DE LA RECHERCHE À L'INDUSTRIE

CHARACTERIZATION OF CLOUD WATER DISSOLVED ORGANIC MATTER USING FT-ICR-MS.

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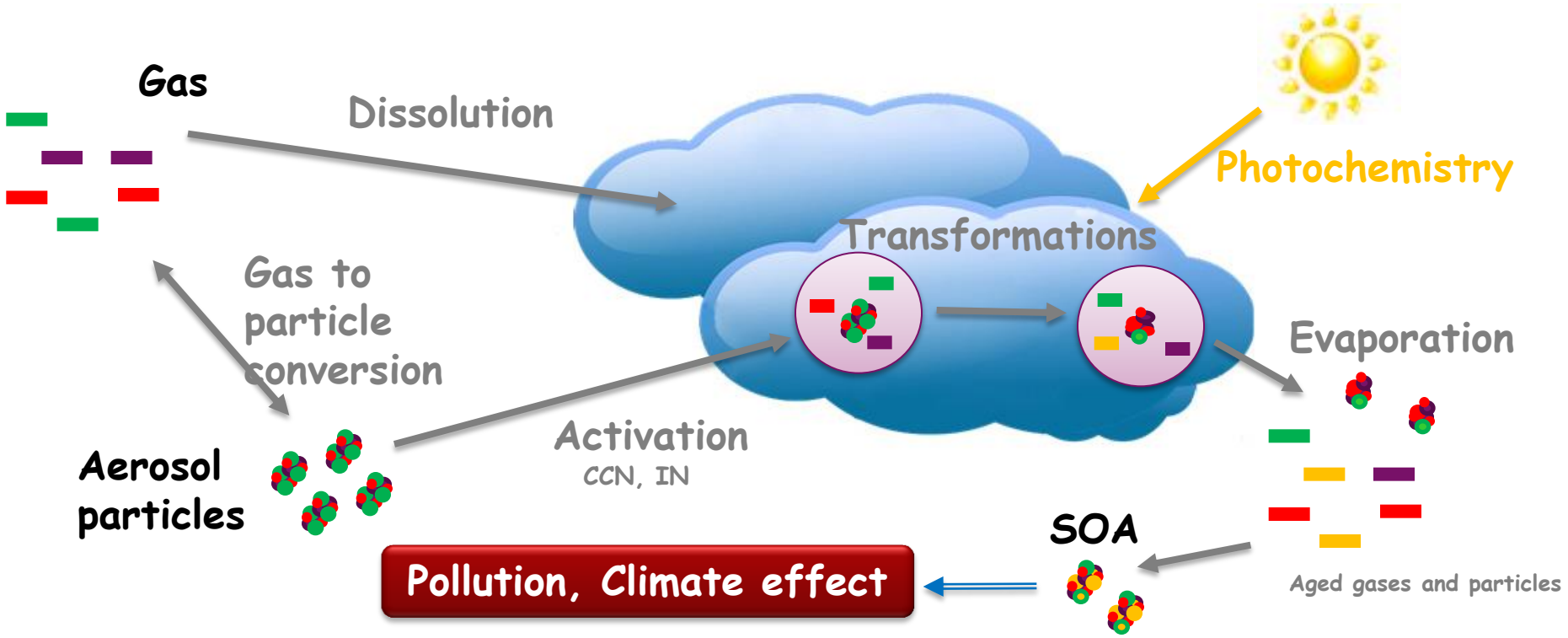
INTRODUCTION AND CONTEXT OF THE STUDY

Gas, particles and cloud: global overview of the interactions



INTRODUCTION AND CONTEXT OF THE STUDY

Focus on the cloud droplet: chemical reactions

- 1-10 mgC/L DOC in natural cloud water
- 20% characterized

Herckes et al., 2013
Deguillaume et al., 2014
Van Pinxteren et al., 2014

Gas

VOCs

Mass transfer

CLOUD DROPLET

Functionnalization

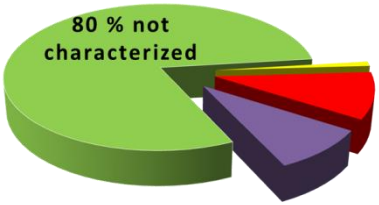
$HO\cdot$ $NO_3\cdot$

Oxidation

$C_xH_yO_z$

Fragmentation

Accretion (oligomers)



