

Carbonaceous species and HUmic
Like Substances in Arctic Snow:
contribution to the speciation of total
carbon and optical properties during
OASIS – Barrow 2009 campaign.

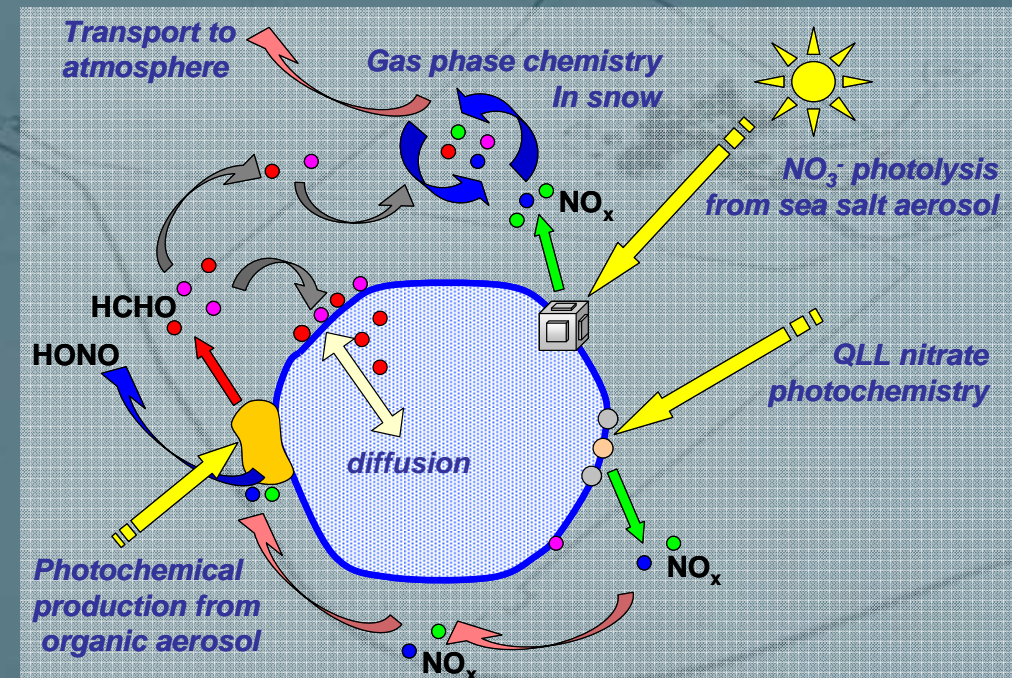
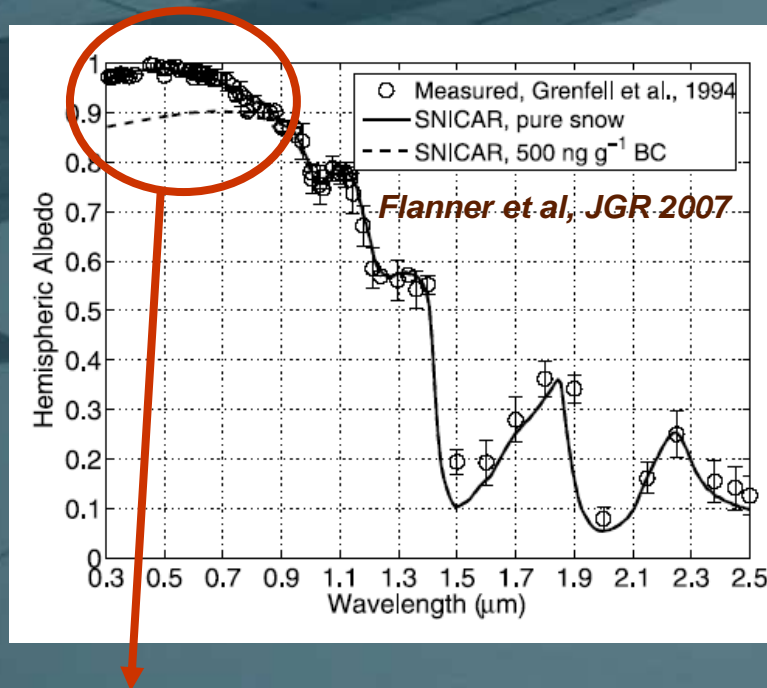
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Why would we look at the carbon content in arctic snowpacks ?

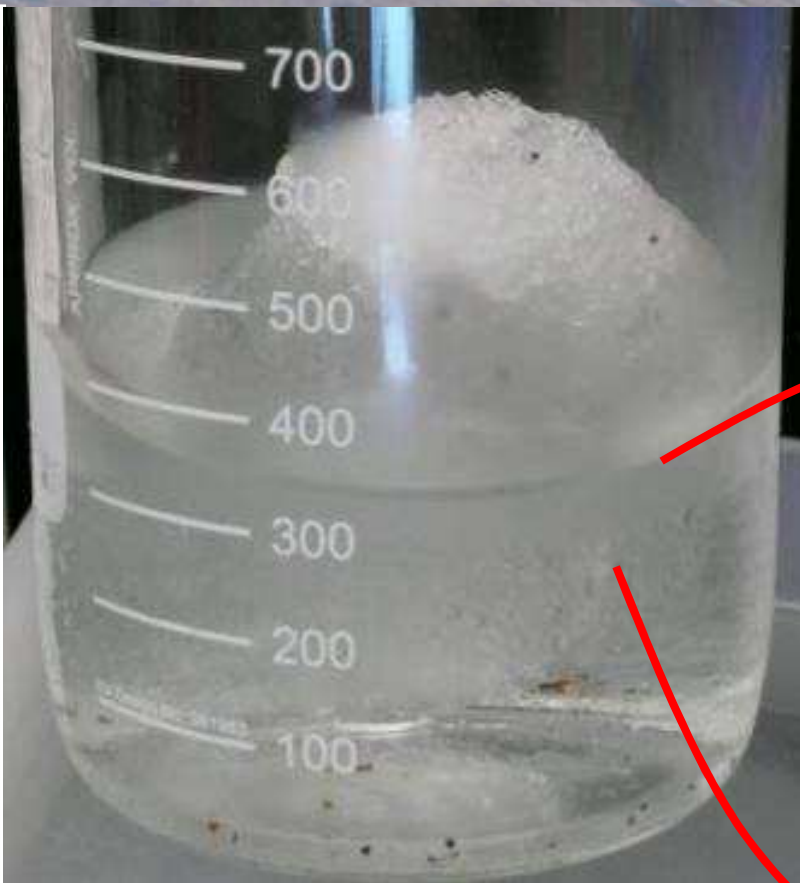


BC lowers snow's albedo, potentially triggering the « snow albedo » climate feedback

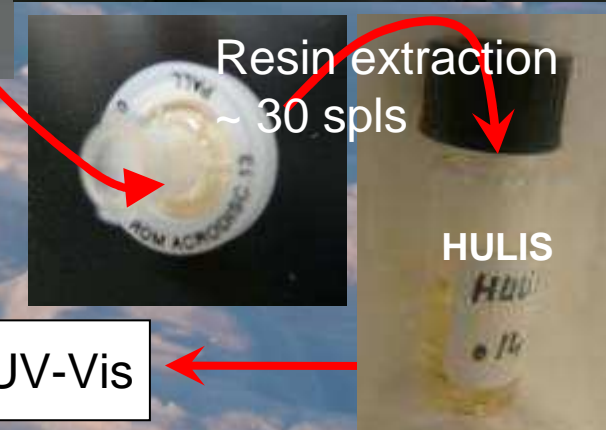
Snowpack photochemistry involves organics
And it influences Boundary Layer chemistry
And it will depends on carbon « speciation »

+ other reasons such as: « it contains all kinds of Persistent Organic Pollutants »

Carbon « Speciation » ?



