# JOINT EFFECT OF ORGANIC AND INORGANIC AEROSOL COMPONENTS ON CLOUD DROPLET ACTIVATION

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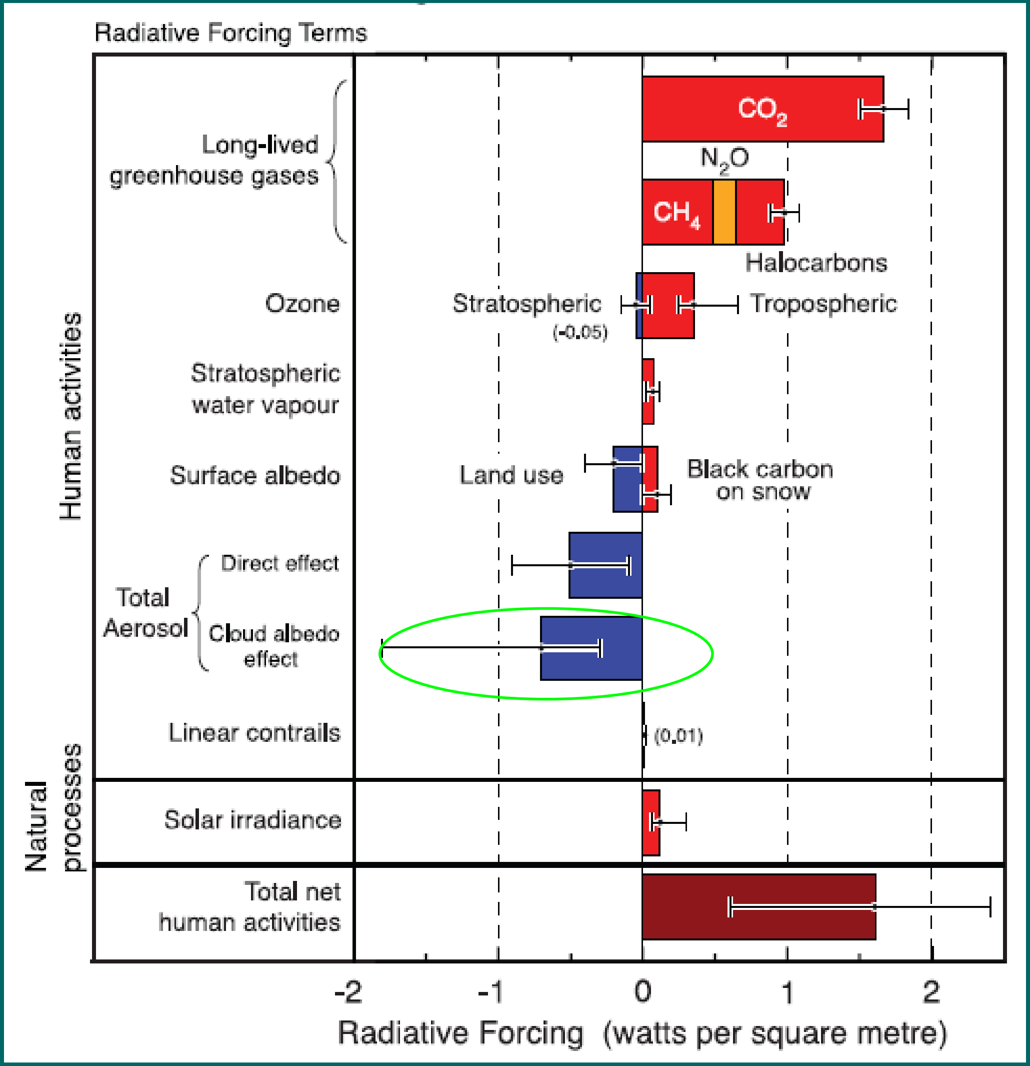
9th International Conference on Carbonaceous Particles in the Atmosphere
Lawrence Berkeley National Laboratory, Berkeley, California,
12-14 August 2008

# IPCC 2007




Reasons for uncertainty…

# Role of organics

Since 1990s: Organic compounds alter the hygroscopic behavior of atmospheric aerosol particles and play a role in cloud formation → They may influence the indirect aerosol radiative forcing *(Novakov and Penner, Nature 1993; Saxena et al., JGR 1996; Novakov and Corrigan, GRL 1996)*

↓

Studies on

• the chemistry of water-soluble organic aerosol components

• CCN ability of organics including ST studies, HTDMA, CCNC measurements, etc.

The organic fraction is very complex. → Simplification → Experiments often performed with single organic compounds (e.g. CCNC studies by *Cruz and Pandis Atm.Env. 1997; Corrigan and Novakov, Atm.Env. 1999; Prenni et al., J. Phys. Chem. 2001; Giebl et al., JAS 2002; Raymond and Pandis, JGR 2002; Kumar et al., ACP 2003; Hartz et al., Atm.Env. 2006)*

# Objectives

Ambient aerosol: mixture of inorganic salts + many organic compounds

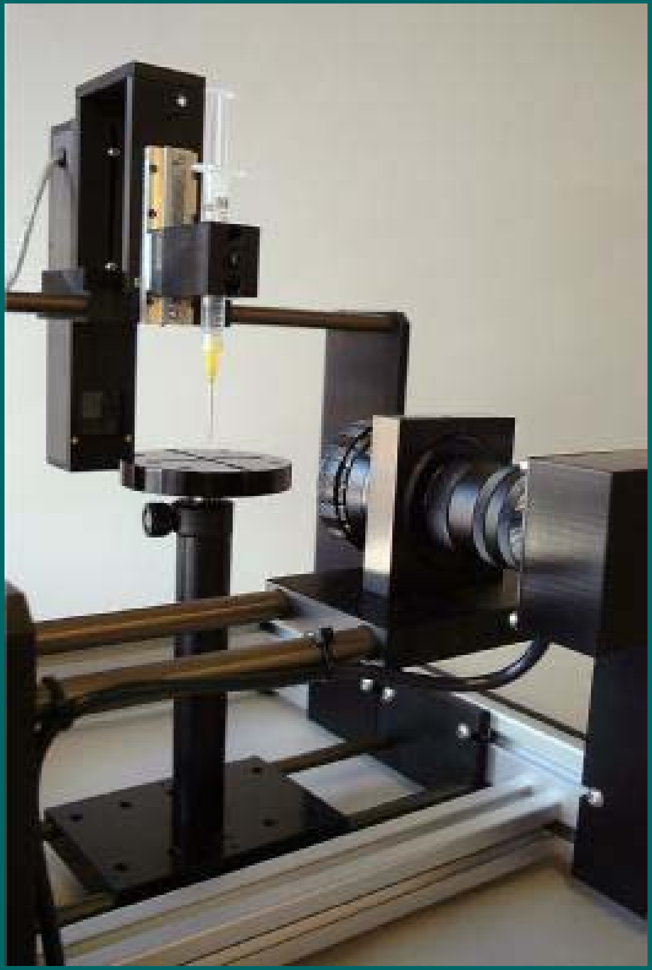
In this study ST and osmometric measurements with

- organic model compounds mixed with inorganic salt
- HULIS isolated from ambient aerosol
- aerosol samples from BB and rural environment

in order to better understand the joint effect of complex mixtures on cloud formation.