1 % aldehydes
10 % carboxylic acids
9 % amino acids

Aerosol particles

Activation

Evaporation

SOA

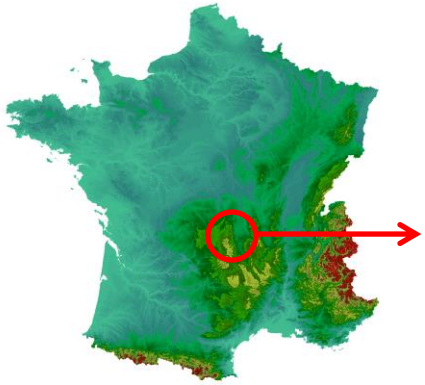
Understanding of chemical composition, properties and reactivity is essential for public health and climate

METHODS

Sampling and sample analysis

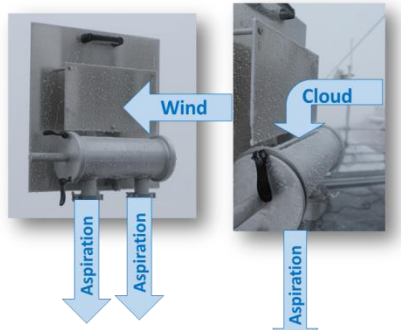
Reasearch Goals:

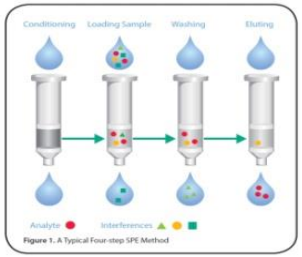
1. **Characterization** of water dissolved organic matter at the molecular level (Spatio / temporal variability) / influence of air masses, …
2. **Reactivity** of organic compounds in cloud water
3. Study the **synergetic/ antagonistic** effects of photochemistry/biodegradation

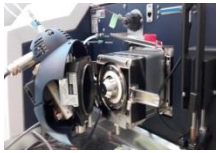


puy de Dôme station

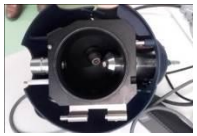
Impactors







ESI



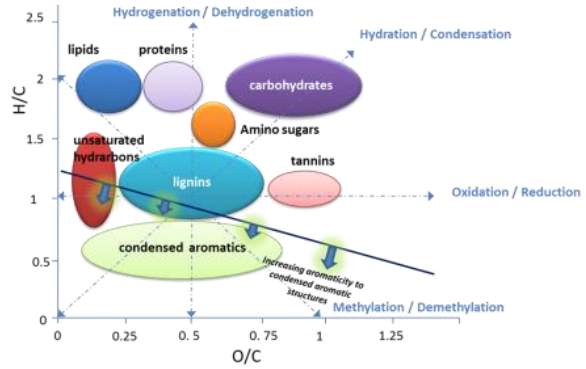
APPI

FTICR (9,4 T)

METHODS

High Resolution mass spectral data processing

Van Krevelen diagram (*commonly used to describe the chemical properties of aerosols*)