Sunset instrument
EC – WinOC



IC

HPLC - fluorimetry

GC - MS

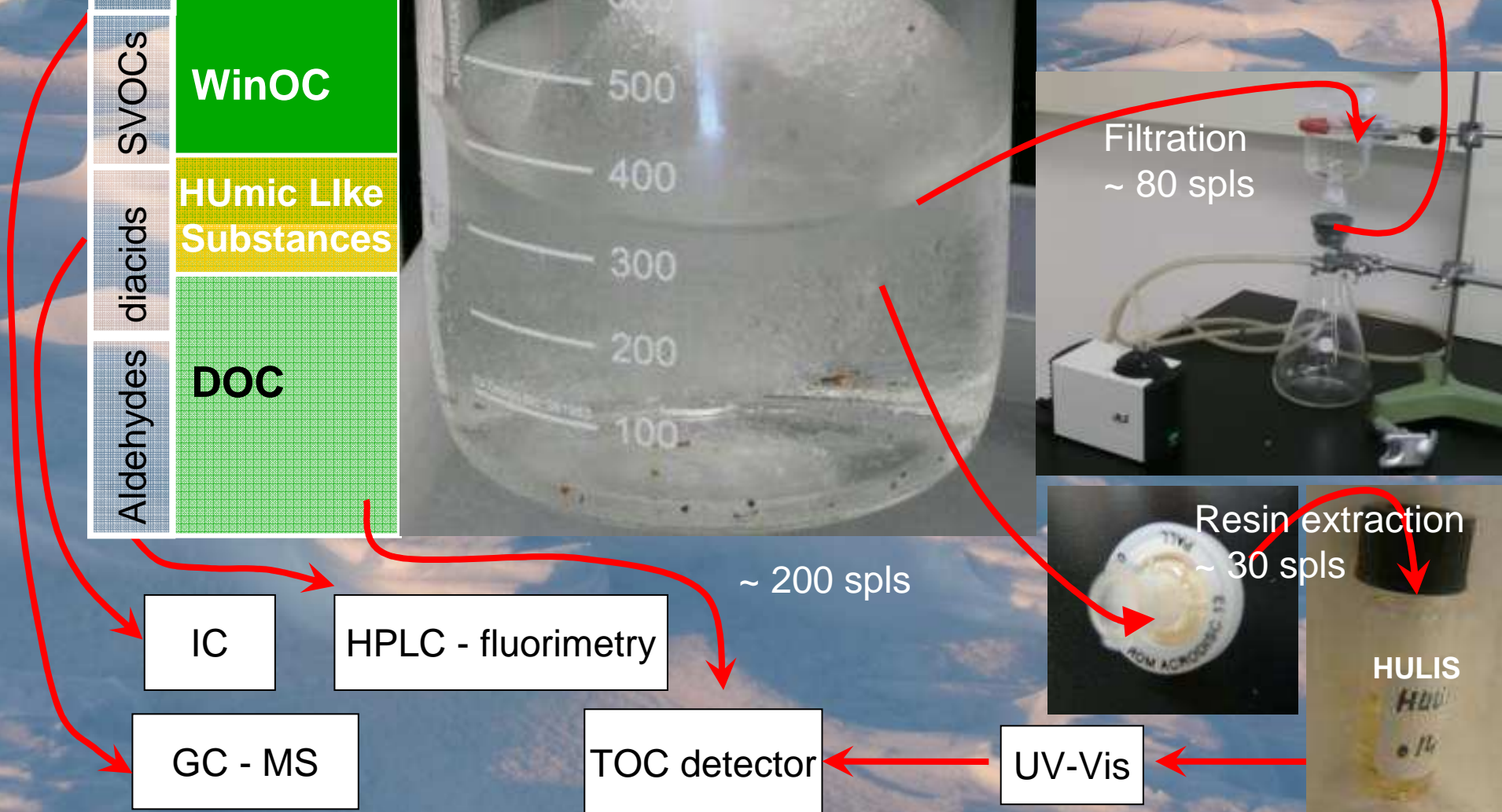
TOC detector

UV-Vis

~ 200 spls

Resin extraction
~ 30 spls

HULIS



HULIS and potential organic absorbers

EC

WinOC

HUmic Like
Substances

DOC

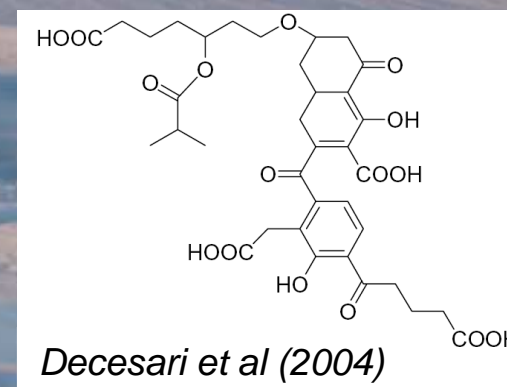
- HULIS are a part of brown carbon (i.e. light absorbing OC)

- polyfunctional oxidized species →

- Photosensitizers !!! Able to « catalyse » photoreactions through excited transition states formed after photon absorption

(cf e.g. Stemmler et al nature 2006, Brigante et al EST 2008)

- What species they actually include depends on specific extraction protocol : ours (cf Baduel et al, ACP 2009) is targeted on polyacidic HULIS



0.5 – 1 L
melted snow

Eluant

DEAE resin

Elimination of
unwanted
compounds

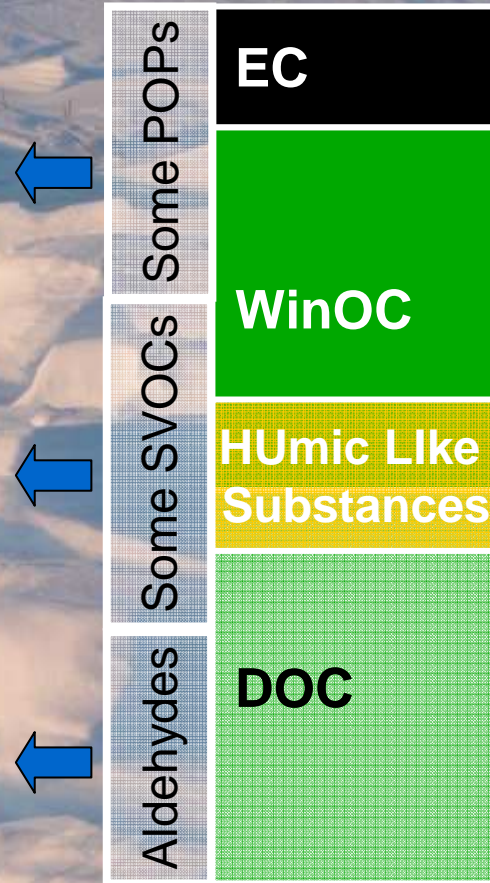
extract
2.3 mL

UV – Vis
(200-600 nm)
1 cm opt. path

TOC detector

How does speciation help ?

More « process – like » snapshots



- How much is there ?
Under which form ?

- What about spatial / temporal variability ?

- Where does it come from ?

- How does it contribute to photochemistry ?

