Organics in Snow and Ice: Recent Findings from Field and Modeling Studies

Amanda M. Grannas
Villanova University

Third workshop on Air-Ice Chemical Interactions (AICI)
June 6-8, 2011
Columbia University

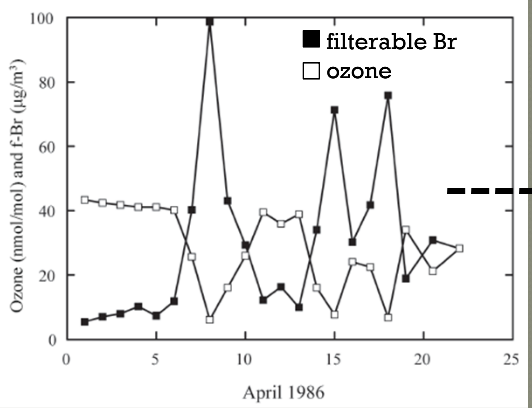
International Global Atmospheric Chemistry
IGAC

National Science Foundation
WHERE DISCOVERIES BEGIN

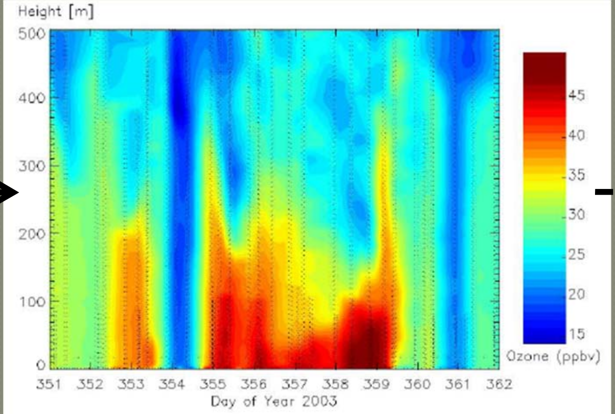
VILLANOVA
UNIVERSITY

It has become increasingly apparent that snow and ice are important media for environmental chemical reactions.

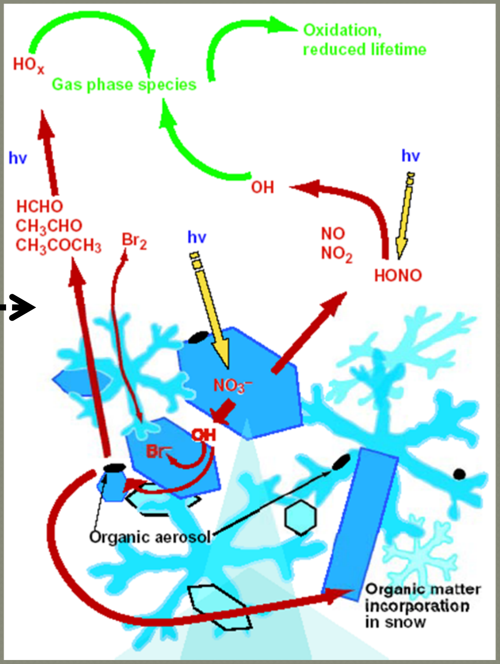
… but it all started with ozone depletion events …

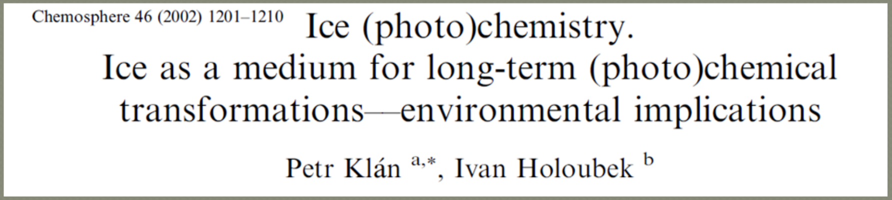


Alert, Canada: Ozone and f-Br
Barrie et al., 1988, Nature



South Pole ODE: Grannas et al., 2007
Figure adapted from Helmig et al., 2007





Chemosphere 46 (2002) 1201–1210

Ice (photo)chemistry.
Ice as a medium for long-term (photo)chemical transformations—environmental implications

Petr Klán [a,*], Ivan Holoubek [b]

30 AUGUST 2002 VOL 297 SCIENCE

REVIEW

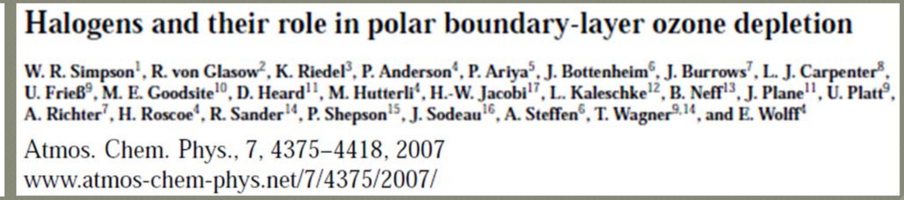
Air-Snow Interactions and Atmospheric Chemistry

Florent Dominé[1]* and Paul B. Shepson[2]*

An overview of snow photochemistry: evidence, mechanisms and impacts

Atmos. Chem. Phys., 7, 4329–4373, 2007

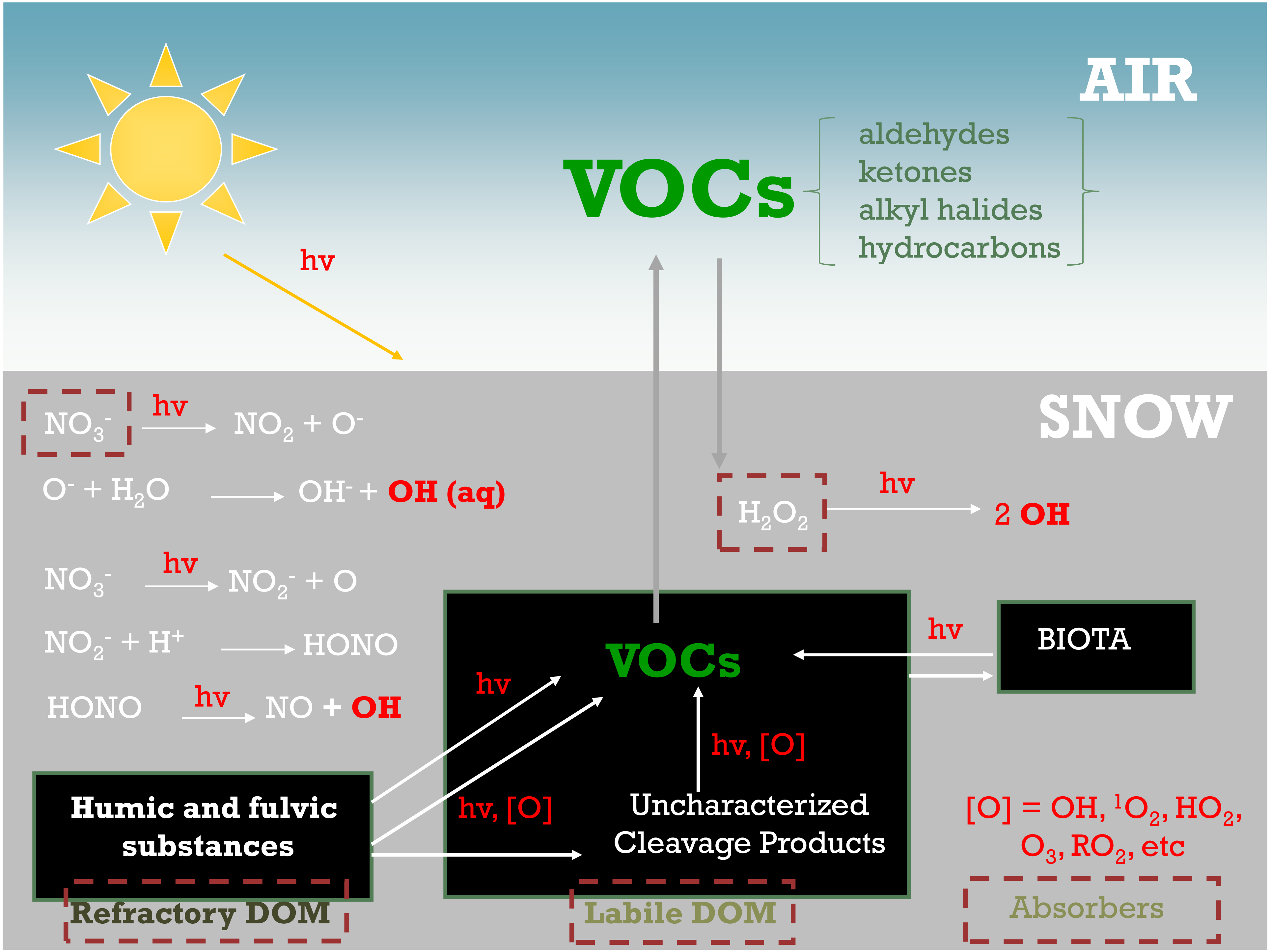
A. M. Grannas[1], A. E. Jones[2], J. Dibb[3], M. Ammann[4], C. Anastasio[5], H. J. Beine[6], M. Bergin[7], J. Bottenheim[8], C. S. Boxe[9], G. Carver[10], G. Chen[11], J. H. Crawford[11], F. Dominé[12], M. M. Frey[12,13], M. I. Guzmán[9,14], D. E. Heard[15], D. Helmig[16], M. R. Hoffmann[9], R. E. Honrath[17], L. G. Huey[18], M. Hutterli[2], H. W. Jacobi[19], P. Klán[20], B. Lefer[29], J. McConnell[21], J. Plane[15], R. Sander[22], J. Savarino[12], P. B. Shepson[23], W. R. Simpson[24], J. R. Sodeau[25], R. von Glasow[26, 27], R. Weller[19], E. W. Wolff[2], and T. Zhu[28]