# Method

1. Preparation of solutions corresponding to different growth factors (GF)
2. Measurement of surface tension of the solutions



FTÅ 125/1000 tensiometer

Method: pendant drop shape

Sample: 1 drop

Parallel analyses

Typical analysis time: 1 minute

# Method

1. Preparation of solutions corresponding to different growth factors (GF)
2. Measurement of surface tension of the solutions
3. Measurement of osmolality of the solutions


← Knauer K-7000 vapour pressure osmometer

Knauer K-7400 semimicro osmometer ↓


Wide working range (5 mOsm-5 Osm) into $a_w$=0.9-1

Sample size: 1 drop / 150 µl

Typical analysis time: 3 minutes

# Method

1. Preparation of solutions corresponding to different growth factors (GF)
2. Measurement of surface tension of the solutions
3. Measurement of osmolality of the solutions
4. Calculation of water activity from osmolality data
5. Calculation of saturation according to Köhler-theory

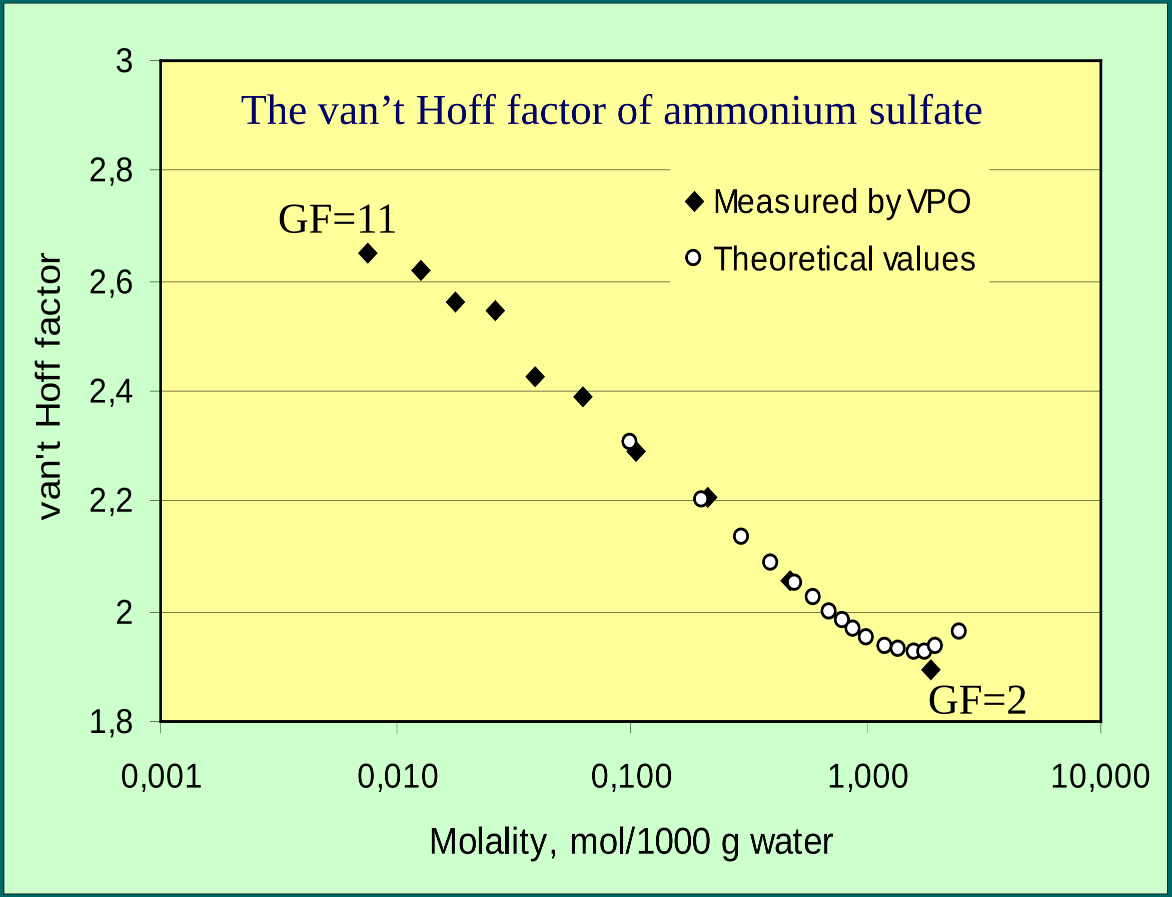
$$p/p_0 = a_w \exp(2\,\sigma\, M_w/(r\,\rho\, R\, T))$$

$p$ = water vapour pressure over the droplet solution
$p_0$ = water vapour pressure over a flat water surface
$a_w$ = water activity in the droplet solution
$\sigma$ = surface tension of the droplet solution
$M_w$ = molecular weight of water
$\rho$ = density of the droplet solution (water)
$R$ = universal gas constant
$T$ = temperature

