30, 32, 35, 37, 38, 40]
N ₂ O	0.16	[10, 21, 26, 27, 41]
Halocarbons	0.34	[5, 36, 45]
O ₃ , Stratosphere	-0.05	[5, 20, 22, 45]
O ₃ , Troposphere	0.35	[14, 29, 47]
Land use change	-0.2	
Black carbon	0.1	[13]
Strat. H ₂ O from CH ₄	0.07	[28, 30, 32, 35, 37, 38, 40]
Direct aerosol	-0.5	[24, 39]
Cloud albedo	-0.7	
Solar Irradiance	0.12	
<u>Total^c</u>	<u>1.6</u>	[42, 52, 53]
Atmospheric ions ^d	< 1.2	[2, 3, 46]

Table 1. Factors driving climate change from 1750 to present. All are chemical effects, with the exceptions of land use change and solar irradiance.

^aData From IPCC, 2007 [52]. Uncertainties omitted for brevity.

^bCO is the major *in situ* source of CO₂, producing 1/6 of the total. Thus CO alone has a radiative forcing of 0.3 W m⁻².

^cThe ‘atmospheric ion’ effect is excluded from the total, in accordance with the IPCC recommendation.

^dThe Sun-Cosmic Ray-Atmospheric ion-Cloud cover hypothesis of Henrik Svensmark is NOT part of the IPCC recommendation. I am the University academic advisor for Martin Enghoff who is doing his PhD with Svensmark at the Danish Space Research Agency.

Isotopic analysis of atmospheric trace gases

The state of Earth’s atmosphere (chemical composition and reactivity) is controlled by gases found at mole fractions of 10⁻³ to < 10⁻⁹. The photochemistry of these gases is important to human society and the environment [52, 53].

Emission of nitrogen oxides, hydrocarbons and CO from transportation, industry and agriculture changes the chemical composition of the atmosphere leading to air pollution. Air pollution includes particles and tropospheric ozone, both important for climate forcing and health. Stratospheric ozone depletion, over the poles and at mid-latitudes, is linked to the chloro-fluoro carbons. The emissions of greenhouse gasses including CO₂, CH₄, N₂O and the halocarbons are a matter of significant concern.

Trace gases are further characterized by the distributions of stable nuclei such as ²H (D), ¹³C, ¹⁵N, ¹⁷O, ¹⁸O, and ³³S, ³⁴S and ³⁶S. The isotopic mass balance equation (1) links the enrichment of an isotope in a gas sample δ_{obs} to the enrichments δ_i and strengths S_i of the emissions sources and the isotopic fractionation ϵ_i and loss rates L_i of the removal processes [18, 41]:

$$\delta_{obs} = \frac{\sum_i \delta_i S_i}{\sum_i S_i} + \frac{\sum_i \epsilon_i L_i}{\sum_i L_i} \quad (1)$$

The ‘delta value’ of sample x is given by $\delta_x = R_x/R_{std} - 1$; R is the isotope ratio in the sample, e.g. [¹³C]/[¹²C]. The reference standards are internationally accepted samples agreed upon by the community.

Isotopic analysis provides additional insight into trace gas budgets that cannot be obtained by other means. For example methane (CH₄) and nitrous oxide (N₂O) are mainly produced by bacteria [52, 53]. It is a challenging task to

determine the source terms S_i for these gases by integrating over the relevant bacteria in the oceans, soil, rhizomes, termites, cows and so on. However, it is possible to measure the isotopic composition of e.g. N_2O produced by bacteria, and it turns out to be notably depleted in ^{15}N and ^{18}O . In a series of articles combining experiment [26], advanced modeling of photolysis using time-dependent wavepacket propagation [10, 27] and a 3D Chemical Transport Model [21], I have shown that the isotopically light bacterial source is balanced by an isotopic enrichment in the one reaction removing 90% of N_2O from the atmosphere, namely stratospheric photolysis. It is typical of the atmosphere that the loss reactions L_i are specific, basic photochemical reactions while trace gas sources S_i are complex. Like N_2O , CH_4 has bacterial sources and a majority (> 95%) is removed by a single reaction, in this case $CH_4 + OH$. Inverse modeling combines the isotopic signature of the atmospheric chemical reactions ε_i with measurements of delta values δ_i and δ_{obs} to constrain the values S_i , the source terms in equation 1. My research has used laboratory studies to determine the isotopic fractionations ε_i of atmospheric chemical and photolysis reactions, modeling to explore the implications of these results, and theoretical studies to uncover the fundamental origin of the effects. This research complements and extends the work of the small army of research groups throughout the world with isotope ratio mass spectrometers who measure the delta values of samples collected in the field.