Visualization

of sample composition

Comparison

Sample molecular composition with

1. Cloud physico-chemical parameters
2. Air mass origin
3. Photochemistry
4. Microbial activity

Data Filtering

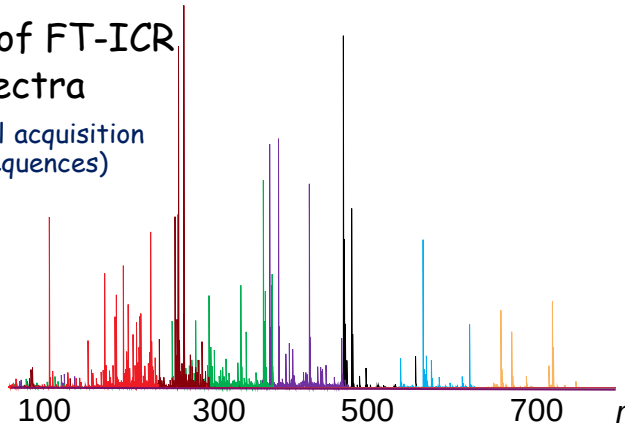
- SPE bkd subtraction
- S/N <3
- MD > 5

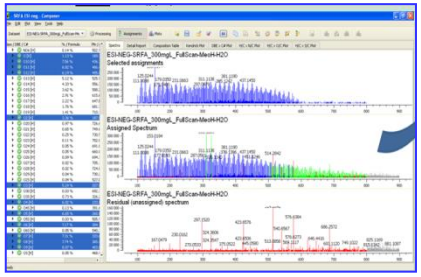
Composer™

1. Data import (*peak list m/z/ Intensity*)
2. Internal recalibration of the peak list / assign highly accurate m/z values
3. Assign elemental compositions to each peak list and review of chemical class and component abundance
4. Visualization of sample composition and comparison of samples through use of graph and tables

Acquisition of FT-ICR MS spectra

Sequential acquisition
(7 m/z sequences)