# Inorganic salts

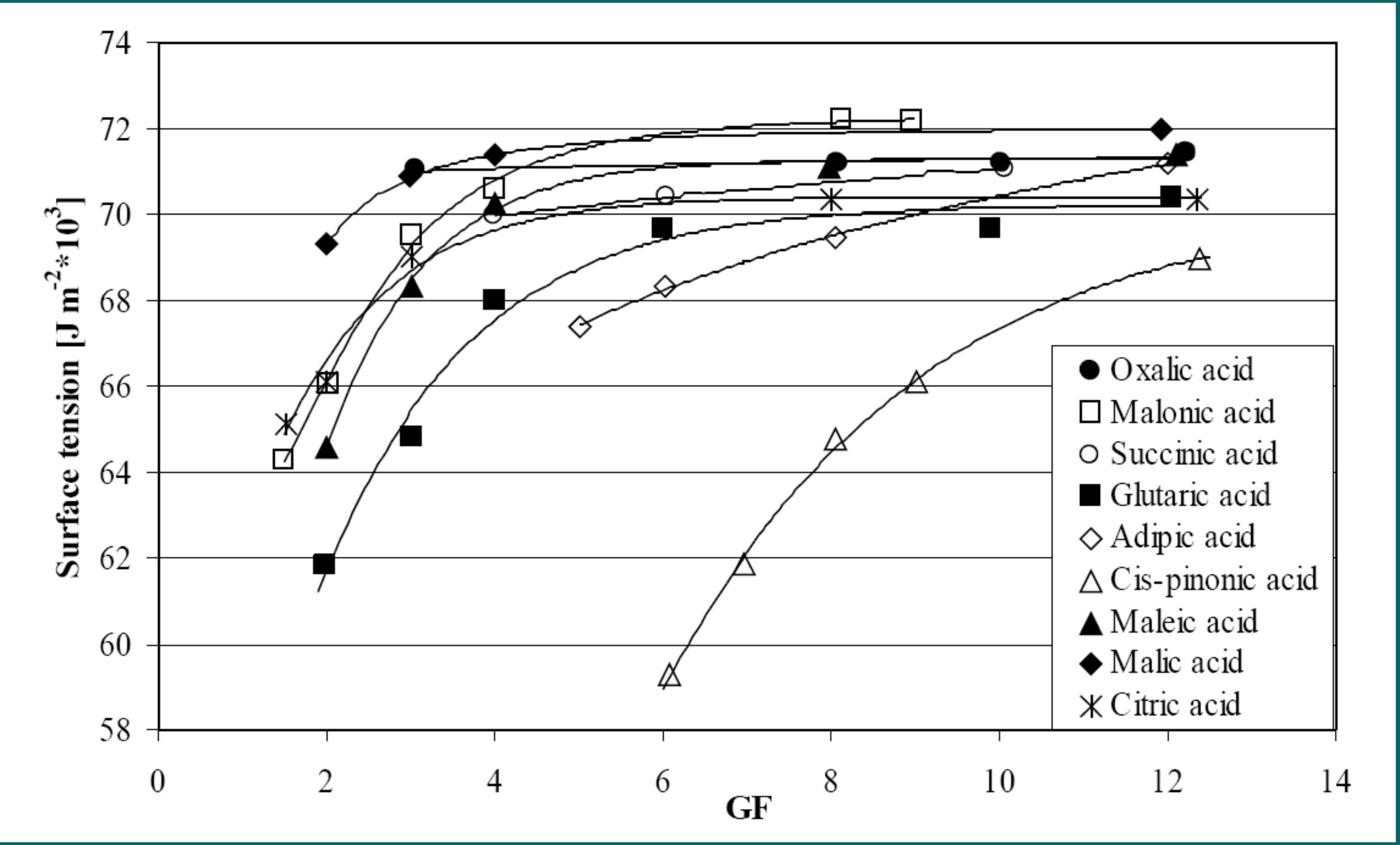
1. No effect on surface tension
2. Remarkable effect on water activity (← dissociation)