« bulk assessments »

Snowpack variability

Eroded old wind pack

Surface Hoar appearing

Old depth hoar resurfacing

older drift

11 march drift

10 march drift

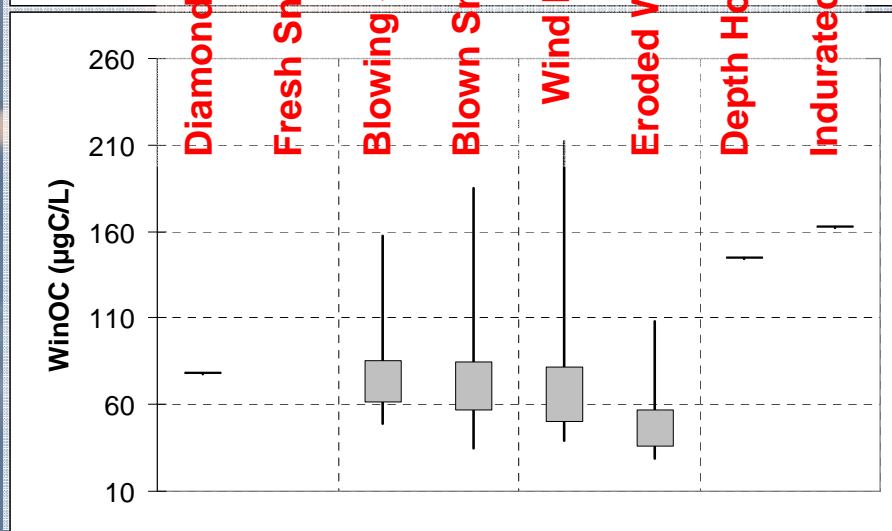
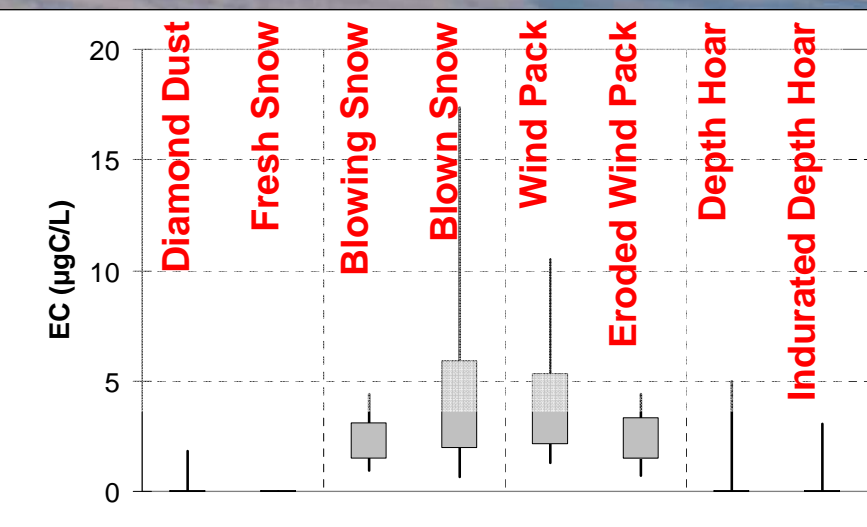
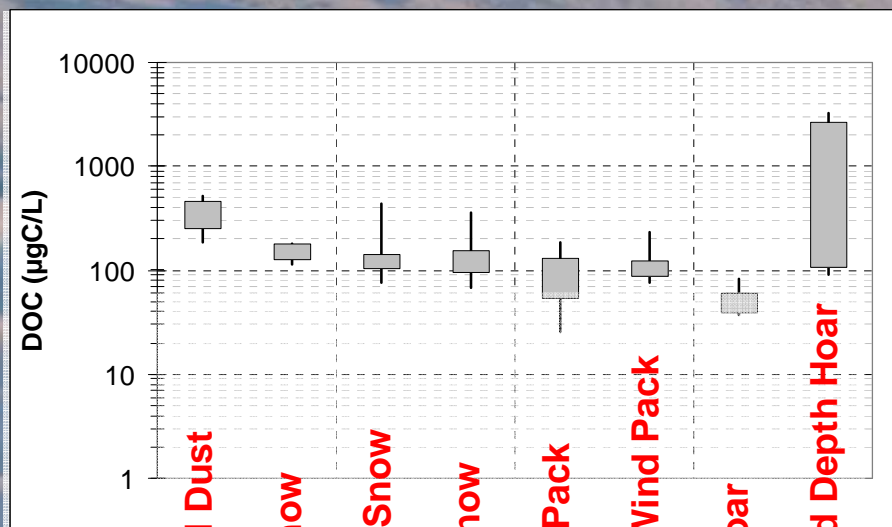
13 march drift

12 march drift, very eroded

- Stratigraphy is not continuous
- Older is not always deeper
- Snow type as indicator ?

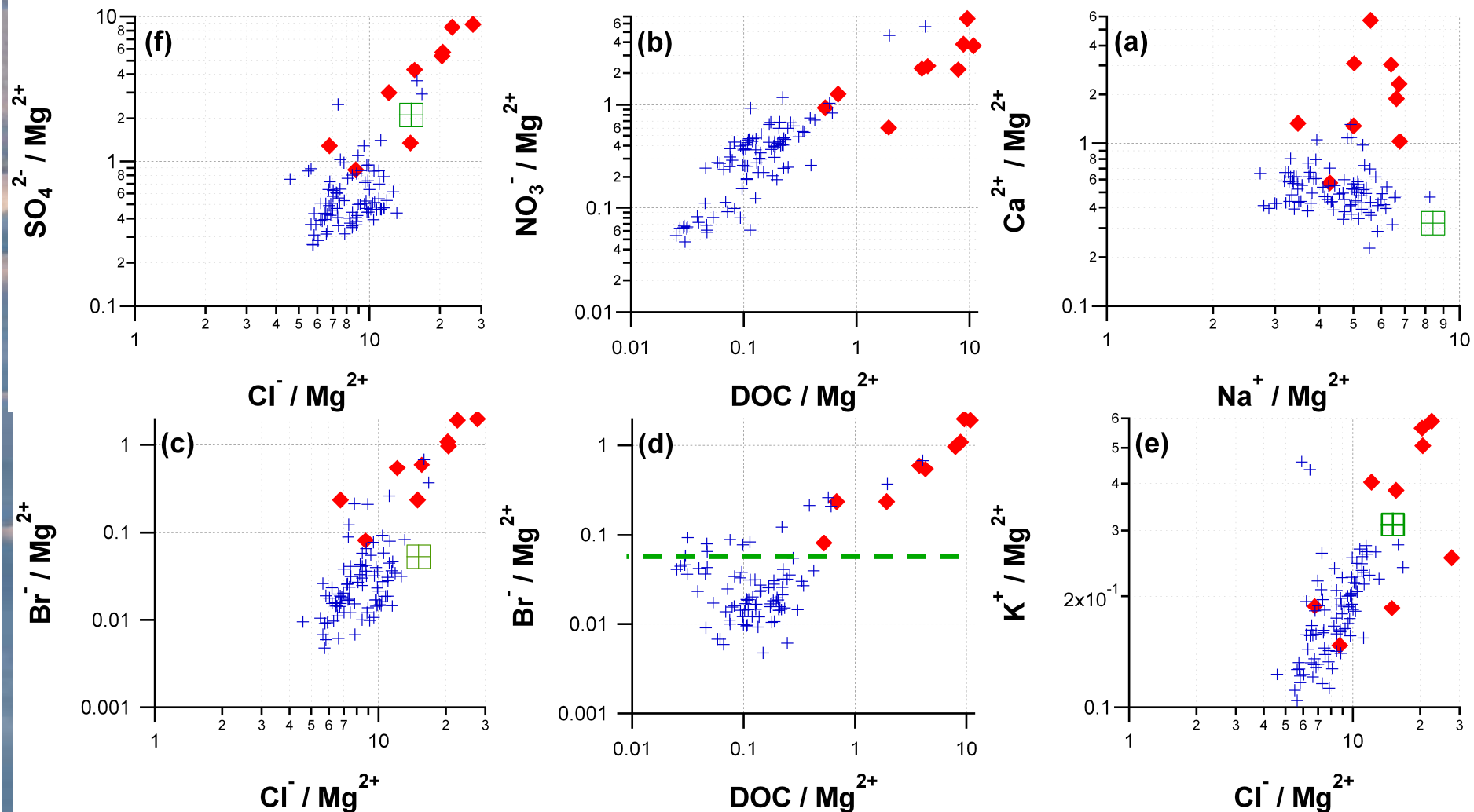
All pictures taken within 200 m radius, on the same day