Halogens and their role in polar boundary-layer ozone depletion

W. R. Simpson[1], R. von Glasow[2], K. Riedel[3], P. Anderson[4], P. Ariya[5], J. Bottenheim[6], J. Burrows[7], L. J. Carpenter[8], U. Frieß[9], M. E. Goodsite[10], D. Heard[11], M. Hutterli[4], H.-W. Jacobi[17], L. Kaleschke[12], B. Neff[13], J. Plane[11], U. Platt[9], A. Richter[7], H. Roscoe[4], R. Sander[14], P. Shepson[15], J. Sodeau[16], A. Steffen[6], T. Wagner[9,14], and E. Wolff[4]

Atmos. Chem. Phys., 7, 4375–4418, 2007
www.atmos-chem-phys.net/7/4375/2007/



AIR

hv

VOCs

aldehydes
ketones
alkyl halides
hydrocarbons

SNOW

$NO_3^- \xrightarrow{hv} NO_2 + O^-$

$O^- + H_2O \longrightarrow OH^- +$ **OH (aq)**

$NO_3^- \xrightarrow{hv} NO_2^- + O$

$NO_2^- + H^+ \longrightarrow HONO$

$HONO \xrightarrow{hv} NO +$ **OH**

$H_2O_2 \xrightarrow{hv} 2$ **OH**

VOCs

hv

BIOTA

hv

hv, [O]

hv, [O]

Uncharacterized Cleavage Products

Humic and fulvic substances

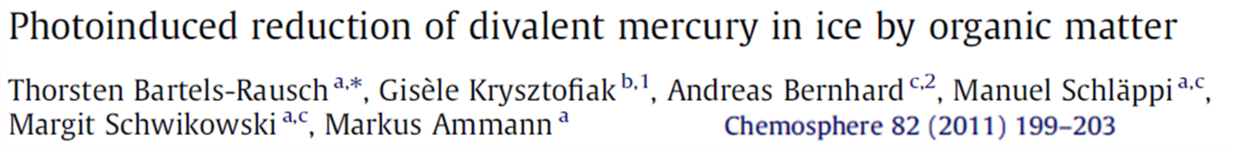
Refractory DOM

Labile DOM

$[O] = OH, {}^1O_2, HO_2, O_3, RO_2,$ etc

Absorbers

A variety of chemistry occurs in/on snow and ice, including photochemical, redox and biologically-mediated reactions.



Photoinduced reduction of divalent mercury in ice by organic matter

Thorsten Bartels-Rausch[a,*], Gisèle Krysztofiak[b,1], Andreas Bernhard[c,2], Manuel Schläppi[a,c], Margit Schwikowski[a,c], Markus Ammann[a]

Chemosphere 82 (2011) 199–203

P. A. Ariya et al., *Environ. Chem.* **2011**, *8*, 62–73. doi:10.1071/EN10056 www.publish.csiro.au/journals/env

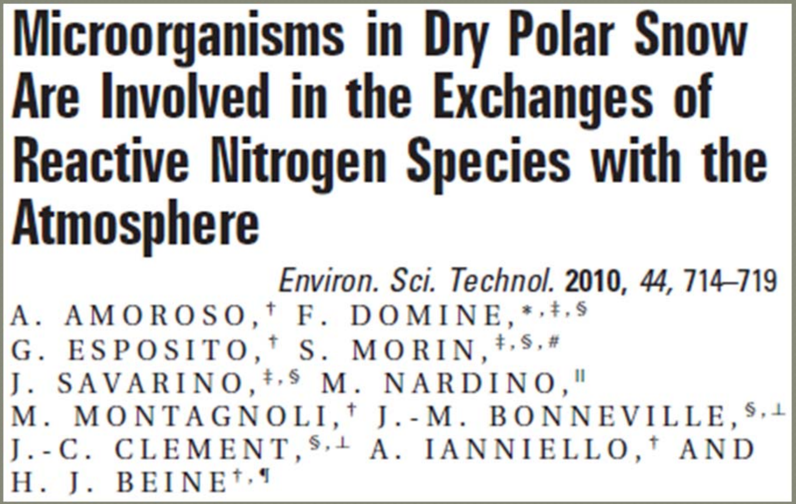
Snow – a photobiochemical exchange platform for volatile and semi-volatile organic compounds with the atmosphere

P. A. Ariya,[A,B,H] F. Domine,[C] G. Kos,[B] M. Amyot,[D] V. Côté,[B] H. Vali,[E] T. Lauzier,[C] W. F. Kuhs,[F] K. Techmer,[F] T. Heinrichs[G] and R. Mortazavi[A]

Enhanced Redox Conversion of Chromate and Arsenite in Ice

Kitae Kim and Wonyong Choi*

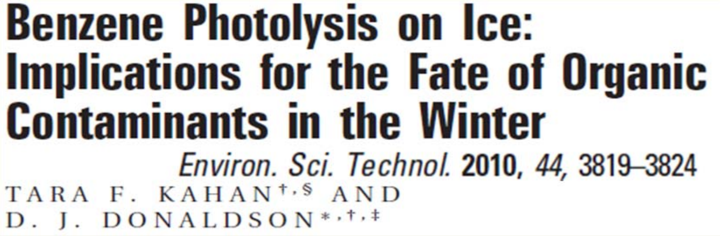
Environ. Sci. Technol. 2011, 45, 2202–2208



Microorganisms in Dry Polar Snow Are Involved in the Exchanges of Reactive Nitrogen Species with the Atmosphere