   van’t Hoff factor describes dissociaton and non-ideality




*Low, Journal de Recherches Atmospheriques 1969*

# Surface tension of organic acids

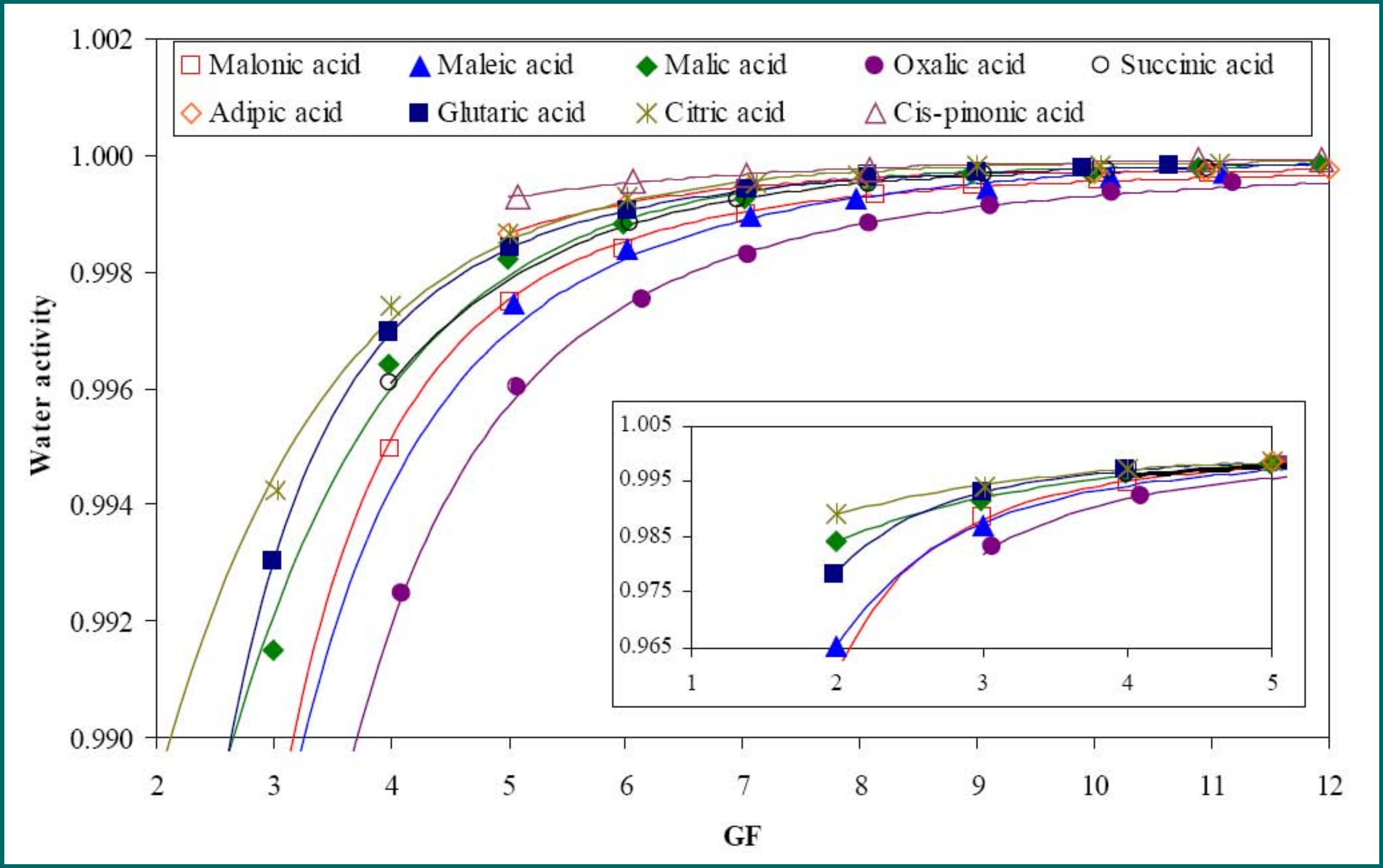



*Varga et al., ACP 2007*

Moderate ST depression

Two extremes: oxalic acid ↔ cis-pinonic acid

# Water activity of organic acids

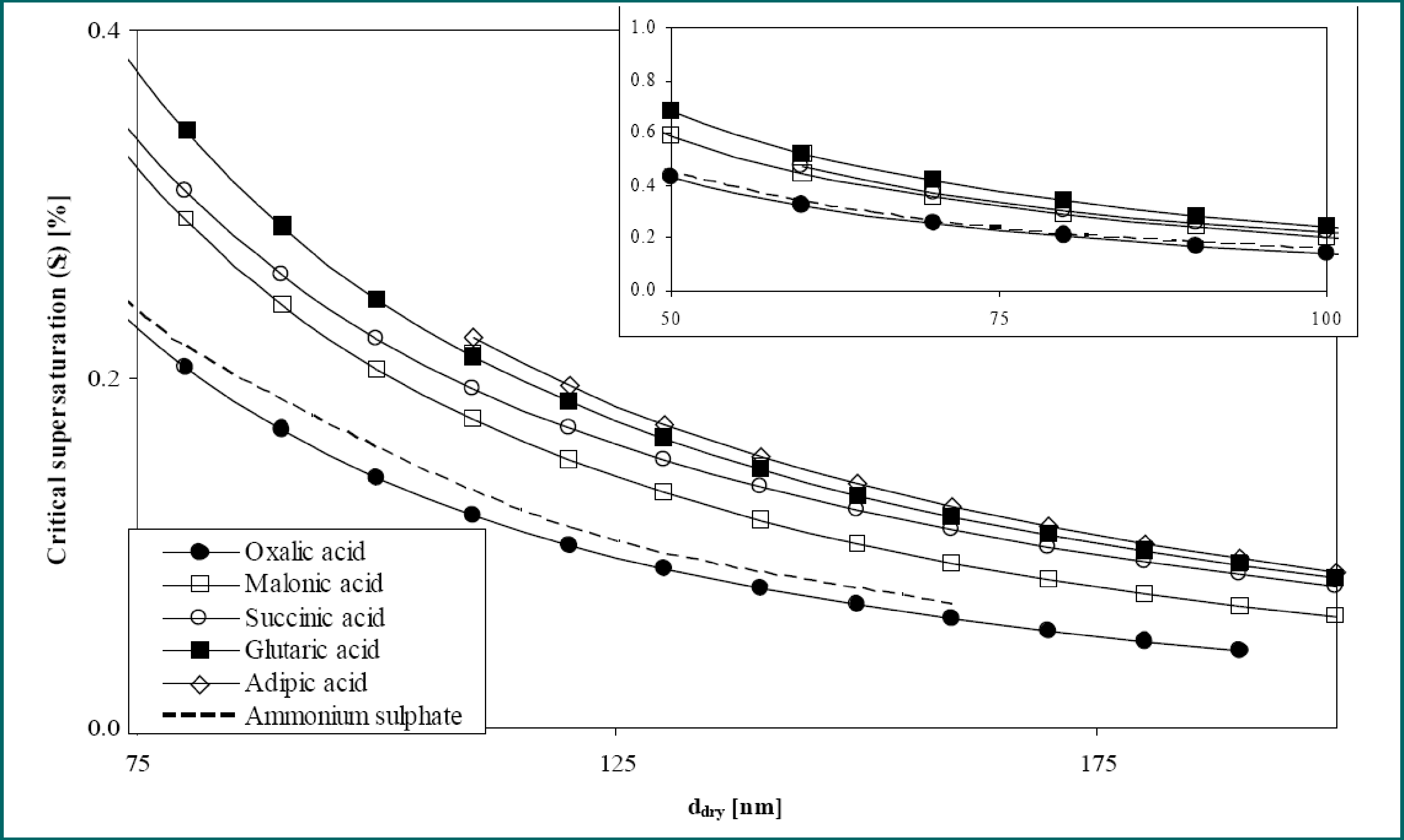



Key parameters: density, MW, pK

The effect of low MW stronger acids (oxalic, maleic, malonic) is considerable.

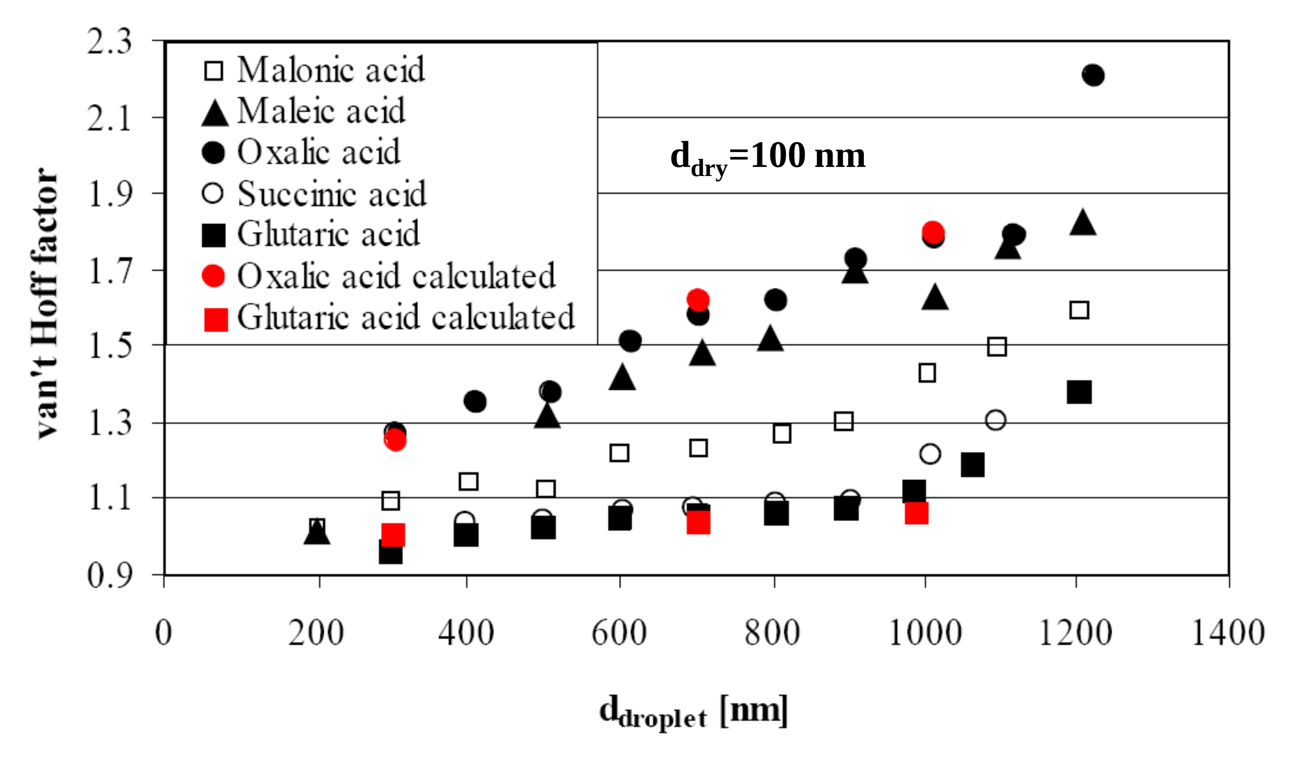
The effect of cis-pinonic acid is negligible