Carbon content vs snow type



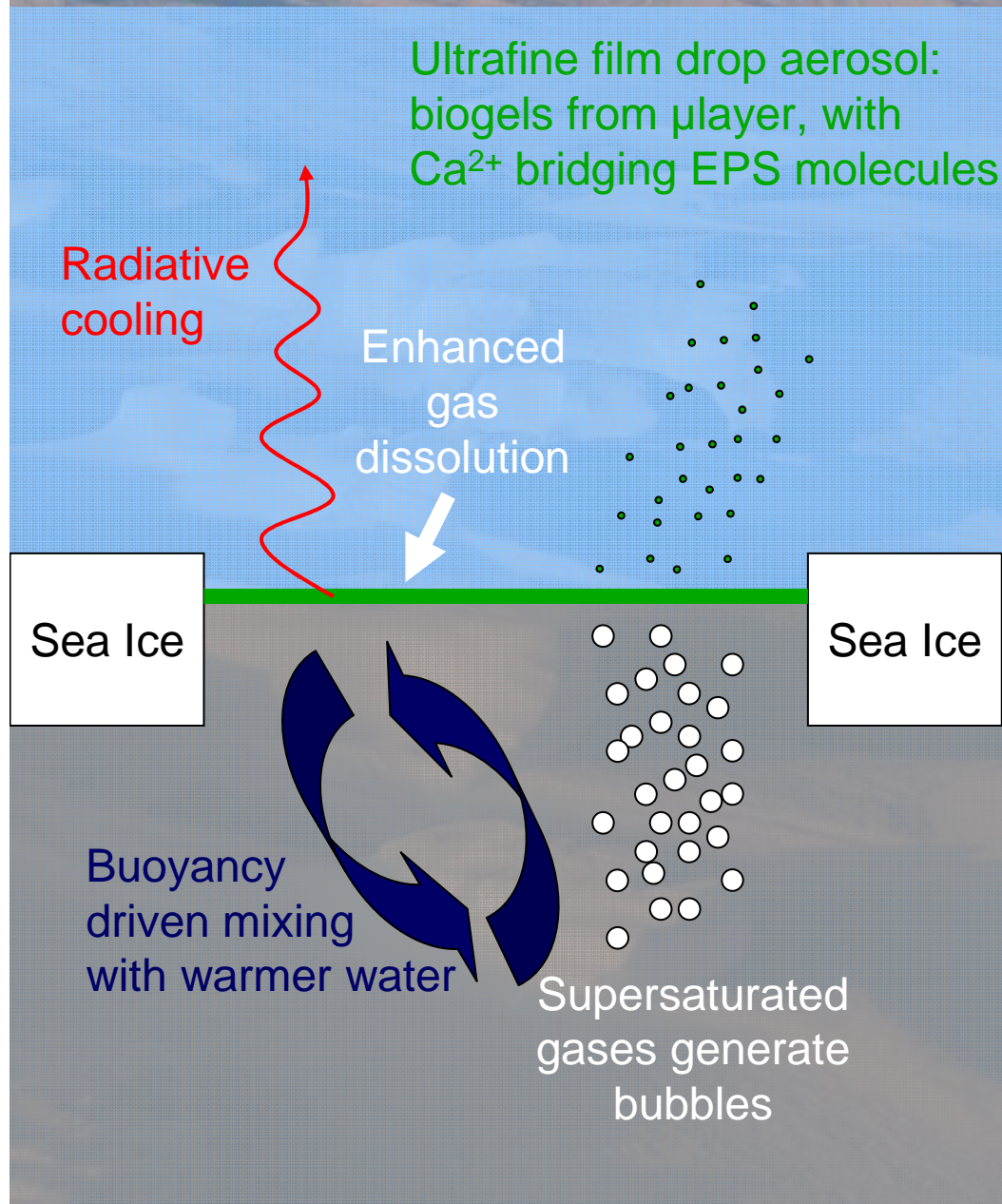
- EC (~BC) is only a minor contributor (<5%)
- DOC major contributor to snowpack carbon
- DOC maximum for
 - Indurated Depth Hoar (Iced Herbal Tea)
 - Diamond Dust → atmospheric origin
- DOC remobilisation ?

DOC Ocean-Atmosphere input



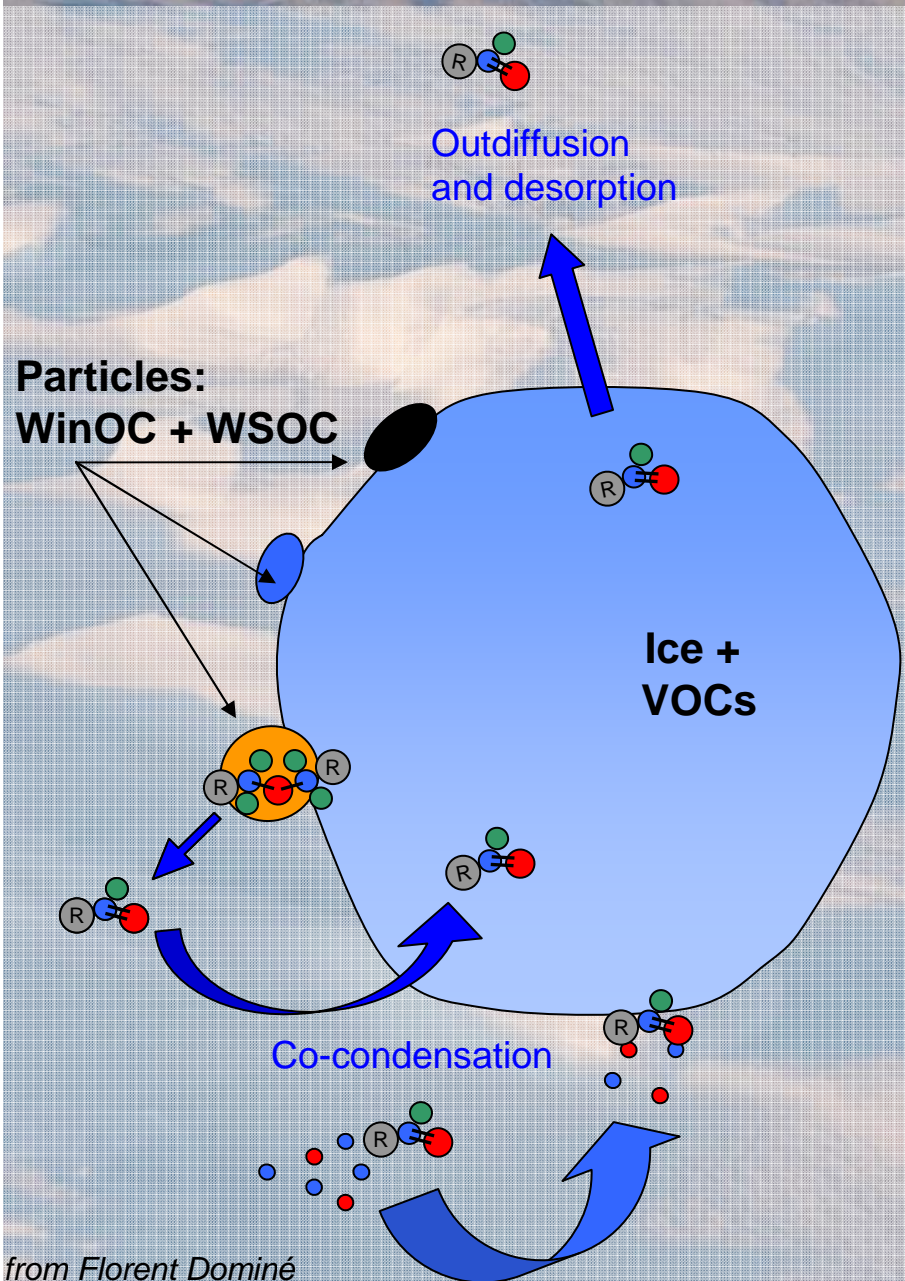
- Relative enrichments in DOC, Cl⁻, Br⁻, NO₃⁻; maybe even SO₄²⁻ could be from ODEs
- K⁺, Ca²⁺, Na⁺ can't be explained from gas phase: biogels from ocean μ player, with Ca²⁺ bridging ExoPolySaccharides molecules