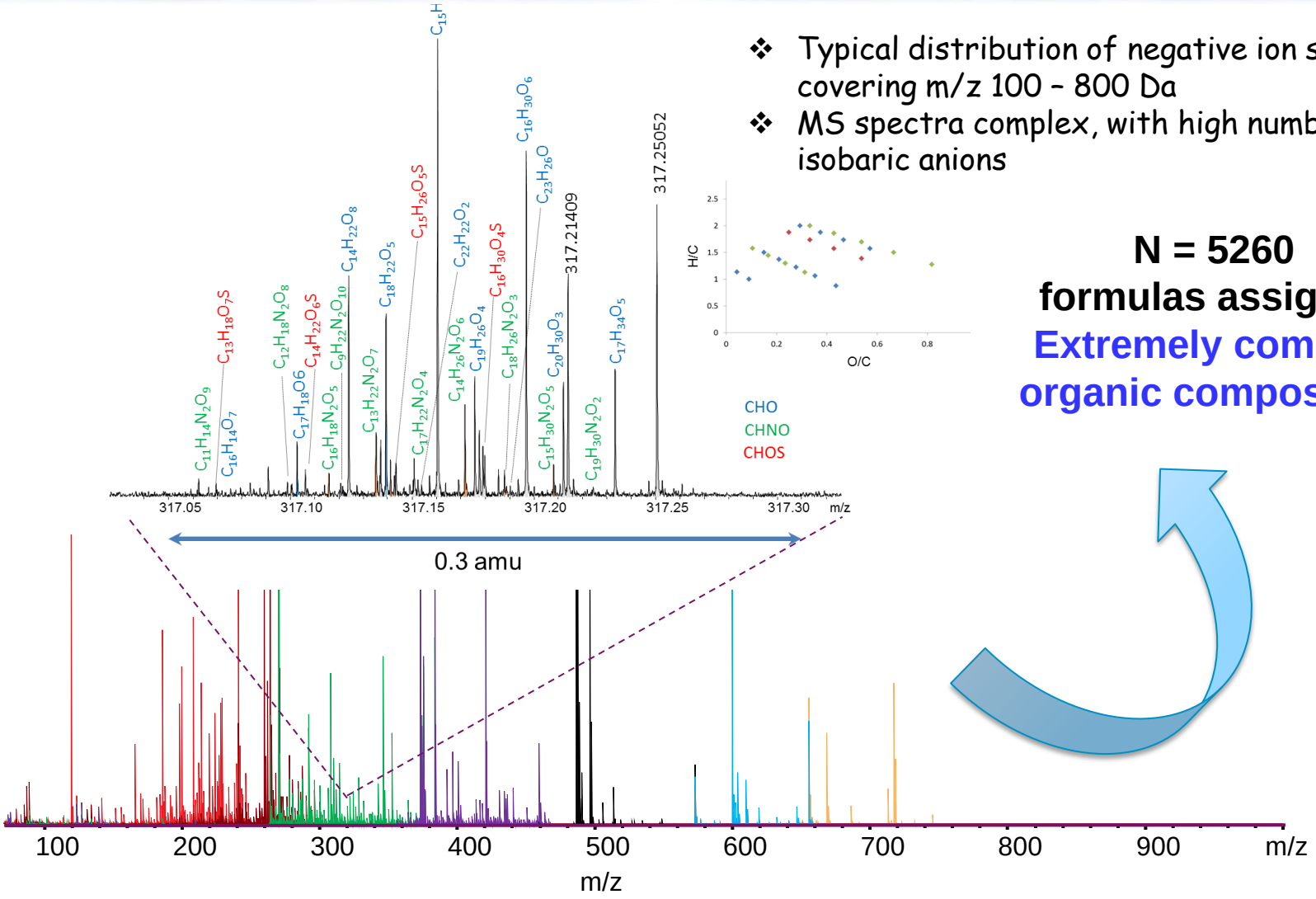




RESULTS

FT-ICR MS spectra of cloud water collected on 010616

- ESI FT/ICR MS spectrum (SPE background subtracted) from 01/06/2017



- ❖ Typical distribution of negative ion signals covering m/z 100 – 800 Da
- ❖ MS spectra complex, with high number of isobaric anions

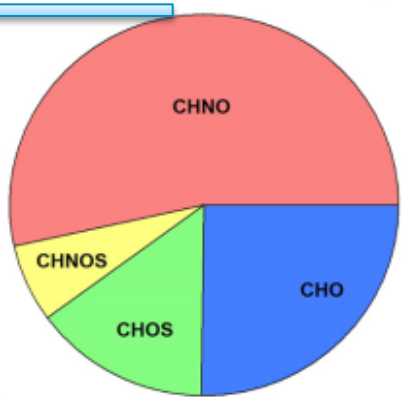
N = 5260 formulas assigned

Extremely complex organic composition

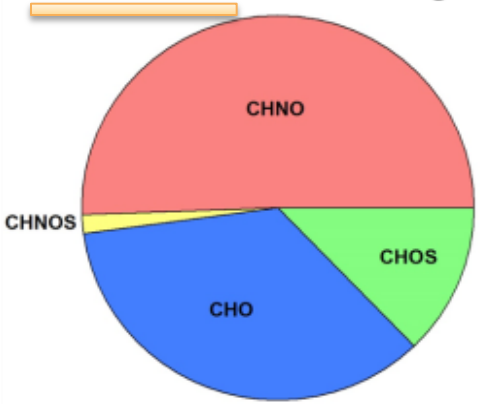
RESULTS

Molecular Class distribution

Cloud 01/06/2016 ESI analysis
5260 molecular formula assigned



Cloud 02/07/2016 ESI analysis
2894 molecular formula assigned



% of assigned molecular formulae

- 53,5% CHNO
- 21,3 % (CHOS + CHONS)
- 25,2 % CHO

- 50,6 % CHNO
- 14,3 % (CHOS + CHONS)
- 35,1 % CHO

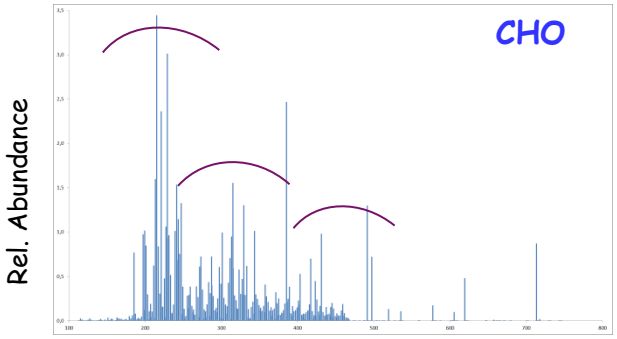
- Four subgroups of molecular formulas determined based on their elemental composition
- High abundance of nitrogen containing compounds (over $\frac{1}{2}$ the compositional space)
- Considerable contribution of sulfur containing organic compounds (in line with other studies of water soluble atmospheric aerosols)