# $S_{crit}$ of dicarboxylic acids as a function of dry diameter




Oxalic acid ~ ammonium sulfate

# Organic + inorganic mixtures




**Water activity**

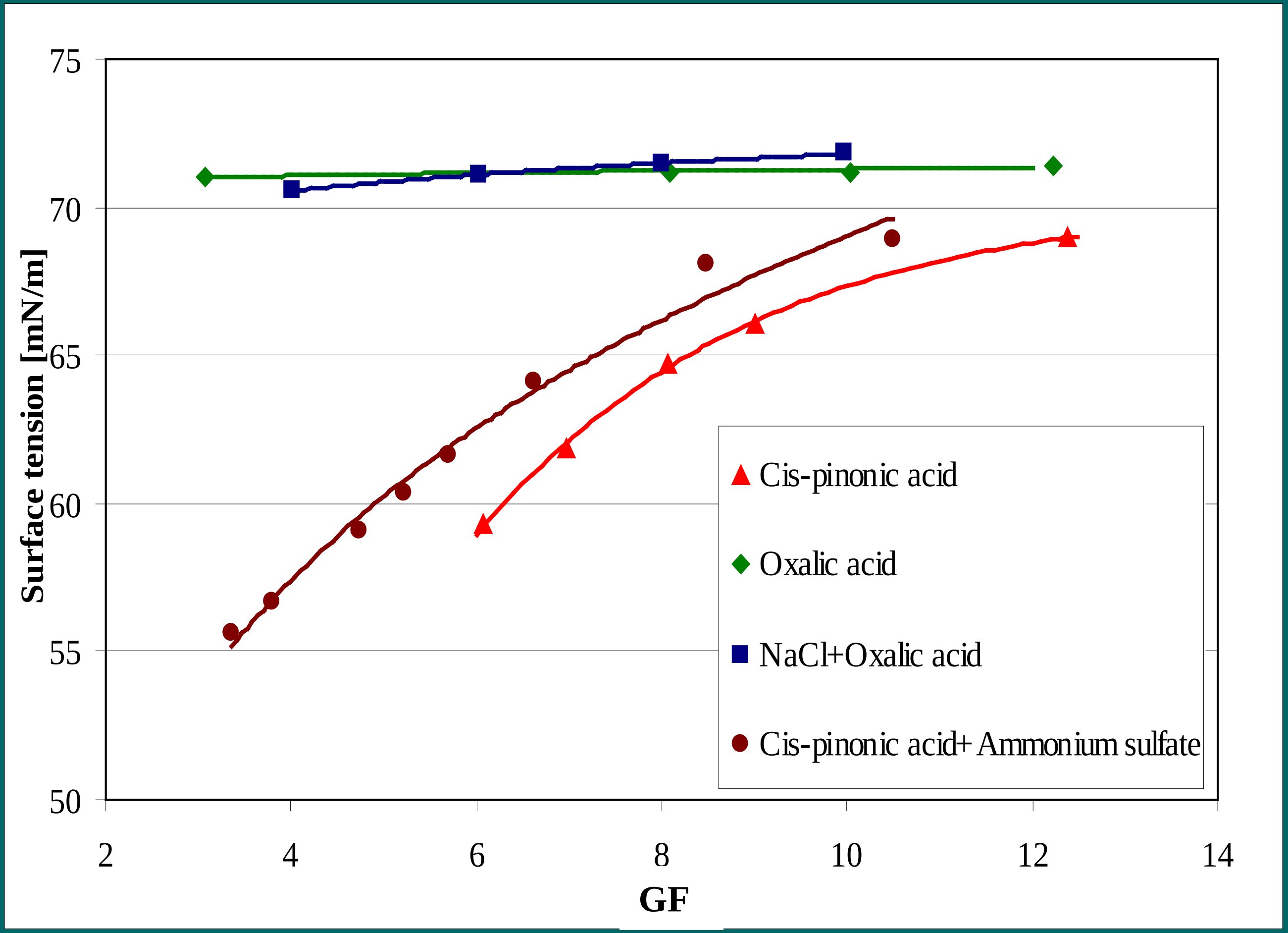
Inorganic salts may suppress dissociation of organic acids (i.e. reduce *i*)