The carbon cycle

The carbon cycle links air chemistry, air quality, and global change. Reduced hydrocarbons such as methane and isoprene are photochemically oxidized in the atmosphere in a process that is catalyzed by nitrogen oxides and produces ozone air pollution and atmospheric particles. Figure 1 shows that the atmospheric concentration of methane (which has doubled since the agricultural and industrial revolutions) is no longer increasing. This surprising finding is very likely linked to changes in emissions but no-one can say with certainty exactly what has changed. Theories include reduced use of natural gas following the economic collapse of the Soviet state, stabilization of emissions from livestock and rice paddies, increased drought, repairs to the natural gas distribution network and decreased emissions by coal mines. A previously unknown source, *aerobic* methanogenesis by green plants, has been identified [54]. Models of climate futures include predictions of the atmospheric concentrations of greenhouse gases and there is a clear difficulty in projecting future concentrations of methane and other greenhouse gases when we cannot explain where they are coming from in today's atmosphere. The IPCC has emphasized the need to improve trace gas budgets [52].

The atmospheric chemical reaction mechanism of methane is shown in Figure 2, for both the CH_4 and CH_3D isotopologues. The mechanism connects the key greenhouse gas methane with formaldehyde, carbon monoxide and dihydrogen. In addition to modulating the concentrations of greenhouse gases, the carbon cycle controls the oxidation capacity of the atmosphere, which is what determines the atmospheric lifetime of a majority of pollutants.

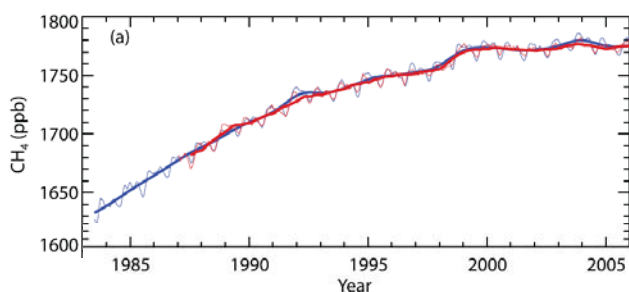


Figure 1. Atmospheric concentration of methane [52]. Although the atmospheric concentration of methane has doubled since pre-industrial times, it is no longer increasing. The reasons for this are debated.

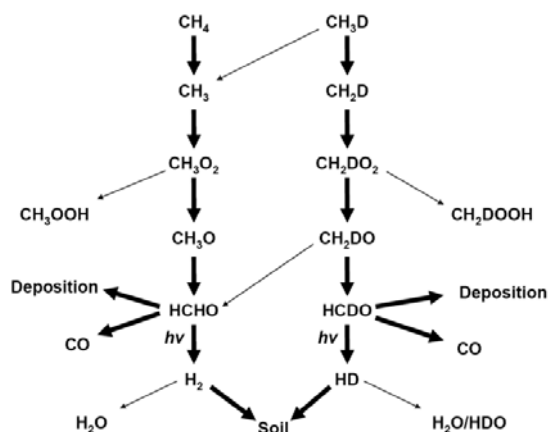


Figure 2. Propagation of deuterium through the atmosphere. Deuterium found in atmospheric methane is propagated via methyl, methperoxyl and methoxyl to formaldehyde, which produces carbon monoxide and dihydrogen. Figure from Nilsson et al. [37].