EPS biogels from open lead μ layer



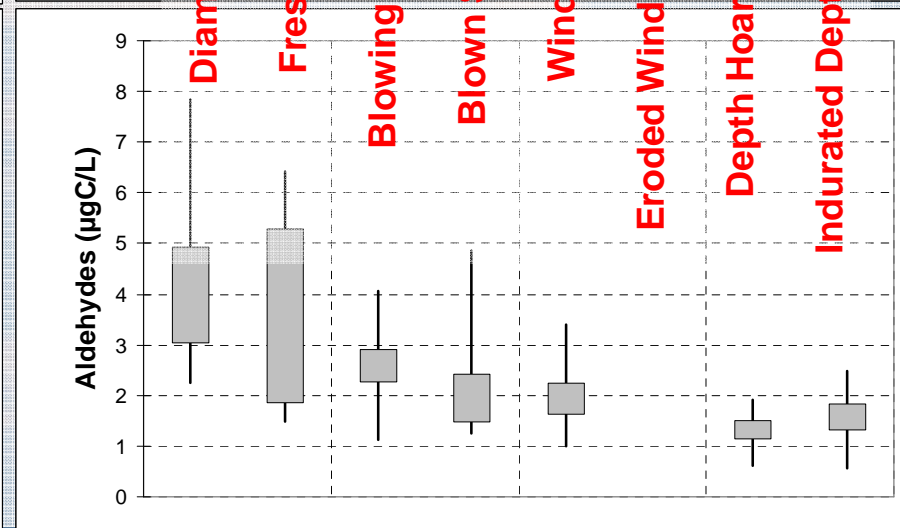
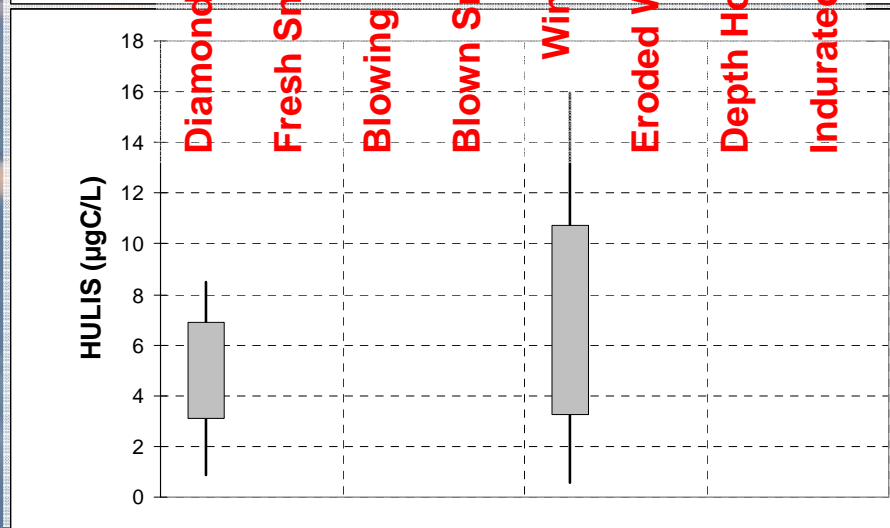
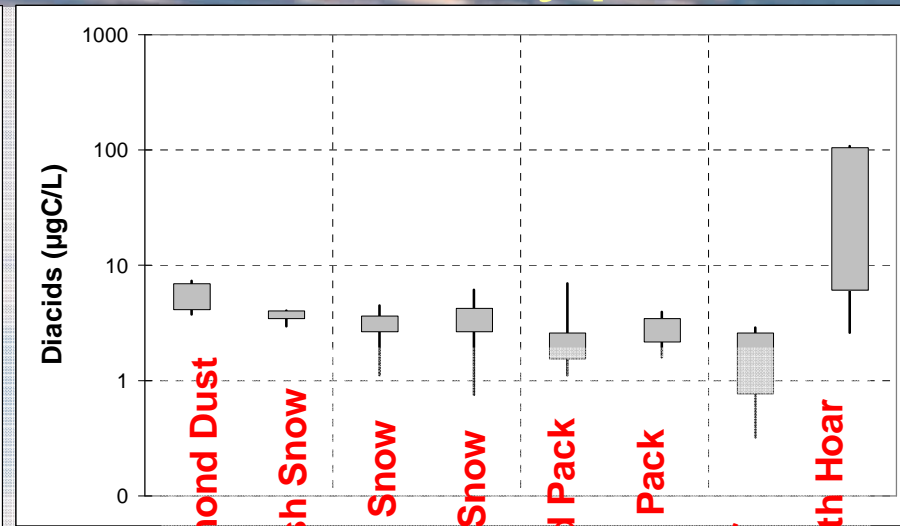
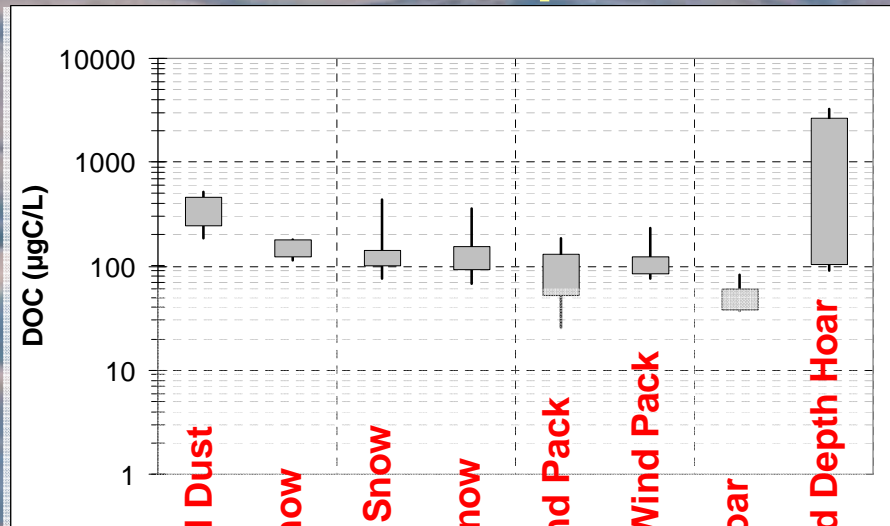
- Bubbling mechanism:
Norris et al, *Ocean Sci* 2011
- Bacterial counts on Frost Flowers, suggesting an active μ layer in the spring too: Bowman and Deming, *GRL* 2010
- Chemical signature of EPS biogels:
Leck and Bigg, *AST* 2010
- in Barrow:
 - MODIS shows an open lead right north of our sampling site
 - backtrajectories coming from north
- implication: EPS biogels as Ice Forming Nuclei ?