Environ. Sci. Technol. **2010,** *44,* 714–719

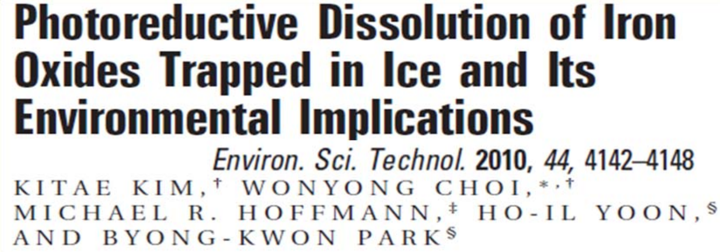
A. AMOROSO,[†] F. DOMINE,[*,‡,§] G. ESPOSITO,[†] S. MORIN,[‡,§,#] J. SAVARINO,[‡,§] M. NARDINO,[‖] M. MONTAGNOLI,[†] J.-M. BONNEVILLE,[§,⊥] J.-C. CLEMENT,[§,⊥] A. IANNIELLO,[†] AND H. J. BEINE[†,¶]



Benzene Photolysis on Ice: Implications for the Fate of Organic Contaminants in the Winter

Environ. Sci. Technol. **2010,** *44,* 3819–3824

TARA F. KAHAN[†,§] AND D. J. DONALDSON[*,†,‡]



Photoreductive Dissolution of Iron Oxides Trapped in Ice and Its Environmental Implications

Environ. Sci. Technol. **2010,** *44,* 4142–4148

KITAE KIM,[†] WONYONG CHOI,[*,†] MICHAEL R. HOFFMANN,[‡] HO-IL YOON,[§] AND BYONG-KWON PARK[§]

Organic components play an important role in many of these processes.

- Reactive Chromophore
- Photosensitizer
- Electron Shuttling
- Biological Carbon Source

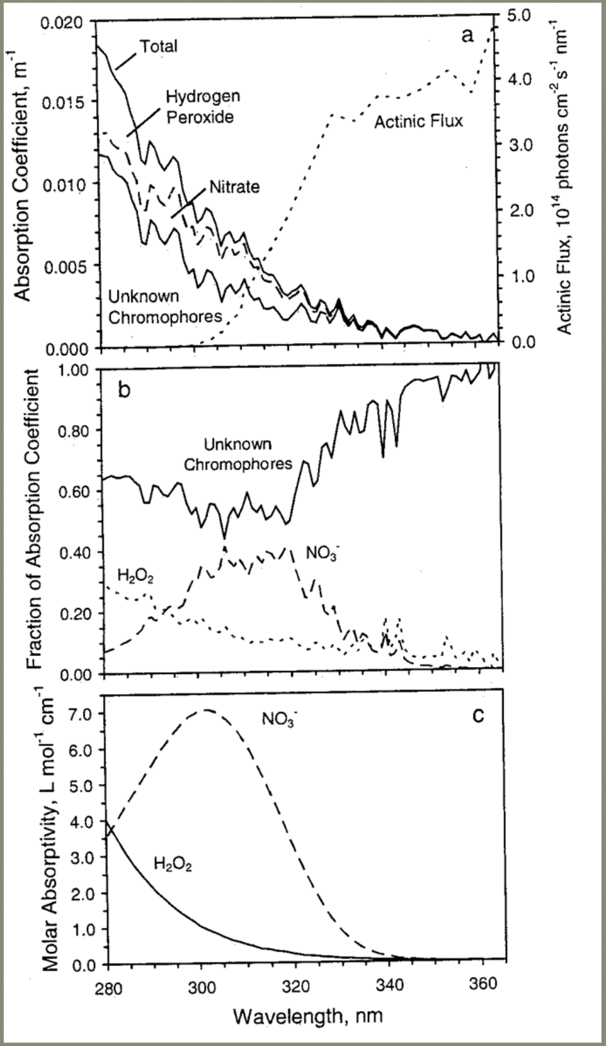
But … just what IS this organic carbon anyway?

- Hydrocarbons
- Carboxylic Acids
- Aromatics
- Monoterpenes
- Proteins / Amino Acids
- Chlorinated , Brominated, and Fluoronated Pollutants
- Phthalates
- “HULIS”
- Bacteria/viruses

Chromophoric Organic Matter

As photochemists, we tend to care most about light absorption by organics

- Initiates chemistry
- Affects albedo, radiative balance
- Snow/ice warming



Anastasio and Robles, JGR-Atm, 112, 2007

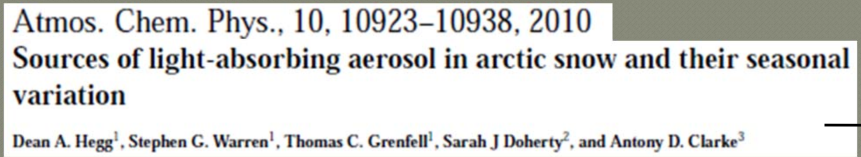
Snow samples from Greenland and Dome C, Antarctica

Dissolved fraction analyzed (filtered to 0.22 µm)

50-90% of the light absorption of dissolved fraction was due to unknown chromophores, presumably organic matter …
H_2O_2 and NO_3^- were remainder

MORE STUDIES COMING FROM THE OASIS 2009 FIELD STUDY IN BARROW ALASKA!

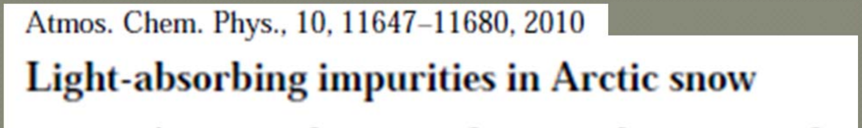
Chromophoric Organic Matter



Atmos. Chem. Phys., 10, 10923–10938, 2010

Sources of light-absorbing aerosol in arctic snow and their seasonal variation

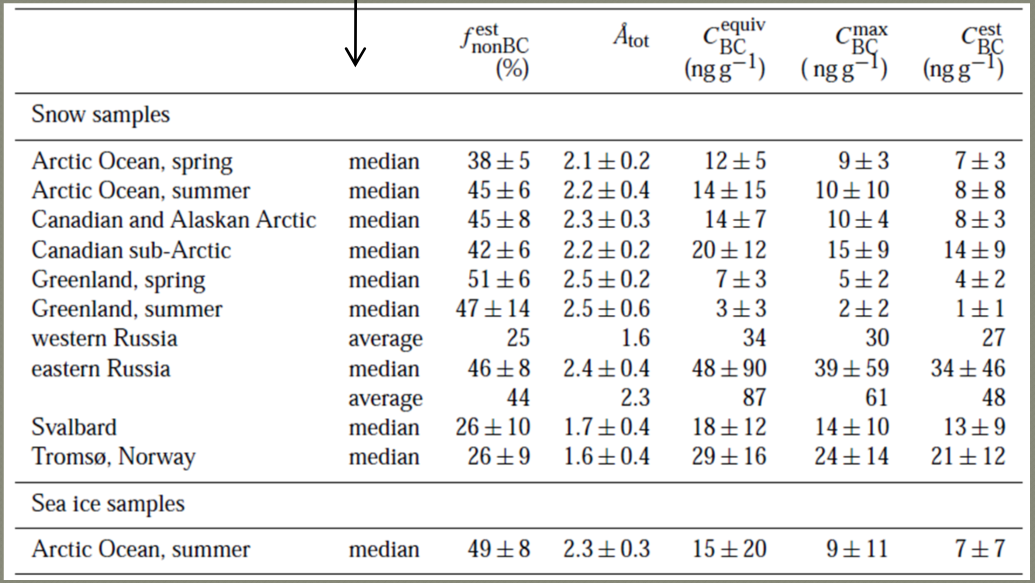
Dean A. Hegg[1], Stephen G. Warren[1], Thomas C. Grenfell[1], Sarah J Doherty[2], and Antony D. Clarke[3]