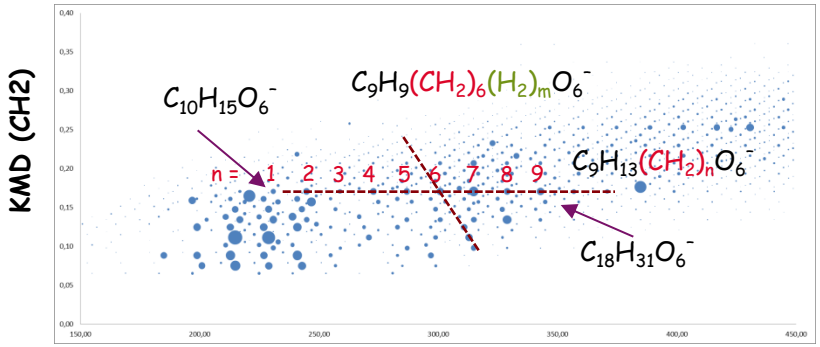
RESULTS

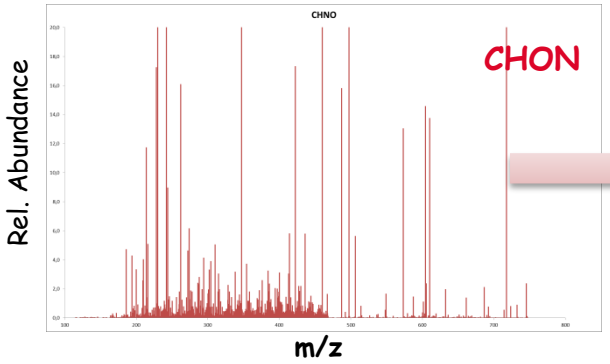
Kendrick Mass Defect,(-CH_2)

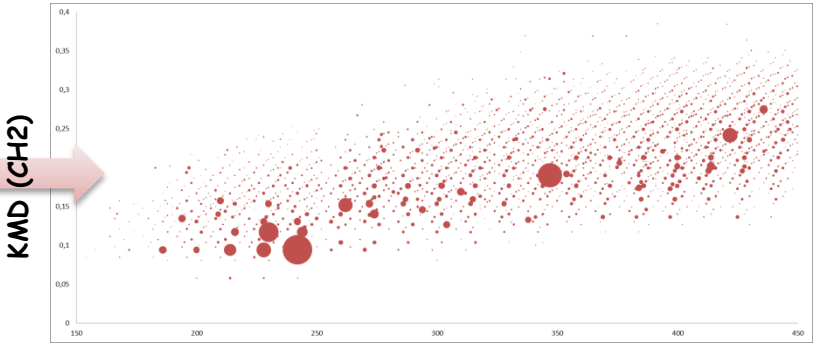
Reconstructed Ion Chromatograms

Kendrick mass defect plots

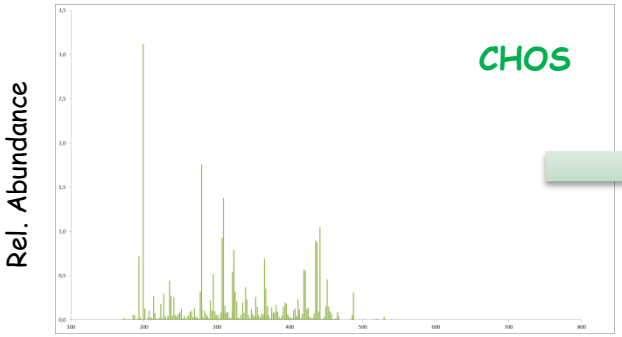


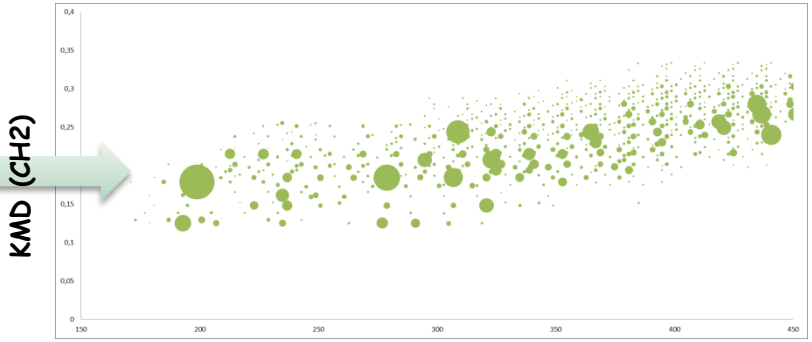






❖ « CH2 » homologous series





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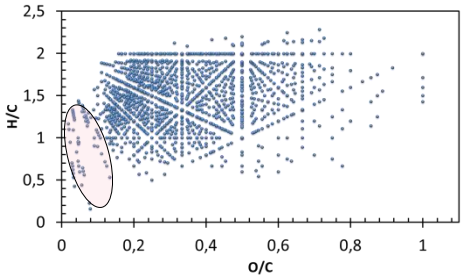
RESULTS