- In concentrated solutions (GF=2-3) *i* ~ 1 for organic acids

- In dilute solutions (GF=8-12) *i* > 1, but the inorganic effect is negligible

Interaction is expected only in the initial phase (GF ~ 2 ) of droplet formation

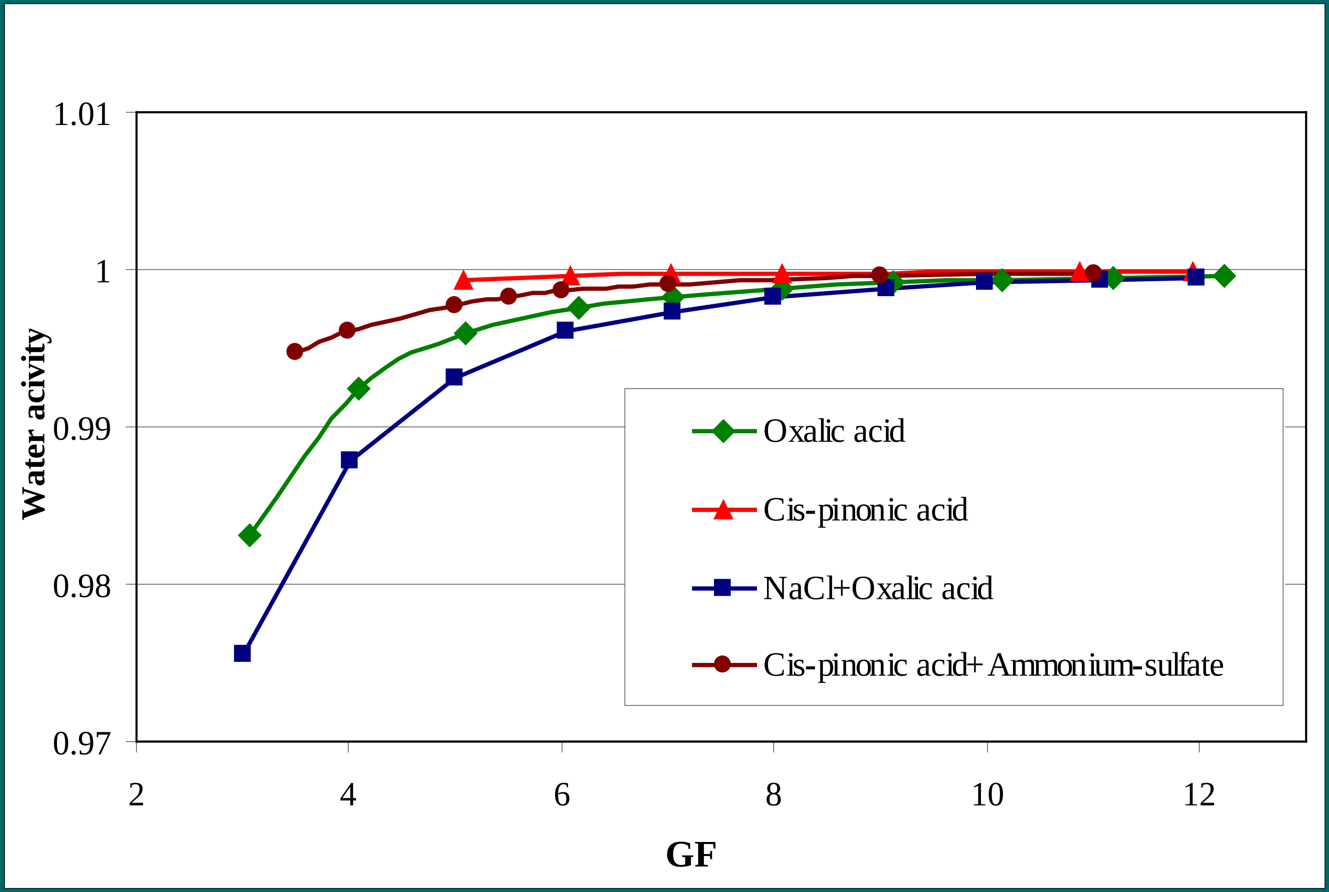
# Surface tension of organic acid+inorganic salt (1:1) mixtures




No change for oxalic acid

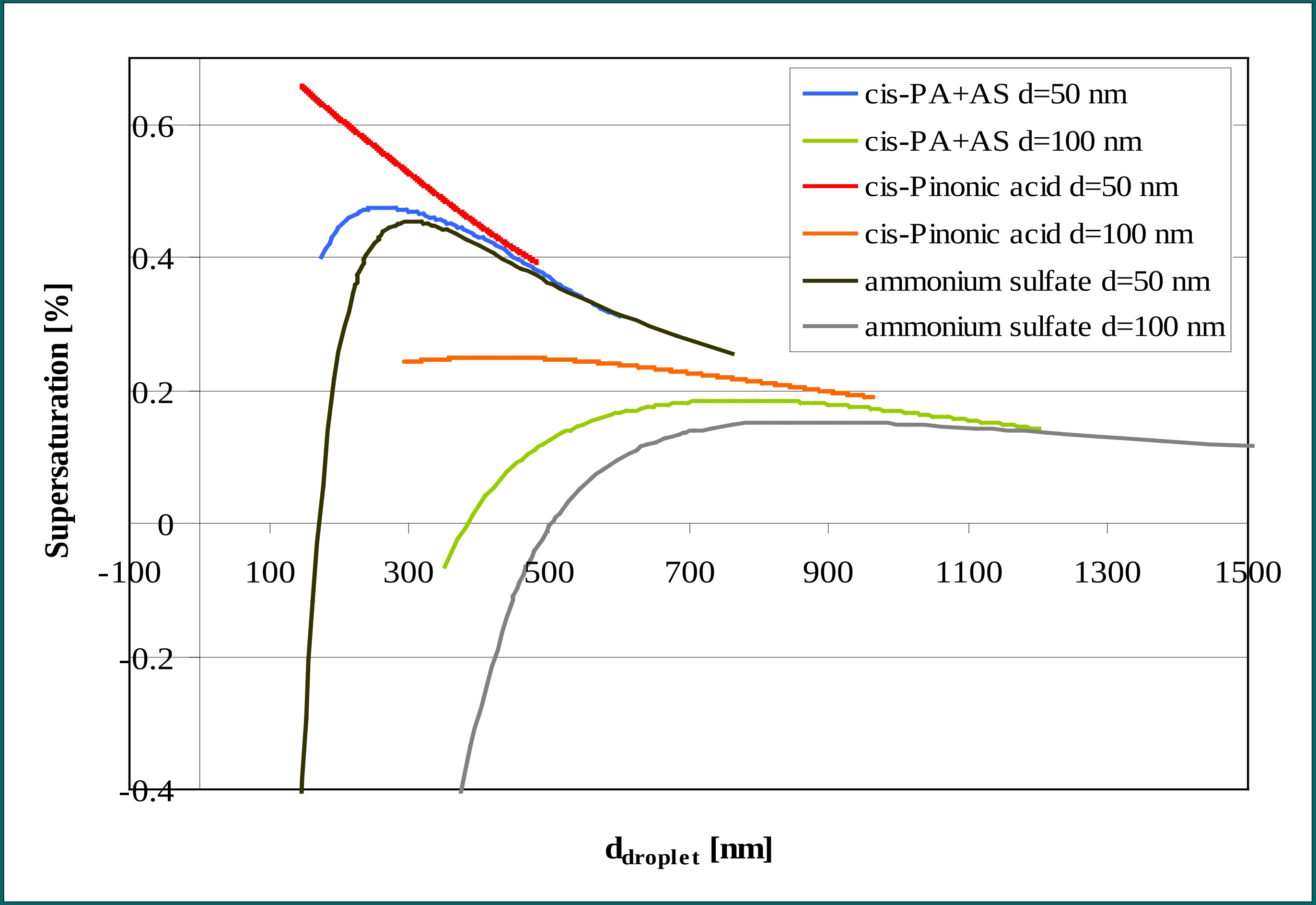
No enhancement of ST depression with cis-pinonic acid (partially replaced!)