Atmos. Chem. Phys., 10, 11647–11680, 2010

Light-absorbing impurities in Arctic snow

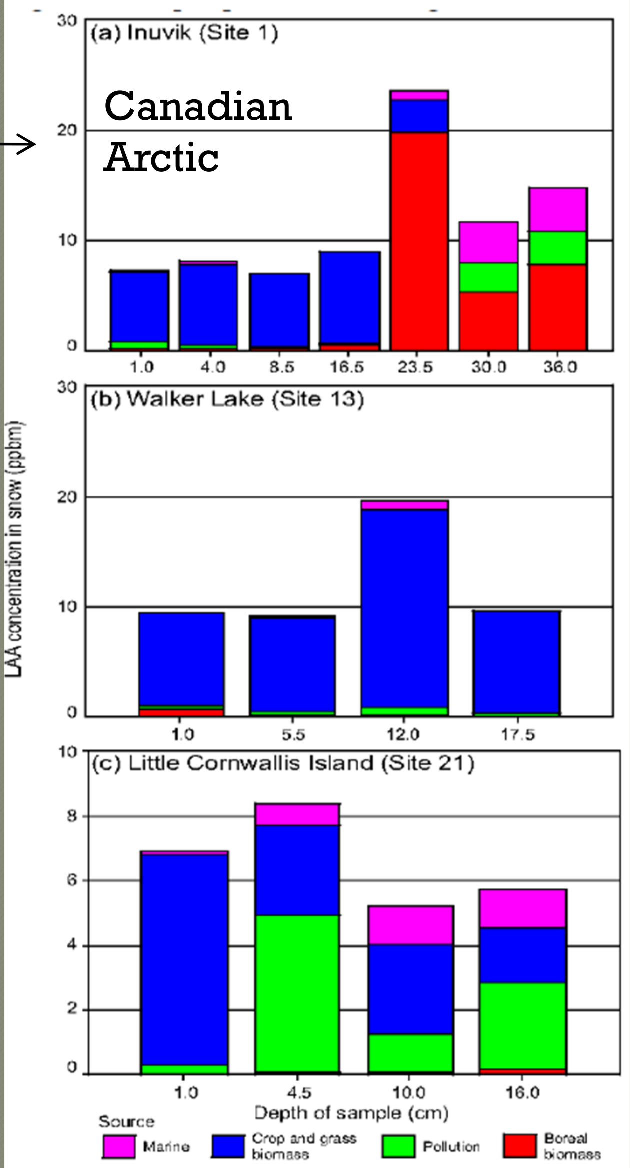
S. J. Doherty[1], S. G. Warren[2], T. C. Grenfell[2], A. D. Clarke[3], and R. E. Brandt[2]



		f^{est}_{nonBC} (%)	$Å_{tot}$	C^{equiv}_{BC} (ng g^{-1})	C^{max}_{BC} (ng g^{-1})	C^{est}_{BC} (ng g^{-1})
Snow samples						
Arctic Ocean, spring	median	38 ± 5	2.1 ± 0.2	12 ± 5	9 ± 3	7 ± 3
Arctic Ocean, summer	median	45 ± 6	2.2 ± 0.4	14 ± 15	10 ± 10	8 ± 8
Canadian and Alaskan Arctic	median	45 ± 8	2.3 ± 0.3	14 ± 7	10 ± 4	8 ± 3
Canadian sub-Arctic	median	42 ± 6	2.2 ± 0.2	20 ± 12	15 ± 9	14 ± 9
Greenland, spring	median	51 ± 6	2.5 ± 0.2	7 ± 3	5 ± 2	4 ± 2
Greenland, summer	median	47 ± 14	2.5 ± 0.6	3 ± 3	2 ± 2	1 ± 1
western Russia	average	25	1.6	34	30	27
eastern Russia	median	46 ± 8	2.4 ± 0.4	48 ± 90	39 ± 59	34 ± 46
	average	44	2.3	87	61	48
Svalbard	median	26 ± 10	1.7 ± 0.4	18 ± 12	14 ± 10	13 ± 9
Tromsø, Norway	median	26 ± 9	1.6 ± 0.4	29 ± 16	24 ± 14	21 ± 12
Sea ice samples						
Arctic Ocean, summer	median	49 ± 8	2.3 ± 0.3	15 ± 20	9 ± 11	7 ± 7

1200 samples analyzed in study from all over Arctic region …

20-50% of light absorption in particulate fraction was due to non-black carbon components ("brown carbon")



Seasonal contributions to light absorbing constituents inferred from snow depth profiles

Organic Matter Sources

GEOPHYSICAL RESEARCH LETTERS, VOL. 37, L10803, doi:10.1029/2010GL042831, 2010

Arctic organic aerosol measurements show particles from mixed combustion in spring haze and from frost flowers in winter

P. M. Shaw,[1] L. M. Russell,[1] A. Jefferson,[2] and P. K. Quinn[3]

Barrow AK
2008-2009

FTIR
analysis of
Teflon filters

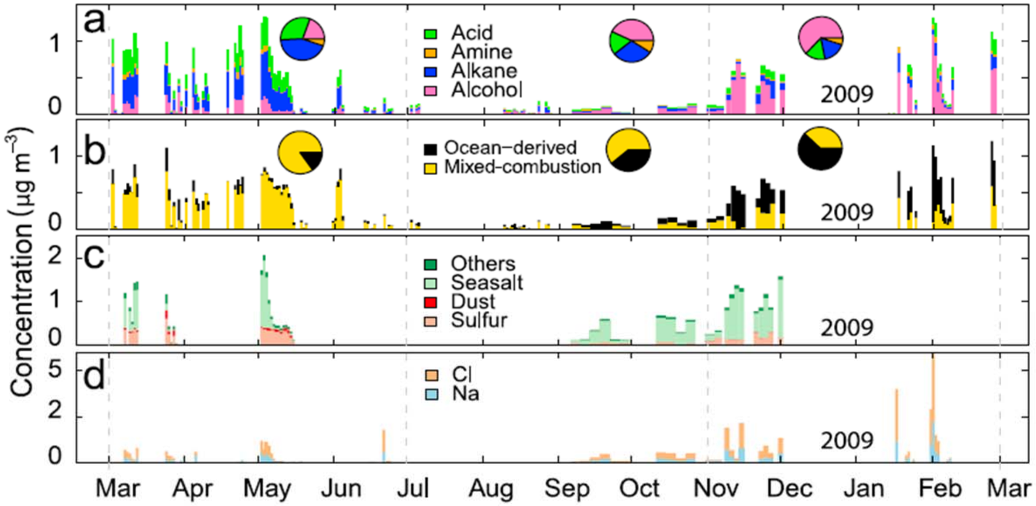


Figure 1. Time series of measured atmospheric aerosol component concentrations. (a) FTIR organic functional groups; (b) PMF factors; (c) XRF trace metals; (d) IC sea salt. Bar widths correspond to durations of collected filters. Inset pies indicate time weighted seasonal averages.

Alkane and carboxylic acids dominate spring OM; organic hydroxyl in winter

Ocean-derived OM: broad organic hydroxyl absorbance, representative of carbohydrate-like compounds

Winter had higher correlation of particle concentration to wind-speed attributed to production from frost flowers

Little OM at low wind speeds or above 8 m s^{-1}

What advances have been made in the identification and characterization of organic matter in snow/ice?

Detection and Structural Identification of Dissolved Organic Matter in Antarctic Glacial Ice at Natural Abundance by SPR-W5-WATERGATE ^{1}H NMR Spectroscopy

Brent G. Pautler,[†] André J. Simpson,[*,†] Myrna J. Simpson,[*,†] Li-Hong Tseng,[‡] Manfred Spraul,[‡] Ashley Dubnick,[§] Martin J. Sharp,[§] and Sean J. Fitzsimons[||]

ES&T, 2011

Antarctic glacial DOM studied here was predominantly composed of a mixture of small recognizable molecules differing from DOM in marine, lacustrine, and other terrestrial environments.

Major constituents detected were:

- lactic and formic acid
- free amino acids
- a mixture of simple sugars and amino sugars

Authors suggest that the detection of free amino acid and amino sugar monomer components of peptidoglycan within the ice suggests that Antarctic glacial DOM likely originates from in situ microbial activity.