Van Krevelen diagrams

- Van krevelen diagram by class for 01/06/2016

CHO



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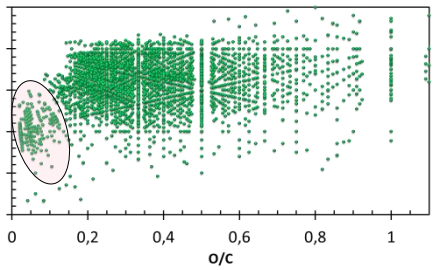

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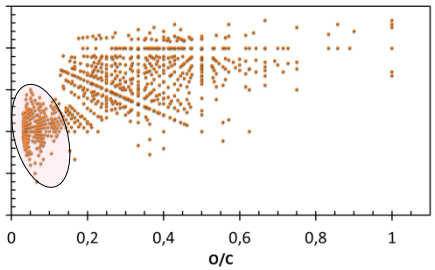

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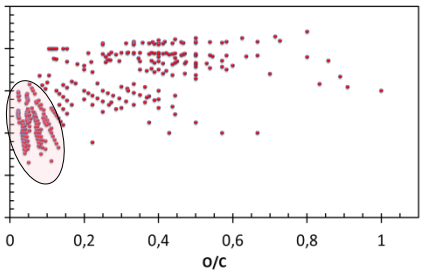

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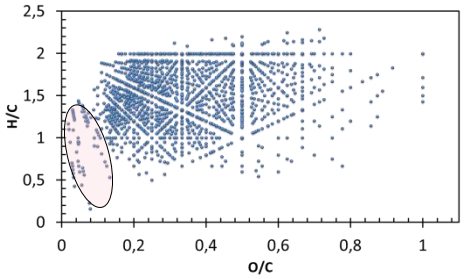

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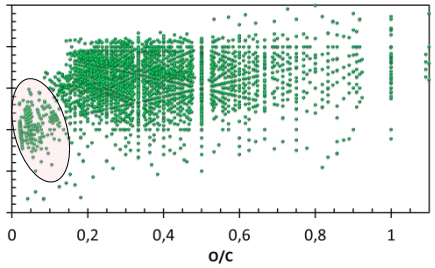

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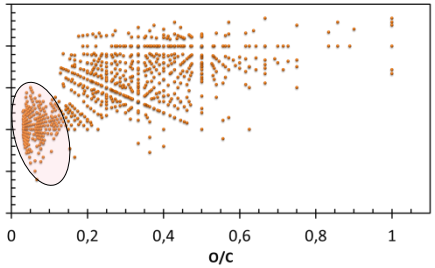

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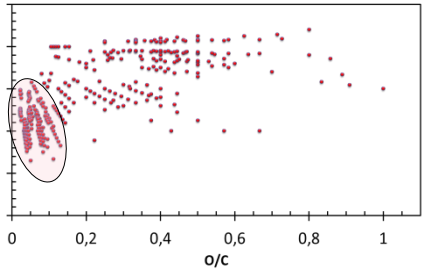

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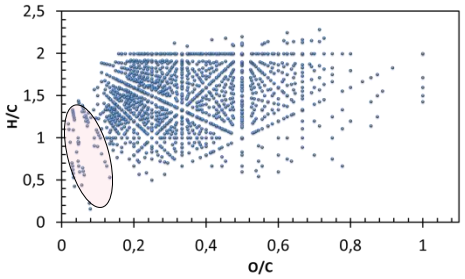

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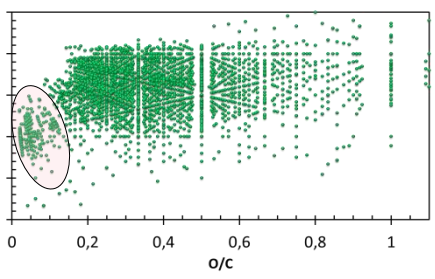