We have characterized the isotope effects in the atmospheric carbon cycle in a series of papers dealing with methane [30], methoxy [37], formaldehyde [32, 35, 38, 40] and carbon monoxide [11, 16, 31]. Formaldehyde is a key intermediate in the mechanism and produces half of the dihydrogen in the atmosphere. This molecule is the focus of research due to the 50% increase in stratospheric water vapor since the 1950s and an anticipated increase in

atmospheric H₂ given more widespread use of hydrogen fuel. According to the isotope budget the dihydrogen produced from methane via formaldehyde photolysis should be enriched in deuterium. However our research showed two interesting things. Deuterated formaldehyde is photolysed more slowly in sunlight than normal formaldehyde [35]. In addition to this, deuterated formaldehyde has a significantly lower branching ratio for dihydrogen production relative to the main isotopologue [35]. This seeming paradox was solved in subsequent research involving hydrogen abstraction from the methoxy molecule [37]. We generated CH₂DO in an atmospheric simulation chamber:



Analysis of the infrared spectra of the product formaldehyde showed that reaction 2a occurs only 12% of the time, while deuterated formaldehyde is formed 88% of the time. All together the enrichment in deuterium occurring in 2 is only partially offset by the photolytic depletion, explaining the overall enrichment predicted by budget models. The key is that the reach and grasp of models and field studies are greatly increased once the chemical mechanism is known.

We have shown that HCHO, HCDO and DCDO have essentially equal UV absorption cross sections [38], meaning that they absorb sunlight at the same rate. The very different photodissociation rates and yields for the isotopologues must therefore be due to a dynamical effect. We are researching the origin of this effect together with Theis Sølling and Solvejg Jørgensen in the Department of Chemistry [40, 41].

Future work will include examination of the site-specific deuterium enrichment in plant isoprene and the site-specific chemical reaction enrichment coefficients for the formaldehyde produced from isoprene. In addition we will use the CCAR photochemical reactor to examine the wavelength, temperature and pressure dependence of the dramatic deuterium isotope effects.

A reactor for studies of atmospheric photochemistry

Elna Nilsson and I have built a photochemical reactor at the Copenhagen Center for Atmospheric Research [47]. The reactor includes a number of technical advances that make it the best system of its kind in the world. 1) A unique, specially designed mounting system for the multipass mirrors counteracts alignment problems associated with pressure and temperature changes. 2) The cell itself is a 2 m long quartz tube made by a specialist in Sweden. Quartz allows photolysis of molecules at short wavelengths (200 – 300 nm) necessary to directly generate OH radicals from O₃. This is not possible on standard Pyrex-glass systems. 3) Radical generation via UV-A, UV-C or Sun lamp systems, under computer control. 4) The entire reaction cell sits inside a temperature control chamber to allow experiments at atmospherically relevant temperatures, -30 °C to +45 °C with a stability of ± 0.1 °C. 5) The entire optical path, including the spectrometer, is under vacuum to eliminate problems with overlapping absorptions from atmospheric CO₂ and H₂O.



Figure 3. *The photochemical reactor.* System components pictured include custom gold-coated multipass optics, solid quartz reaction cylinder, double O-ring sealing of end flanges, lamp systems and temperature control housing.

The instrument has been in continuous use since it came on-line in the summer of 2007.

List of ongoing research projects with the Photochemical Reactor:

1. *Atmospheric impact of biofuels.* MSc thesis project of Vibeke Friis Andersen. Use of biofuels is increasing exponentially and studies have shown that 1 - 2% of all transportation fuel escapes to the atmosphere unburned. We have completed initial kinetics studies of the reactivity of representative biofuels. Collaboration with Prof. O. J. Nielsen (University of Copenhagen) and Dr. T. J. Wallington of Ford Motor Company.
2. *Isotopic analysis of the atmospheric sulfur cycle.* MSc thesis project of Carsten Eskebjerg. We are completing studies that will allow the first complete isotope budget for stratospheric sulfate, which is important for climate and ozone depletion. The unsolved question regards the source of non-volcanic aerosol. Collaboration with Prof. N. Yoshida

and S. Danielache of the Tokyo Institute of Technology with several visits in both directions. Our work on SO₂ spectroscopy has just been accepted at *Journal of Geophysical Research, Atmospheres* [43].