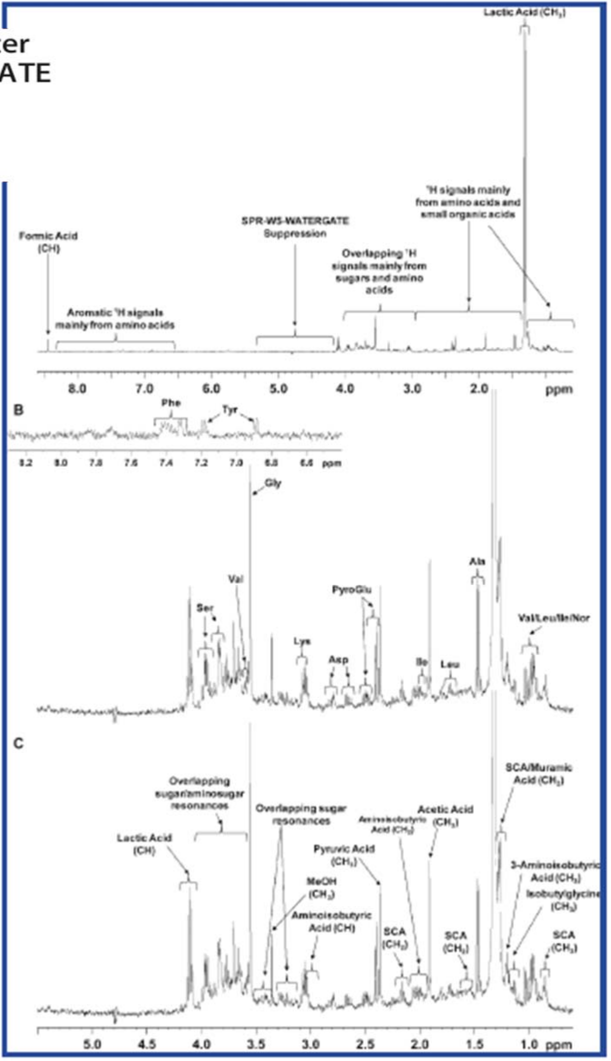
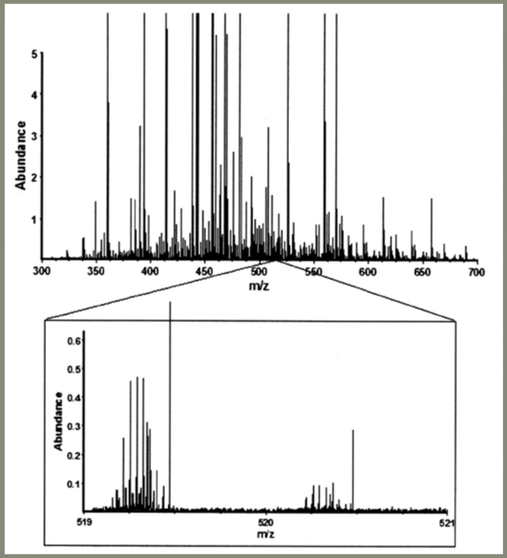
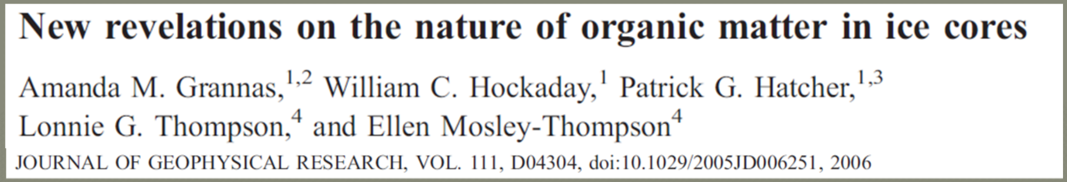


Figure 1. SPR-W5-WATERGATE ^{1}H NMR spectra of Victoria Upper Glacier ice sample from the glacial-basal ice contact, (A) Entire spectrum highlighting the major spectral ^{1}H regions, the suppressed ^{1}H water signal region, along with the lactic and formic acid ^{1}H chemical shift assignments; (B) The same sample spectrum magnified to highlight the resonances assigned to amino acids, inset: aromatic ^{1}H region with amino acid assignments; (C) Magnified spectrum highlighting sugar and amino sugar ^{1}H overlap, and other biologically relevant acid ^{1}H resonances within the ice.

What advances have been made in the identification and characterization of organic matter in snow/ice?

FTICR - MS

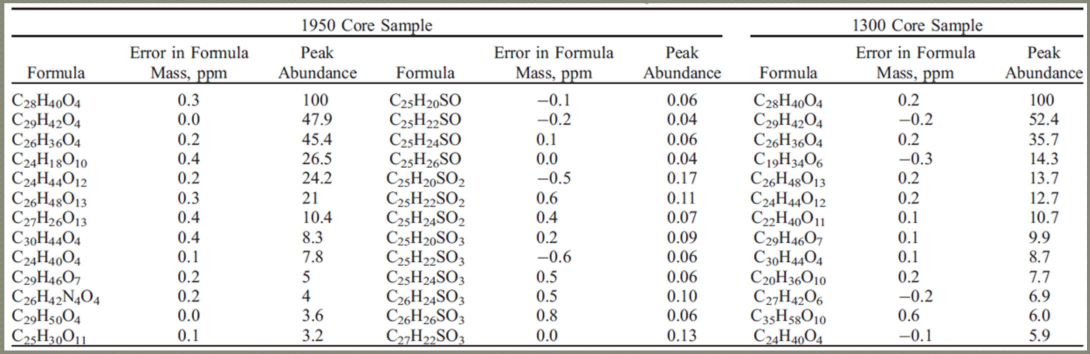




New revelations on the nature of organic matter in ice cores

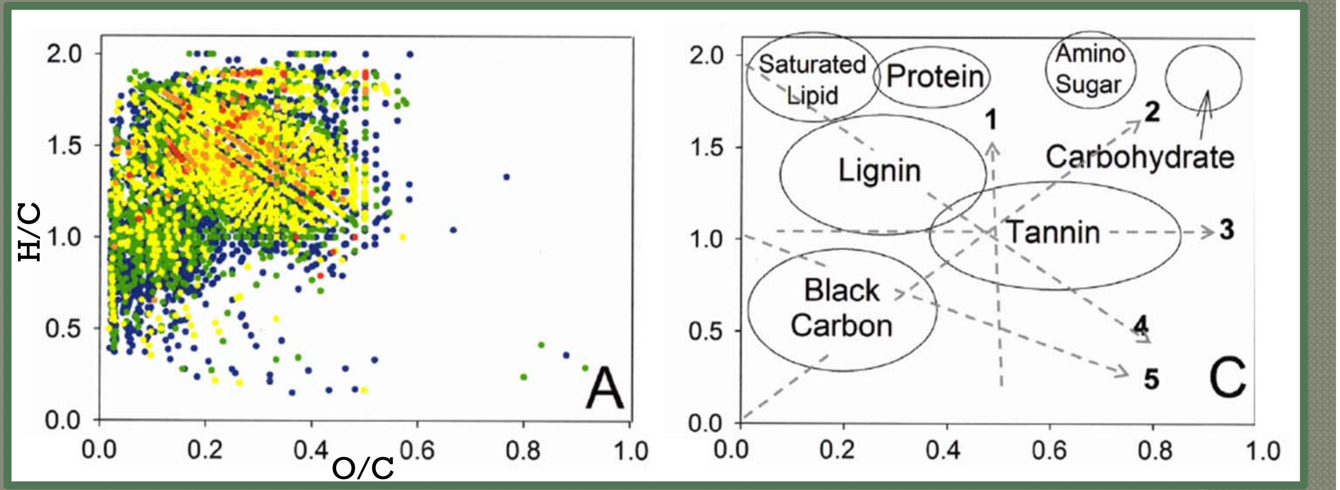
Amanda M. Grannas,[1,2] William C. Hockaday,[1] Patrick G. Hatcher,[1,3]
Lonnie G. Thompson,[4] and Ellen Mosley-Thompson[4]