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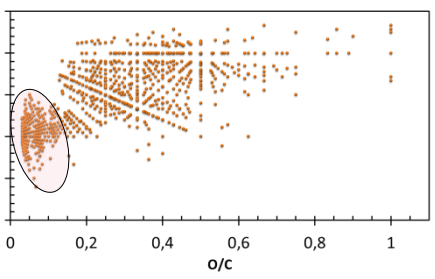

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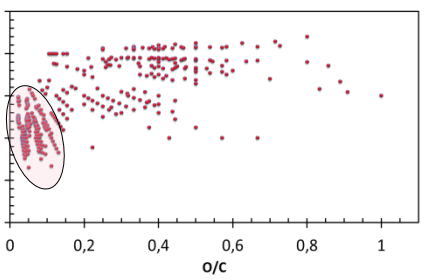

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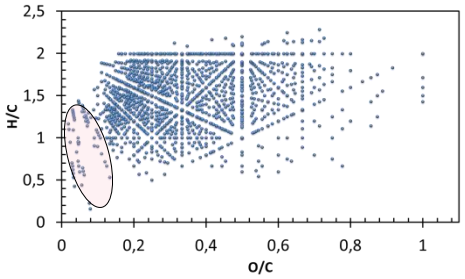

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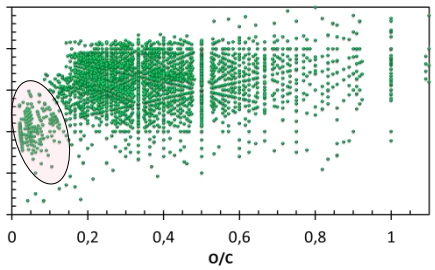

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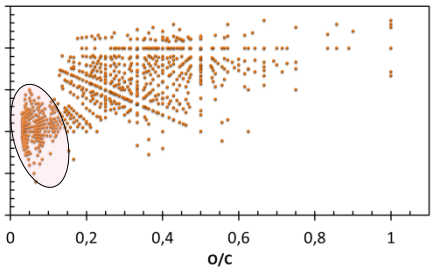

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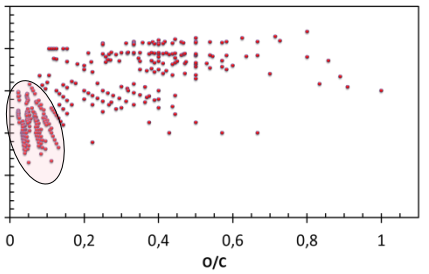

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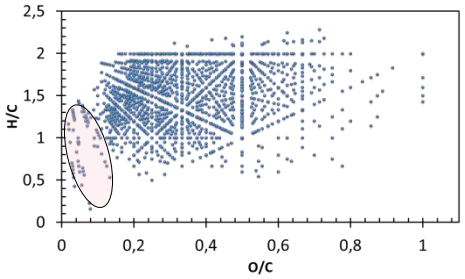

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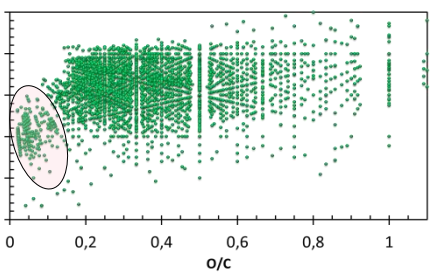