3. *Kinetics of CFC replacements*. Collaboration with Prof. O. J. Nielsen (University of Copenhagen), T. J. Wallington (Ford Motor Company), R. R. Singh (Honeywell Inc.) [45, 50].
4. *Carbon cycle: Formaldehyde reactions*. The desire is to learn the effects of temperature, pressure and wavelength on the dramatic deuterium isotope effects we have observed. This will give insight into the fundamental dynamical origin of the phenomenon, and provide parameters for atmospheric models. Collaboration with Prof. T. Röckmann (University of Utrecht) for isotope ratio mass spectrometric analysis, Assoc. Prof. S. Jørgensen (University of Copenhagen) for theory, Professor C. J. Nielsen (Oslo) for scientific and moral support.
5. *Carbon cycle: Methane reactions*. There is indirect evidence concerning the ratio of OH that reacts with D vs. H in CH₃D (cf. Figure 2). We will do the first direct measurements of this branching ratio. Collaboration with Dr. T. J. Wallington of Ford Motor Company.

Electrodynamic Balance

Post-docs Christophe Delval and Philipp von Hessberg and I have built an instrument based on an electrodynamic balance that is capable of levitating single aerosol particles, generated either from a liquid solution using a piezoelectric injector, or from powder samples (Figure 4). The environment around the particle is controlled allowing studies of the effect of temperature, relative humidity and the addition of reactive gases such as O₃, NO₂ and NH₃ on the particle.

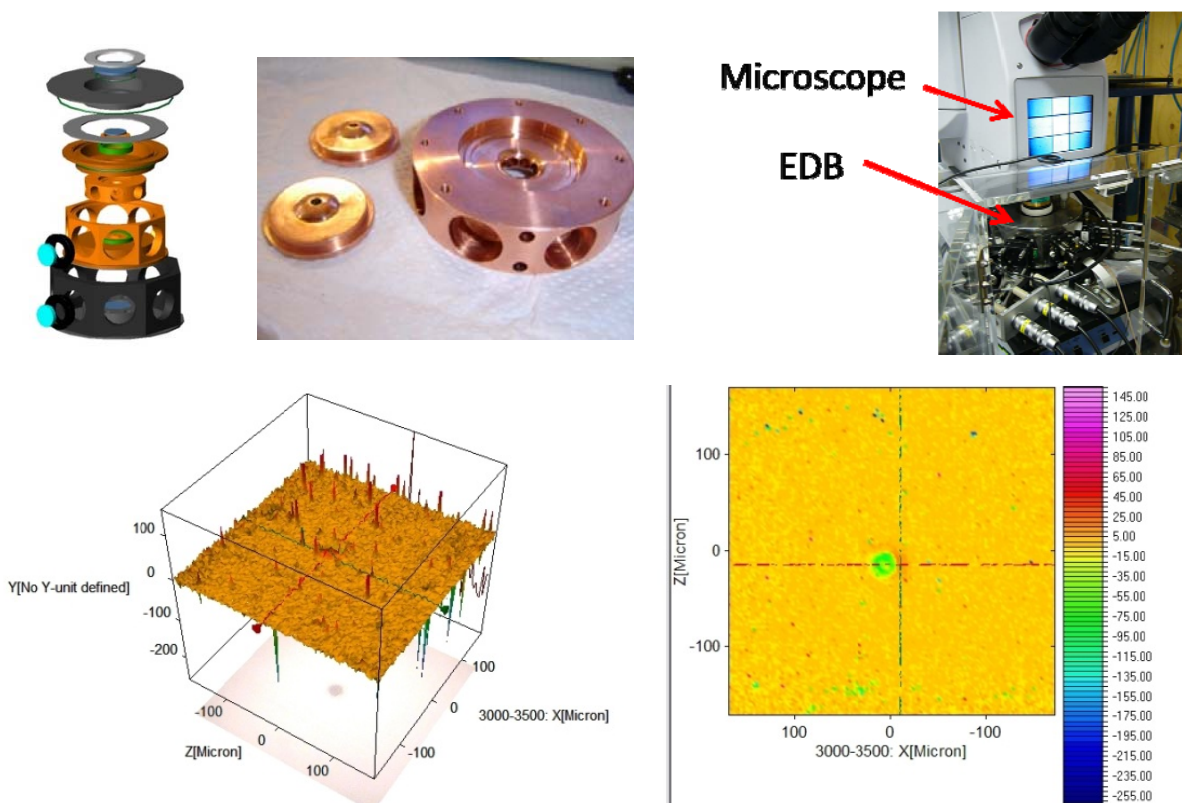


Figure 4. The electrodynamic balance particle trap.