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 111, D04304, doi:10.1029/2005JD006251, 2006

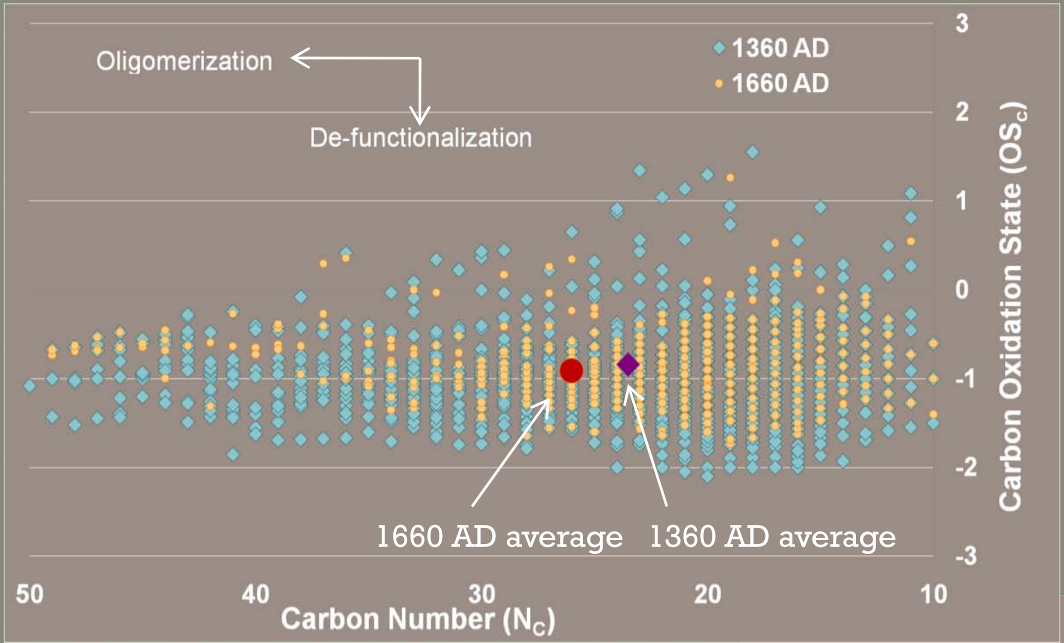


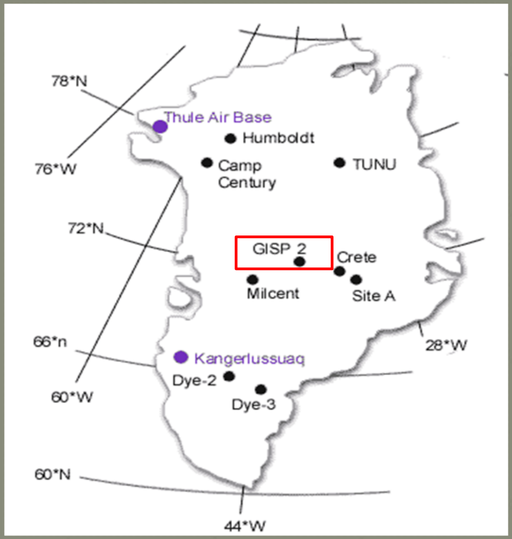
1950 Core Sample						1300 Core Sample		
Formula	Error in Formula Mass, ppm	Peak Abundance	Formula	Error in Formula Mass, ppm	Peak Abundance	Formula	Error in Formula Mass, ppm	Peak Abundance
$C_{28}H_{40}O_4$	0.3	100	$C_{25}H_{20}SO$	−0.1	0.06	$C_{28}H_{40}O_4$	0.2	100
$C_{29}H_{42}O_4$	0.0	47.9	$C_{25}H_{22}SO$	−0.2	0.04	$C_{29}H_{42}O_4$	−0.2	52.4
$C_{26}H_{36}O_4$	0.2	45.4	$C_{25}H_{24}SO$	0.1	0.06	$C_{26}H_{36}O_4$	0.2	35.7
$C_{24}H_{18}O_{10}$	0.4	26.5	$C_{25}H_{26}SO$	0.0	0.04	$C_{19}H_{34}O_6$	−0.3	14.3
$C_{24}H_{44}O_{12}$	0.2	24.2	$C_{25}H_{20}SO_2$	−0.5	0.17	$C_{26}H_{48}O_{13}$	0.2	13.7
$C_{26}H_{48}O_{13}$	0.3	21	$C_{25}H_{22}SO_2$	0.6	0.11	$C_{24}H_{44}O_{12}$	0.2	12.7
$C_{27}H_{26}O_{13}$	0.4	10.4	$C_{25}H_{24}SO_2$	0.4	0.07	$C_{22}H_{40}O_{11}$	0.1	10.7
$C_{30}H_{44}O_4$	0.4	8.3	$C_{25}H_{20}SO_3$	0.2	0.09	$C_{29}H_{46}O_7$	0.1	9.9
$C_{24}H_{40}O_4$	0.1	7.8	$C_{25}H_{22}SO_3$	−0.6	0.06	$C_{30}H_{44}O_4$	0.1	8.7
$C_{29}H_{46}O_7$	0.2	5	$C_{25}H_{24}SO_3$	0.5	0.06	$C_{20}H_{36}O_{10}$	0.2	7.7
$C_{26}H_{42}N_4O_4$	0.2	4	$C_{26}H_{24}SO_3$	0.5	0.10	$C_{27}H_{42}O_6$	−0.2	6.9
$C_{29}H_{50}O_4$	0.0	3.6	$C_{26}H_{26}SO_3$	0.8	0.06	$C_{35}H_{58}O_{10}$	0.6	6.0
$C_{25}H_{30}O_{11}$	0.1	3.2	$C_{27}H_{22}SO_3$	0.0	0.13	$C_{24}H_{40}O_4$	−0.1	5.9

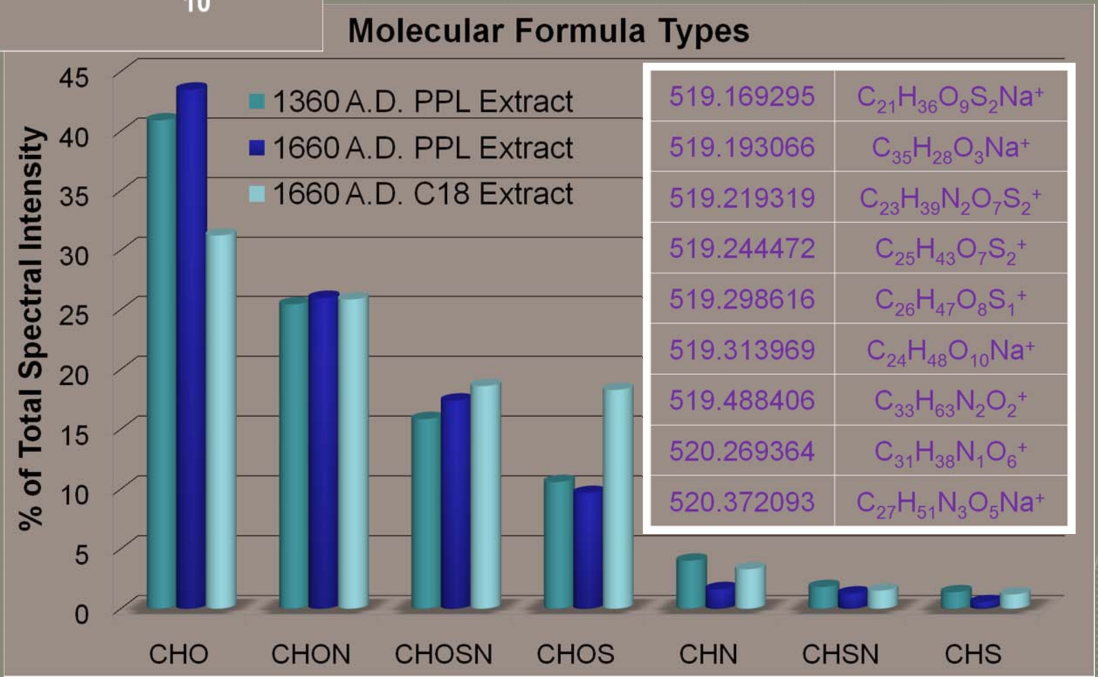
- ➢4000 unique m/z values obtained from sample
- ➢70% of peaks identified by a single molecular formula
- ➢Much greater S and N incorporation in DOM in modern ice