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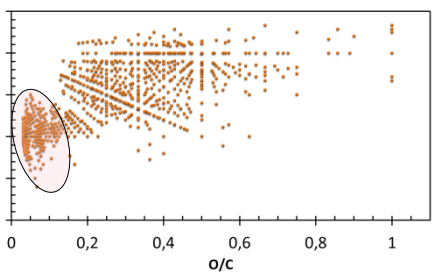
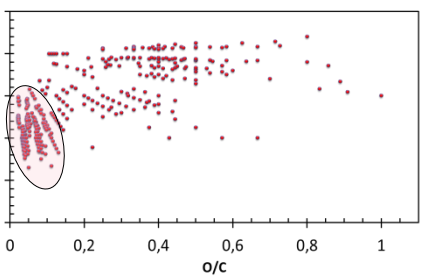
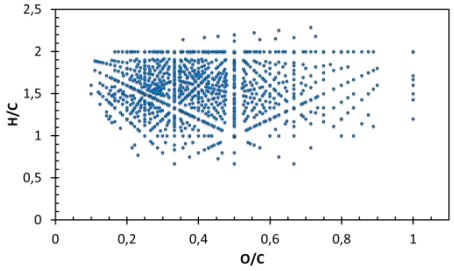
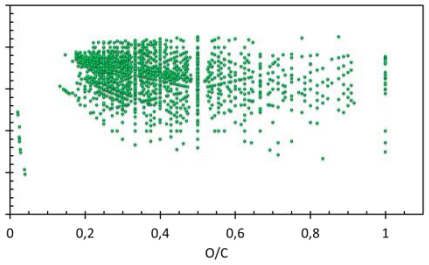


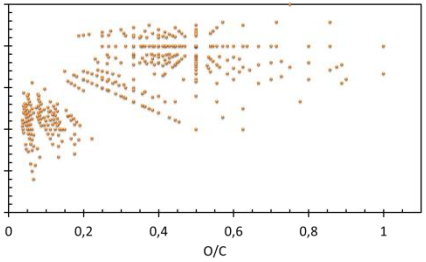
CHONS

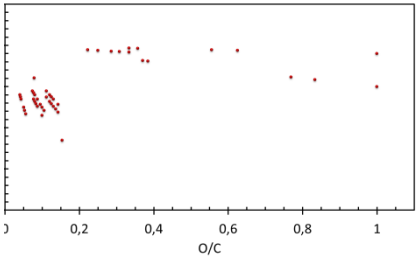


- Van krevelen diagram by class for 02/07/2016









CONCLUSIONS ET PERSPECTIVES

- Molecular composition determined by ultrahigh-resolution Fourier-transform ion cyclotron resonnance mass spectrometry provides unambiguous identification of the cloud water organic anion composition in the Puy de Dôme area

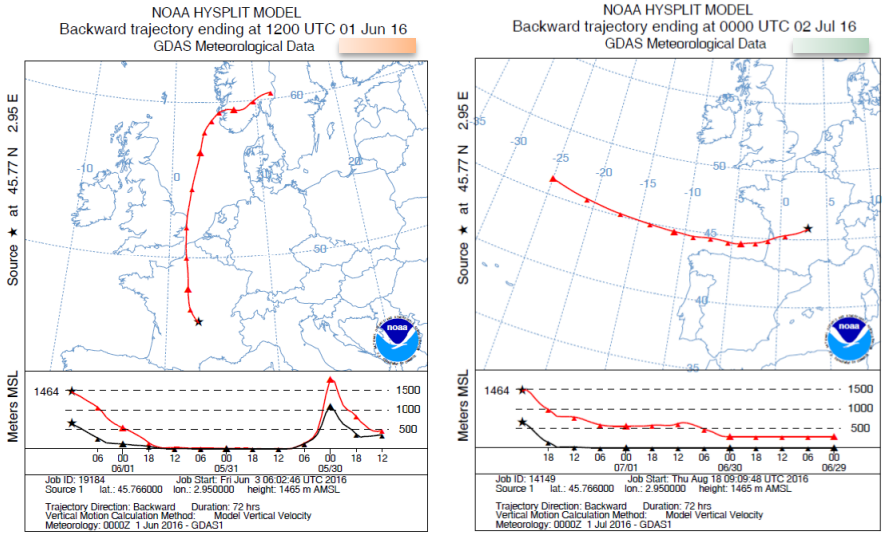
  > 5000 monoisotopic molecular formulae found for sample 01/06/2016

  ~ 3000 molecular formulae found for sample 02/07/2016

- Complex organic compounds containing C, H, N, O, S with MW comprised between m/z 50 and 700 Da

  - significantly more N-containing and S-containing compounds for 01/06/2016

  - Van Krevelen diagrams reveal more unsaturated components from 01/06/2016 sample



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THANK YOU FOR
YOUR ATTENTION…
QUESTIONS ?