# Water activity of organic acid+inorganic salt (1:1) mixtures



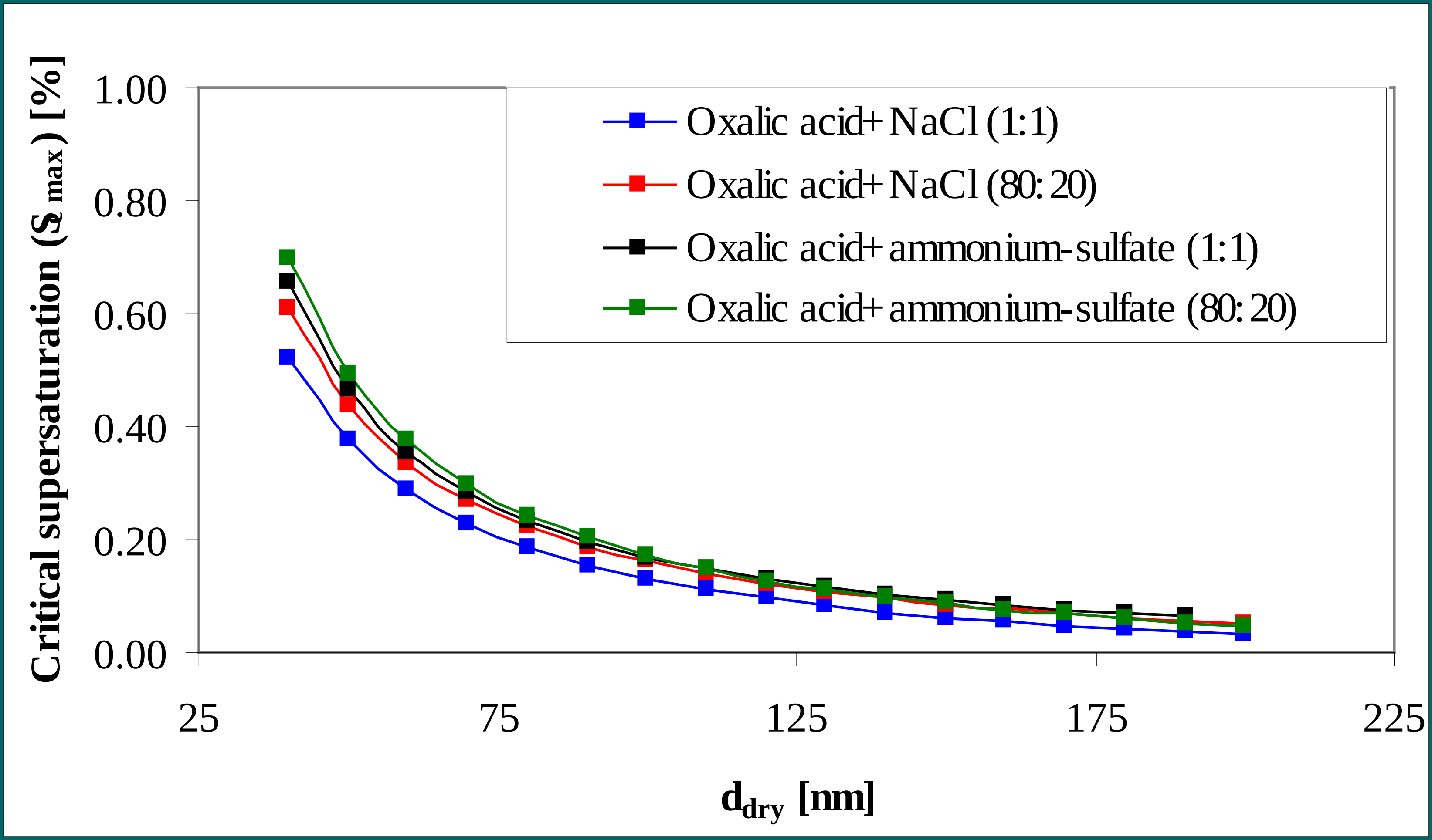

Considerable decrease in water activity by inorganic salts with both organics.

# Köhler curves for cis-PA + ammonium sulfate mixture




Mixture activates at significantly lower $S_c$ than pure cis-pinonic acid but higher $S_c$ than pure ammonium sulfate.

# $S_{crit}$ of oxalic acid + sodium chloride




Mixtures with AS activate at similar $S_c$ as pure AS or oxalic acid.

1:1 mixture with NaCl activates at lower $S_c$ than pure oxalic acid.

# Summary of experiments with model compounds

Kelvin effect:

- Inorganic salts do not enhance ST depression of organic compounds at relevant concentrations
- ST depression of mixed particles at a given GF is less than that for the pure surfactant

Raoult effect:

- Inorganic salts do not suppress the dissociation of organic acids
- Inorganic salts dissociate better than organic acids, so water activity of a solution at a given GF is less than that for the pure surfactant (dominant effect)

↓

Mixtures activate at lower $S_{crit}$ than pure organics studied

# Experiments with HULIS

HULIS isolated from ambient (K-puszta) aerosol samples on an HLB SPE column.