DOC, WinOC and real snow chemistry



- Real snow chemistry question: Where is the carbon ?
 - In organic inclusions ?
 - on the surface ?
 - in the ice lattice ?
- DOC and WinOC operationally defined starting from melted snow
 - WinOC has to come from particles
 - DOC contains
 - species dissolved in the ice lattice
 - some adsorbed species
 - Water Soluble Organic Carbon that came with the particles
- → some more speciation is necessary, specially on DOC

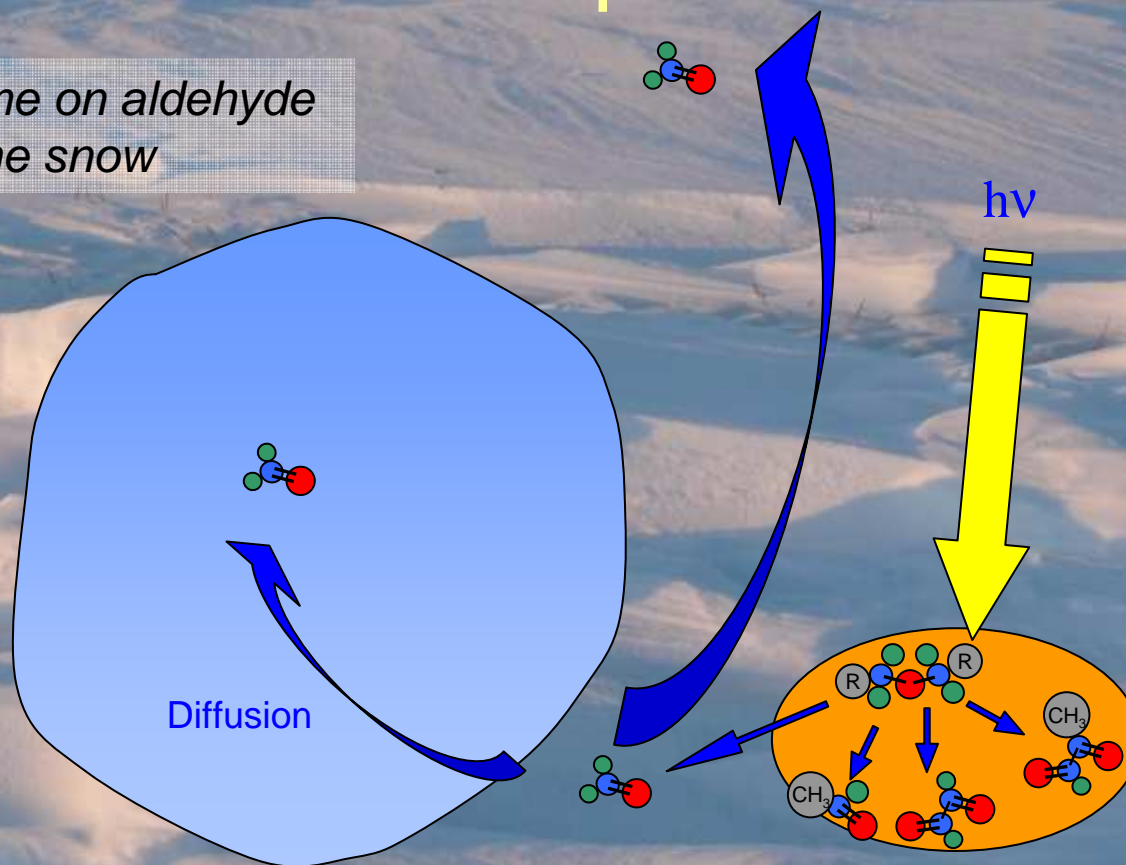
DOC speciation vs snow type



- less than 10% of DOC explained by any single species group
- diacids follow DOC closely: herbal tea source; diamond dust source ?
- most Organic Carbon (DOC and WinOC) largely unknown