Some new data from a Greenland ice core







519.169295	$C_{21}H_{36}O_9S_2Na^+$
519.193066	$C_{35}H_{28}O_3Na^+$
519.219319	$C_{23}H_{39}N_2O_7S_2^+$
519.244472	$C_{25}H_{43}O_7S_2^+$
519.298616	$C_{26}H_{47}O_8S_1^+$
519.313969	$C_{24}H_{48}O_{10}Na^+$
519.488406	$C_{33}H_{63}N_2O_2^+$
520.269364	$C_{31}H_{38}N_1O_6^+$
520.372093	$C_{27}H_{51}N_3O_5Na^+$

Marsh, Boschi, Grannas, Hatcher, Sleighter.
J. of Glaciology, in prep

The fly in the ointment …

- From an analytical standpoint … 99% of methods require we MELT and PREP the sample!
  - Particles filtered from *melted* samples, characterized after isolation
  - Dissolved species obtained from melted sample (better filter it if you are doing chromatography!)
    - Can be analyzed as is, or acidified, or extracted, or derivatized, or some combination of all (egad!)
  - How do we know what was originally in dissolved form stays there … How do we know portions of particulates don't become dissolved during workup?
- Evidence that sample work-up can impact results
  - Domine et al., 2010, ACP, 10(3), Acetaldehyde in the Alaska subarctic snowpack

    "We propose that most of the acetaldehyde measured is either trapped or dissolved within organic aerosol particles trapped in snow, or that acetaldehyde is formed by the hydrolysis of organic precursors …when the snow is melted for analysis."

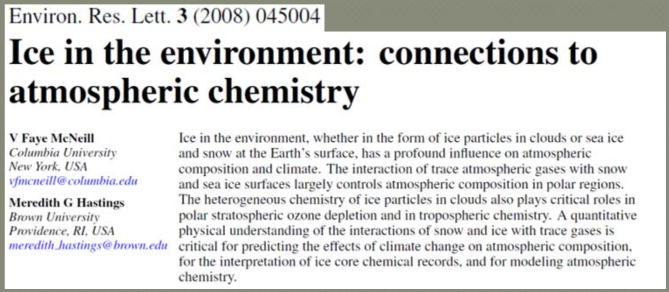
What we need to work on…

- How does sample handing impact dissolved vs. particulate phases? How can we know that what was originally dissolved stays dissolved and vice versa? How do we know sample prep doesn't lead to artifacts? (…and what is an appropriate blank?)

- Which phase is most important for snow photochemistry and generation of VOCs?

- Absorption of light will certainly impact the radiative and energy balances … but from a photochemistry standpoint we care about what reactive intermediates are produced from said absorption
  - If organics are an important photosensitizer, we need to quantify OH, $^1O_2$, ^{3}DOM, RO_2, etc production

These myriad processes all play an important role in the exchange of reactive species between snow and the atmosphere.



Environ. Res. Lett. **3** (2008) 045004

Ice in the environment: connections to atmospheric chemistry

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New York, USA
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Ice in the environment, whether in the form of ice particles in clouds or sea ice and snow at the Earth's surface, has a profound influence on atmospheric composition and climate. The interaction of trace atmospheric gases with snow and sea ice surfaces largely controls atmospheric composition in polar regions. The heterogeneous chemistry of ice particles in clouds also plays critical roles in polar stratospheric ozone depletion and in tropospheric chemistry. A quantitative physical understanding of the interactions of snow and ice with trace gases is critical for predicting the effects of climate change on atmospheric composition, for the interpretation of ice core chemical records, and for modeling atmospheric chemistry.

Environ. Res. Lett. 3 (2008) 045008 (5pp) doi:10.1088/1748-9326/3/4/045008

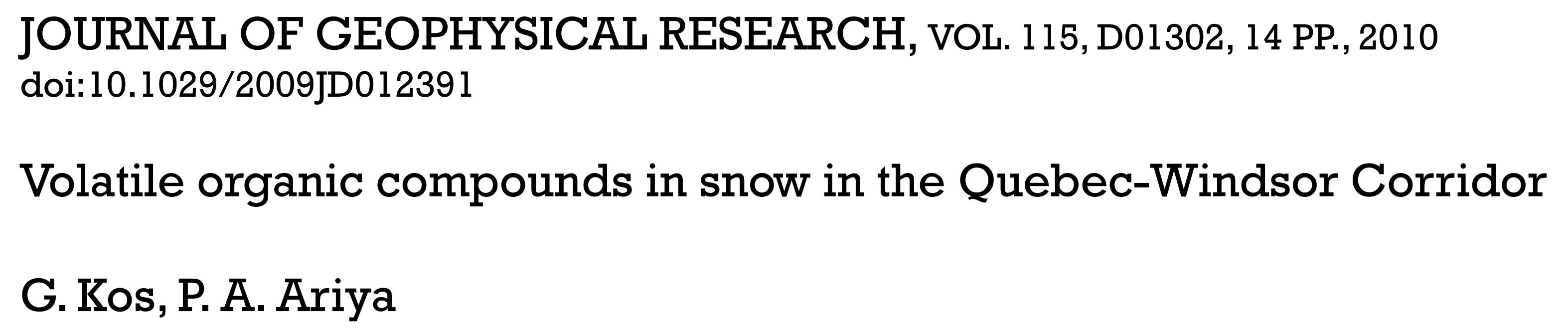
Uptake of acetone, ethanol and benzene to snow and ice: effects of surface area and temperature

J P D Abbatt[1], T Bartels-Rausch, M Ullerstam and T J Ye

Mountain Research and Development Vol 28 No 3/4 Aug–Nov 2008: 222–225 doi:10.1659/mrd.1041

Massimo Pecci

Snow Cover on the Mountains: Still White and Pure?



JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 115, D01302, 14 PP., 2010
doi:10.1029/2009JD012391

Volatile organic compounds in snow in the Quebec-Windsor Corridor

G. Kos, P. A. Ariya

What have we learned about the interaction of snow/ice with VOCs?

Simulating the Influence of Snow on the Fate of Organic Compounds

Environ. Sci. Technol. **2004**, *38,* 4176−4186

GILLIAN L. DALY AND FRANK WANIA*

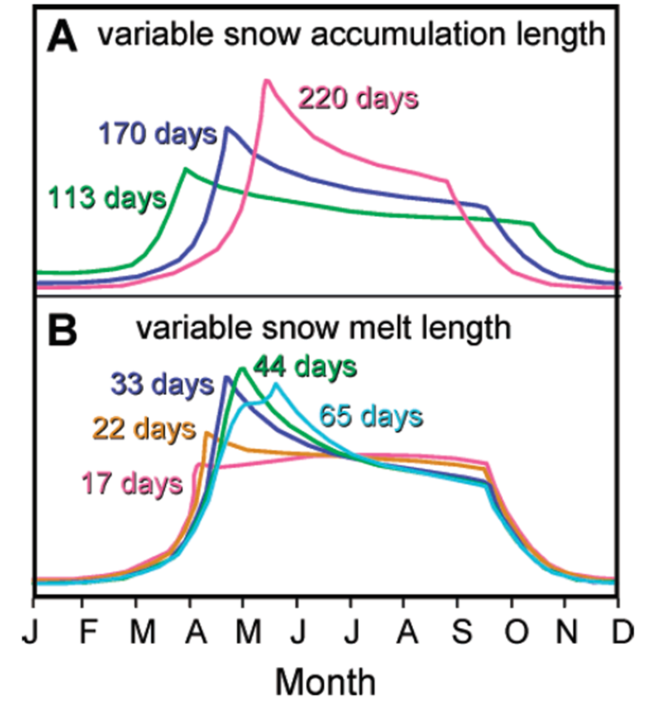


FIGURE 7. Air concentrations of CB-101 over the course of 1 yr assuming various lengths of snow accumulation (A) and snowmelt (B).