4a. Top left, assembly drawing showing the inner and outer vacuum chambers. 4b. Top middle, the three electrodes that form the quadrupole trap. 4c. Top right, The particle trap installed in the infrared microscope at the electron storage ring. 4d. Bottom, the first chemical map of a droplet levitated in the trap, recorded in 2008 using synchrotron infrared microscopy. The microscope's array detector allows infrared spectra to be recorded at 128² points simultaneously in a (100 μm)² grid. A 20 μm diameter polyethylene glycol droplet was injected into the trap. The C-H stretching vibration was integrated to generate the chemical maps shown.

Particles are characterized in several ways by our device. They are filmed using a high speed camera with microscope optics. The particle size is measured using Mie scattering of a HeNe laser beam. Two dimensional chemical maps of

particles have been recorded using infrared microscopy (focal plane array detector and synchrotron light source). The microscope acts as an aperture limiting the area of a light source that can illuminate the sample; introduction of a synchrotron light source makes possible a 10^3 increase in signal intensity [7]. Finally we are preparing for Raman microscopy, for chemical characterization and accurate temperature measurement. The chemical composition and temperature of the region around the particle is controlled. Thus we are in a position to begin many interesting experiments related to heterogeneous chemistry in the atmosphere, including absorption and reaction kinetics, partitioning within particles, supercooling behavior and the role of surfactants.

There are three ongoing collaborations involving the EDB. 1) Aging of pollen by photochemical air pollution with Assoc. Prof. S. Jørgensen of the University of Copenhagen. 2) Effect of surfactants on particle properties with Prof. M. Bilde of the University of Copenhagen. 3) Chemical mapping of particles using an EDB and synchrotron infrared microscopy with Prof. P. Uvdal of the University of Lund.

Green Air Systems

I have recently begun a collaboration with *Green Air Systems*, a startup environmental technology company in Sweden. This project is an exciting combination of fundamental physical chemistry, atmospheric chemistry and engineering. My role is to provide scientific input to help develop innovative new products. The initiative has led to two promising projects in which the University provides basic research and *Green Air Systems* provides funding for students and equipment.

1. Worldwide, 15% of greenhouse gas emissions are due to heating and cooling of residential and commercial buildings [55]. Indoor air quality is a problem and the only current solution is to dilute the pollution by bringing in fresh air from the outside. In cold climates this air must be heated, and in warm climates it must be dehumidified and cooled. A market analysis indicates that a device to allow recirculation of a greater fraction of indoor air, based on air purification, would save energy and pay for itself. I have created an invention for photochemical air purification and the University of Copenhagen Technology Transfer office has asserted its right to own and develop the invention. A venture capital group in Sweden will be investing 3.7 million DKK in the project in exchange for exclusive rights to market the device on a worldwide basis. The grant involves basic research on a prototype of the air purification device by a PhD student. Collaboration on the aerosol portion of the project with Prof. M. Bilde of the University of Copenhagen.

2. The Danish chemical company *BT Kemi* manufactured pesticides in Skåne, Sweden in the 1960s and buried great quantities of chemical waste. There was a plan to clean up the site by driving the soil to Holland in trucks, where it would be incinerated. Recently the port of Landskrona has denied the project the right to ship the contaminated soil through its harbor, which in practice means that they need another cleanup method. We have conducted initial tests that show that ozonolysis of the soil will remove the pesticides and their residues from the soil. The partners in Sweden are very interested in providing funding to the University of Copenhagen for laboratory equipment and one or more PhD students to study the chemical mechanism of treating contaminated soil using ozonolysis. Collaboration on analysis of pesticides and residues with Prof. F. Lauritsen of the University of Copenhagen who has recently developed an 'artificial nose' mass spectrometer ideally suited to this project.

References

Numbered references 1 through 51 can be found in publications, <http://kl5.ki.ku.dk/~msj/pub.html>.

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