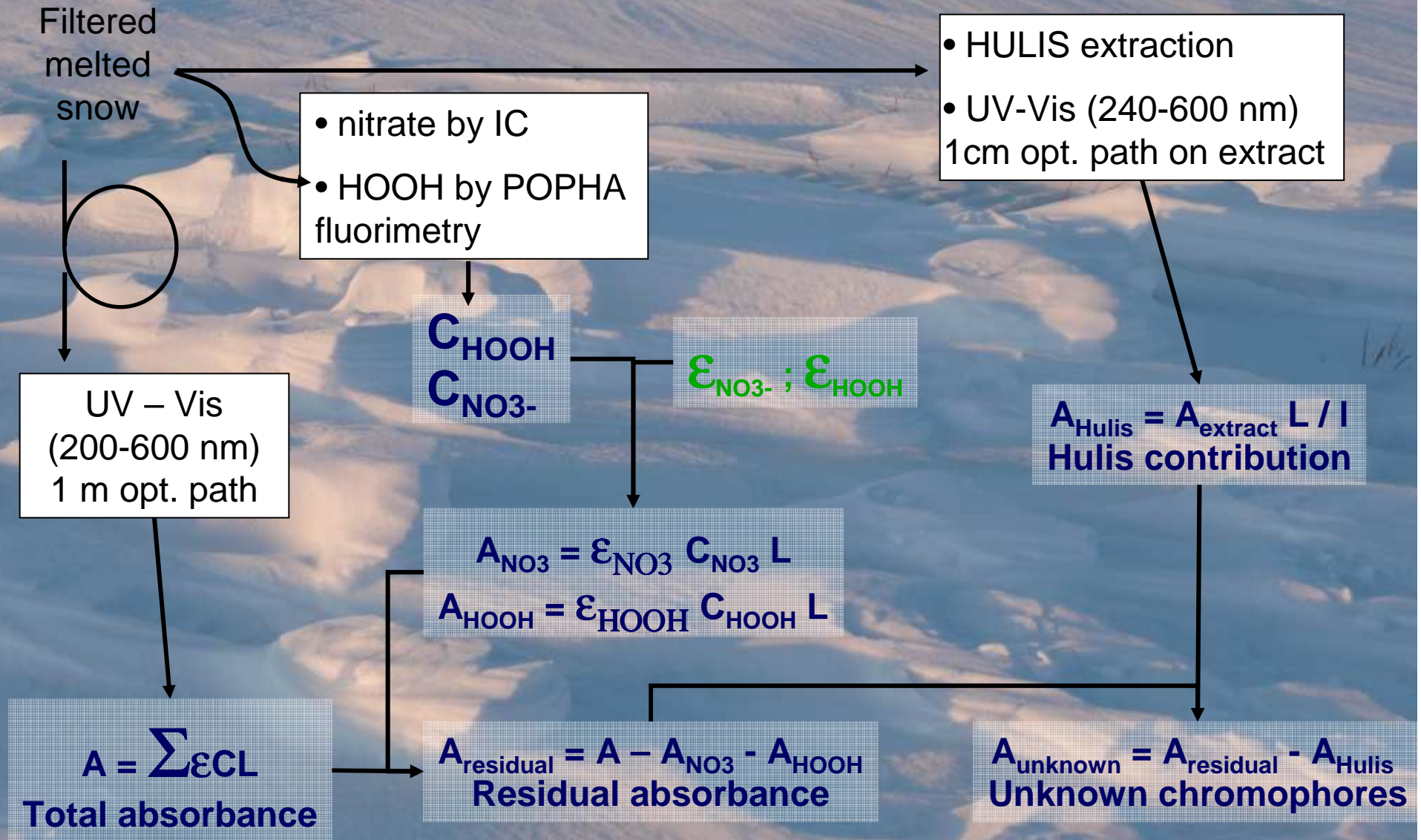
Back to snow photochemistry

Florent's scheme on aldehyde production in the snow

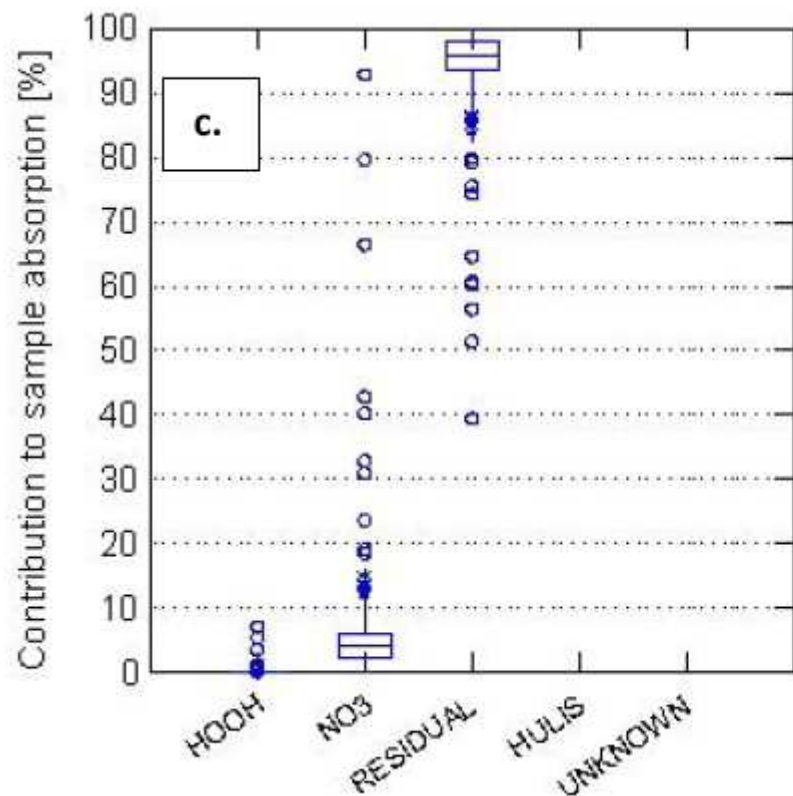


- most OC unknown...
 - but photochemistry starts with absorbing a photon
- look at UV-Vis absorbing species first

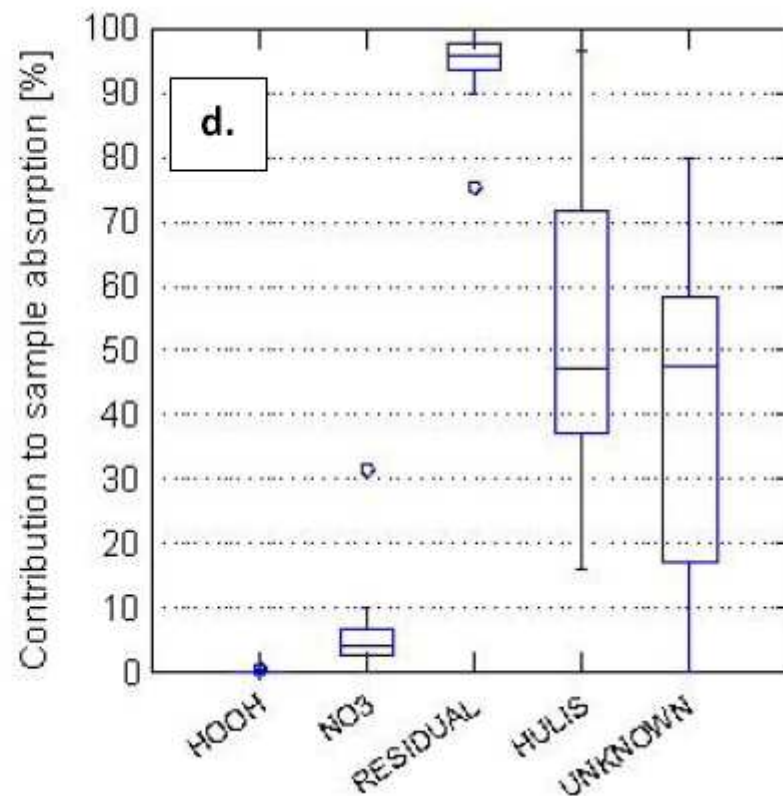
Melted snow total absorbance



Contributions to surface snow integrated absorbance (300 – 450 nm)



no HULIS data (N=350)

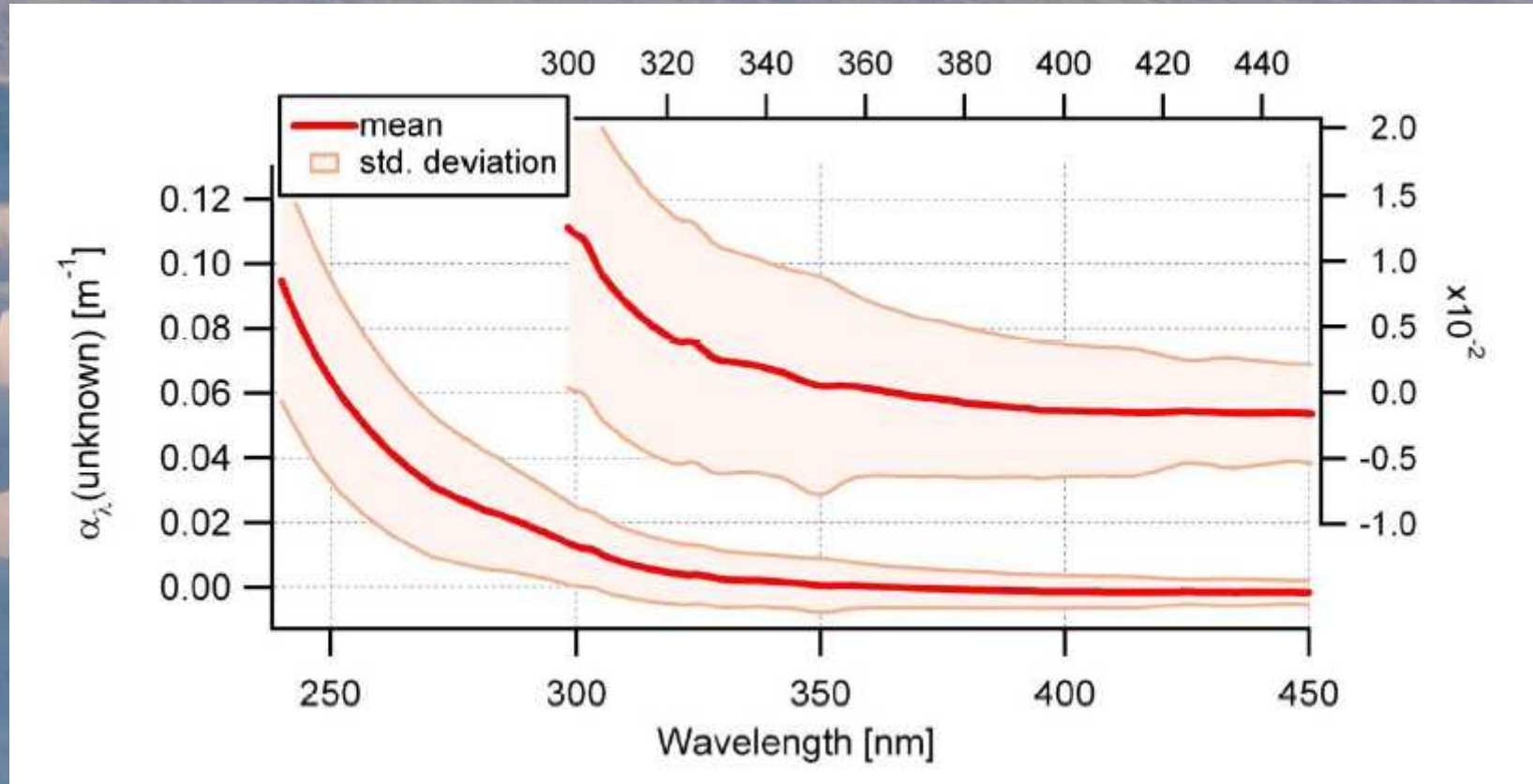


with HULIS data (N=24)