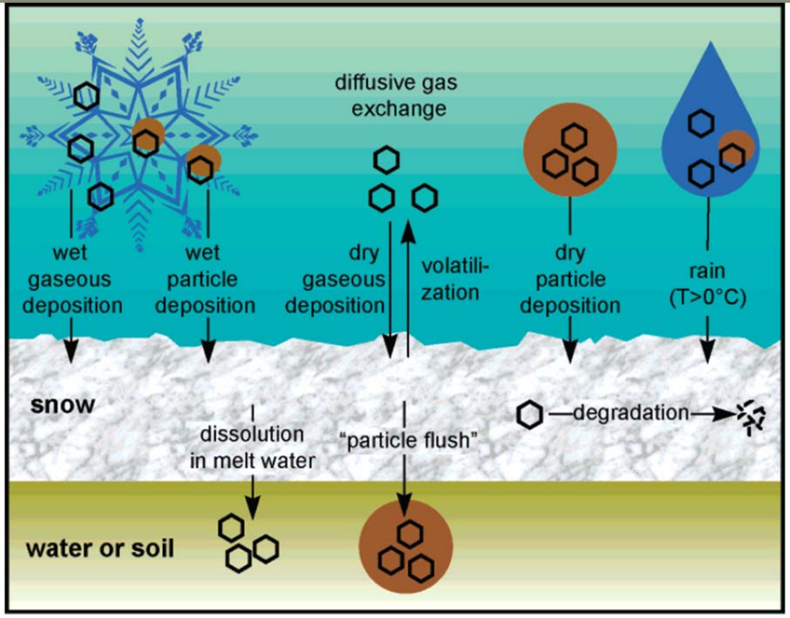


FIGURE 1. Processes involved in the delivery and loss of organic contaminants in a seasonal snow cover and described in the modified CoZMo−POP model.

"The best way to accomplish a model evaluation is to measure with fairly high temporal resolution the air and meltwater concentrations of various organic contaminants prior, during and after melting…"

OASIS field data coming!

Future needs as this study sees it

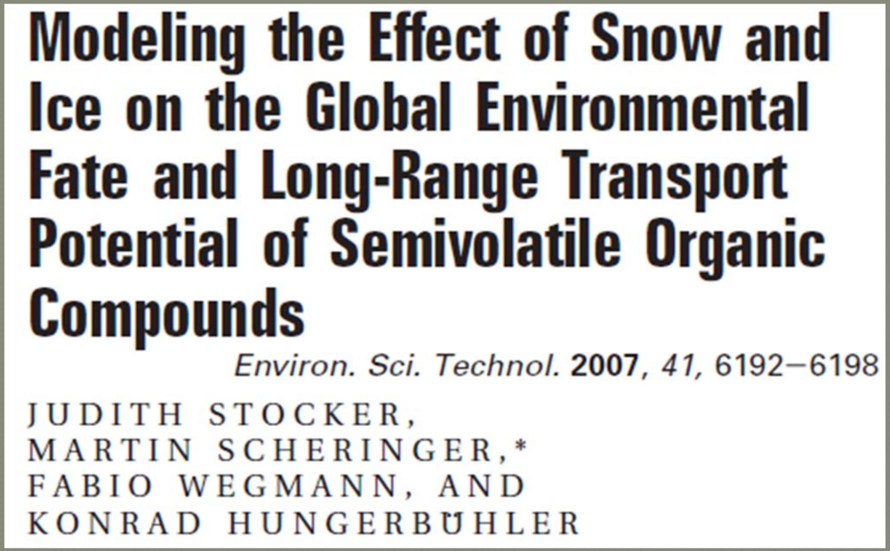
Understanding the fate of particles in snowpack.

Understanding the kinetics of diffusive air/snow exchange.

Better quantification of the interfacial partitioning constant for the snow surface for large organics and of the specific snow surface area.

Quantification of the rate of organic chemical transformations occurring in the snow.

What have we learned about the interaction of snow/ice with VOCs?



Modeling the Effect of Snow and Ice on the Global Environmental Fate and Long-Range Transport Potential of Semivolatile Organic Compounds

Environ. Sci. Technol. **2007**, *41*, 6192−6198

JUDITH STOCKER,
MARTIN SCHERINGER,*
FABIO WEGMANN, AND
KONRAD HUNGERBÜHLER

Snow and ice added to a global multimedia box model (CliMoChem model) to investigate the influence of these media on the environmental fate and LRT of semivolatile organic compouds (HCB, PCBs, PBDEs, HCH, dacthal)

Low latitudes – snow acts as a transfer medium taking up chemicals from air and re-releasing to water or soil during snowmelt

High latitudes – snow and ice shield water, soil, and vegetation from chemical deposition, make air concentrations higher than what is observed in models w/o snowcover.

And what is the role of a changing climate???

From the perspective of organic matter: altered sources and amounts

- Changing transport patterns of organics to polar regions
- Changing atmospheric chemistry of SOA, etc?
- Thawing permafrost – release of previously stored organic carbon
- Higher temps – altered microbial processes, could change nature of organic carbon or its use as a substrate
- Greater export of organic matter from e.g. tundra … altered timing, quantity and quality of organic carbon
- Longer ice-free periods, greater chance of photobleaching of organic carbon, changing reactivity?

From the perspective of snow/ice: changes in precipitation, timing of melt/freeze cycles, sea ice extent

- If the snow goes away … are we out of a job?

So what do we really know???

“There are known knowns; there are things we know we know.
We also know there are known unknowns; that is to say we know there
are some things we do not know. But there are also unknown unknowns
– the ones we don't know we don't know.”

Donald Rumsfeld, Former U.S. Secretary of Defense

Known knowns:

- snow/ice is an important medium for chemical reaction and physical processing of atmospheric constituents
- organic constituents are important from both photochemistry and radiative transfer standpoints

Known unknowns:

- we need better characterization of organic material – what is this stuff?
- we need better accounting of dissolved vs. particulate fractions - what are the absorption and photosensitizing properties of each?
- we need better understanding of WHERE the chemistry occurs – on vs. in?

Unknown unknowns:

“If you thought that science was certain — well, that is just an error on your part.”
Richard Feynman

Where do we go from here?

Who: What organics are the main players in snow/atmosphere interactions? (Answer will depend on what chemistry you are talking about … photoproduction of oxidants? Direct production of VOCs? Electron shuttling for redox processes?)

What: What processes are most important for 1) oxidant production; 2) VOC production; 3) pollutant degradation; 4) biological systems?

Where: In or on, or both?

When: Seasonality of processes, changing characteristics of organics with time (photobleaching, etc)?

Why: Links to atmospheric chemistry, climate, and ecosystem health … and, well, it's just interesting as hell!

How: How do we adequately characterize the substrates and the chemistry, and insure our methods aren't introducing artifacts?

And a final request:

Next week – National Academy of Science IPY workshop

I would greatly appreciate your input regarding what you take as the greatest accomplishments for near-surface atm. chem during/since IPY, and where we need to go from here …

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