In the most photochemically active wavelength range:

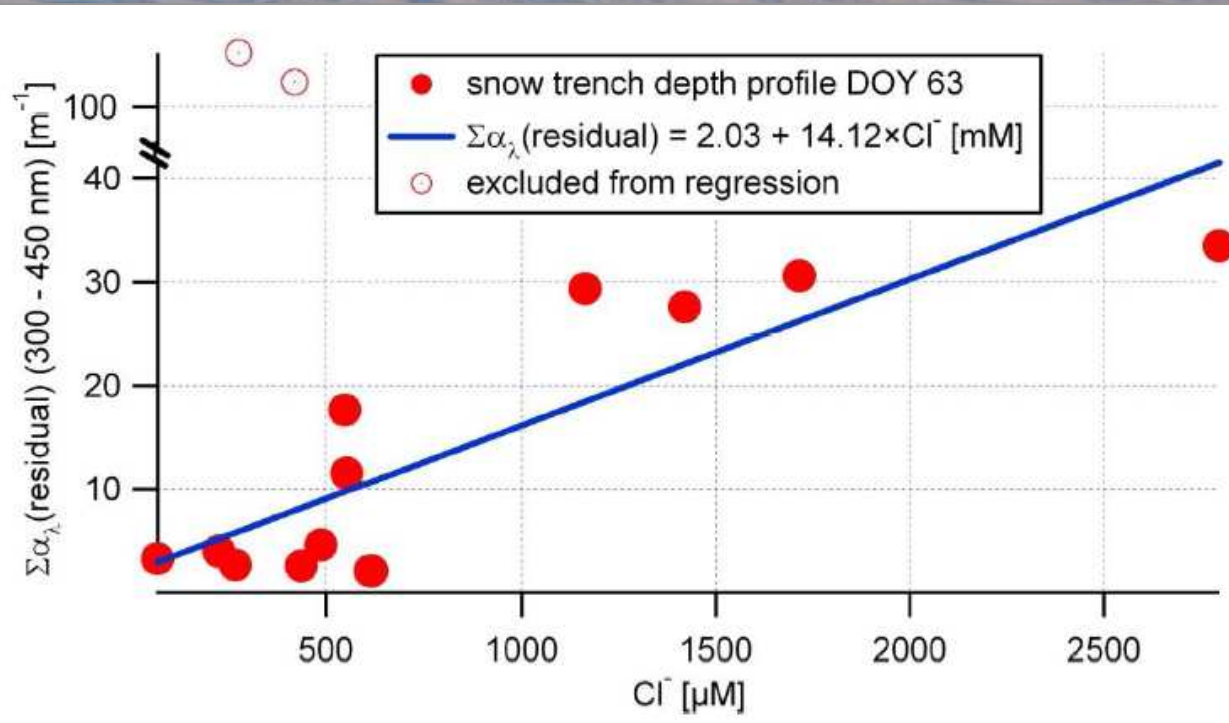
- Nitrate contribute to less than 10% of the integrated absorption
- HULIS contribution is about 50%
- 40 % of the integrated absorption is from unknown chromophores (likely organics)

Absorption from Unknown



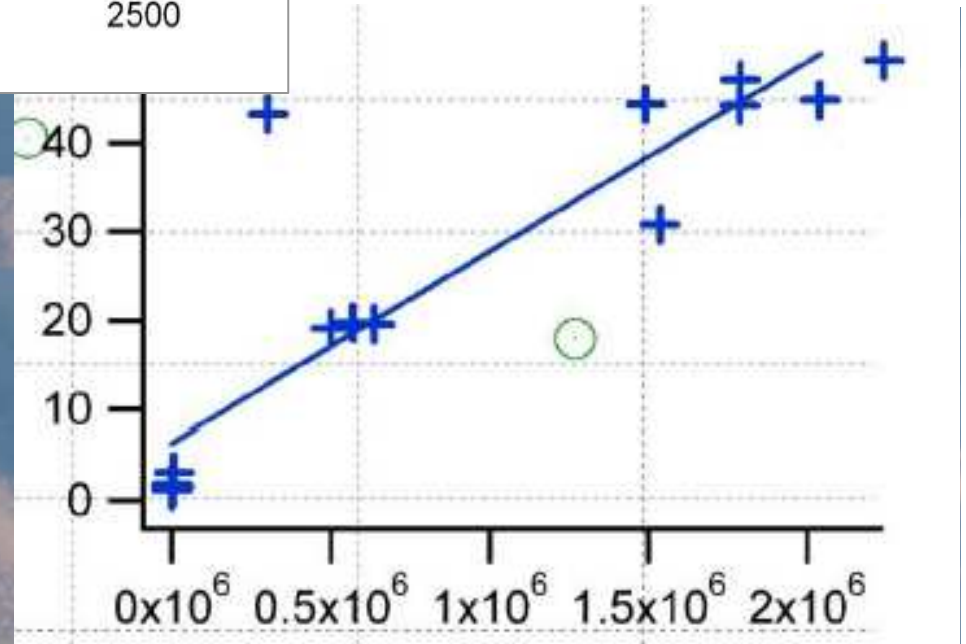
Virtually no absorption above 350 nm from those unknown chromophores

Unknown chromophores : marine origin ?



Sea ice, brine and frost flowers

The observed weak correlation of the residual integrated absorption with Cl^- suggests a marine origin for the unknown chromophores



Conclusions

- Carbon variability linked with snow type and thus the variability of snow transformations
- Carbon probably located essentially in organic inclusions in the snowpack
- Diamond dust enriched in EPS biogels from ocean μ layer: is it a significant DOC source ?
- EC (\sim BC) is a very minor fraction of snowpack carbon.
- HULIS represent $<10\%$ of DOC, yet, it represents more than half of the cumulated melted snow absorption in the UV

Thanks for your attention

Corresponding papers (upcoming OASIS special issue)

- Beine, H. J., C. Anastasio, G. Esposito, K. Patten, E. Wilkening, F. Dominé, D. Voisin, M. Barret, et S. Houdier, Soluble, Light-Absorbing Species in Snow at Barrow, Alaska, *J. Geophys. Res.*, *submitted*.
- Domine, F., J.-C. Gallet, M. Barret, S. Houdier, D. Voisin, T. A. Douglas, J. Blum, H. J. Beine, C. Anastasio, The specific surface area and chemical composition of diamond dust near Barrow, Alaska, *J. Geophys. Res.*, *submitted*.
- Voisin, D., J.-L. Jaffrezo, J. Guilhaumet, S. Houdier, M. Barret, H.W. Jacobi, A. Grannas, H.J. Beine, F. Dominé, Carbonaceous species and Humic Like Substances (HULIS) in arctic snowpack during OASIS field campaign in Barrow, *J. Geophys. Res.*, *in prep*.