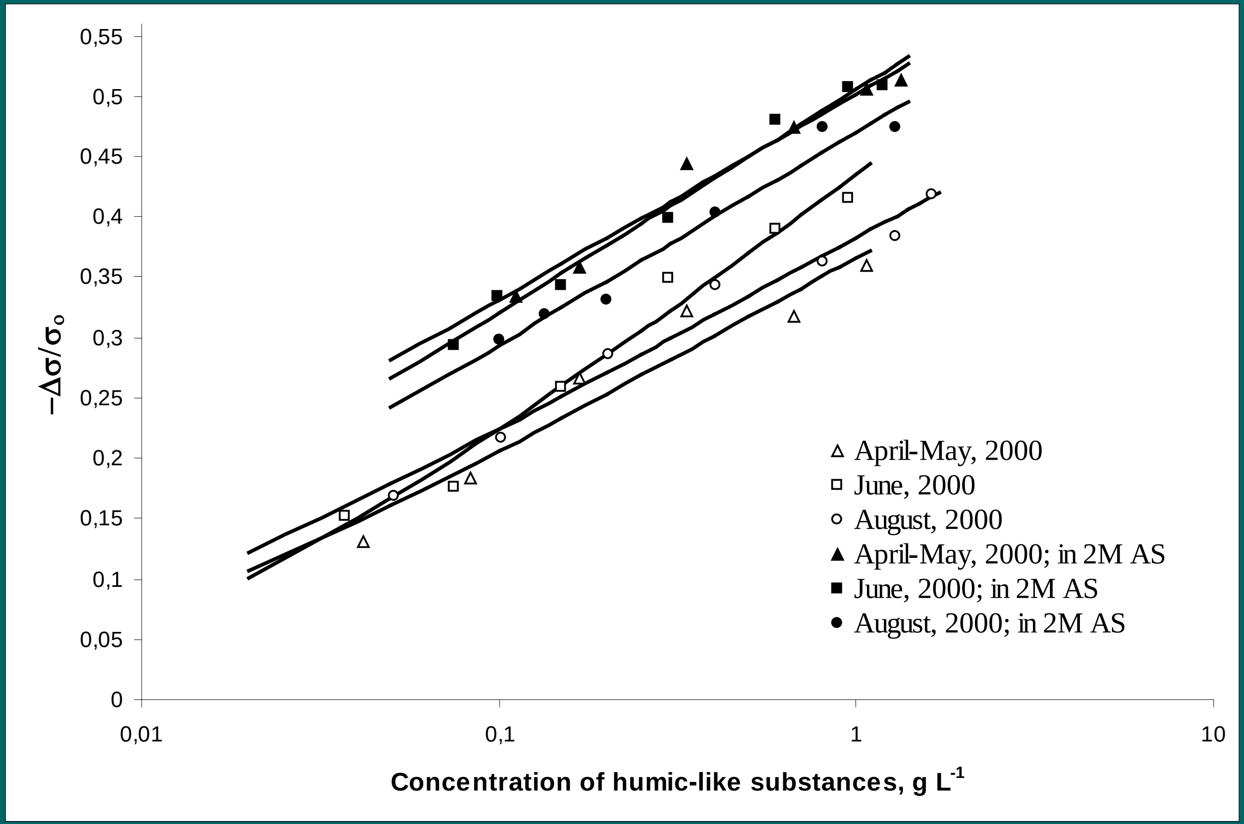
HULIS represent ca. 60% of WSOC

Much more complex than single organic model compounds shown before

The isolated HULIS fraction is practically free from inorganic ions.

Freeze dried aqueous extract of a summer aerosol sample collected at K-puszta, Hungary

# Surface tension depression of HULIS



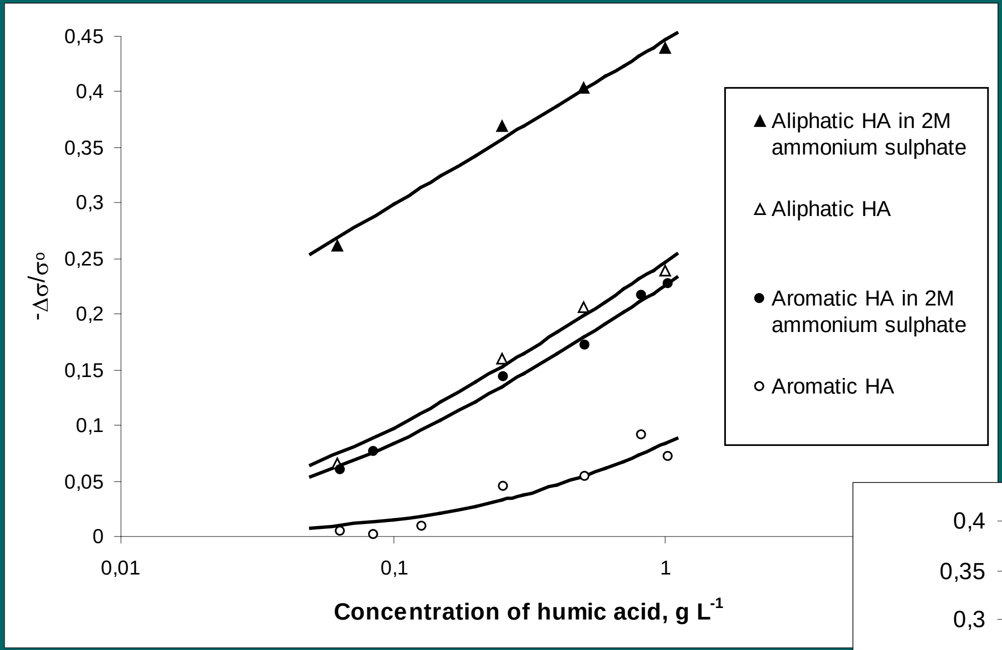

Scaling!

*Kiss et al., J.Atmos. Chem. 2005*

More efficient ST depression than for any model compounds *(Shulman et al., GRL 1996)*
$\sigma$ = 41-47 mN/m at 1 g $l^{-1}$ vs. $\sigma$ = 66-71 mN/m for model compounds above.
Similar result with fog samples:
15-20% decrease at 0.1 gC $l^{-1}$ ~ 0.2 g HULIS $l^{-1}$ *(Facchini et al., Atm. Env. 2000)*
ST depression significantly enhanced in 2M ammonium sulfate (45-52%)!

# Reason for ST depression?

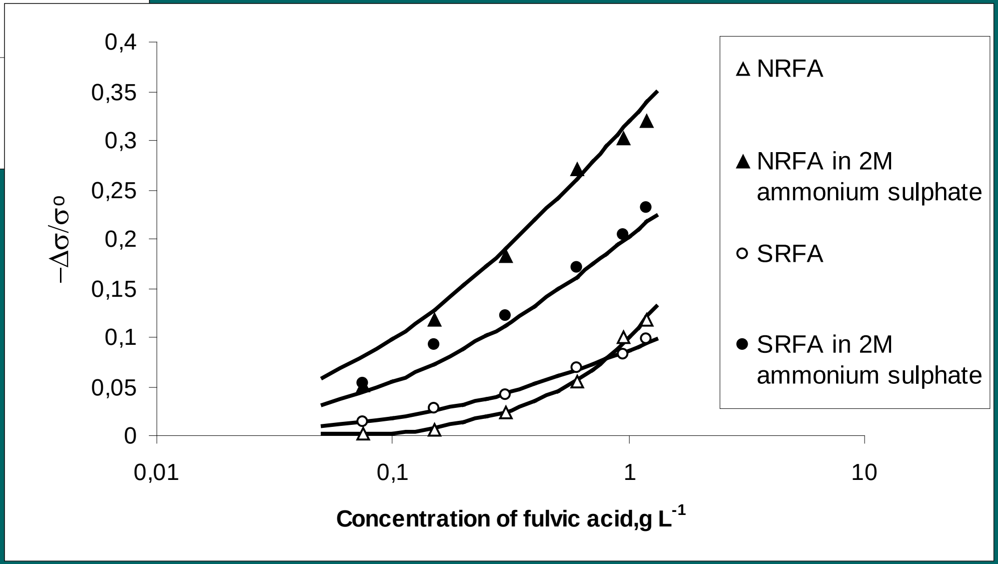
Humic substances are known to be surfactants




7% and 25% decrease ↔ 35-40% HULIS

22% and 43% ↔ 45-52% in 2 M AS

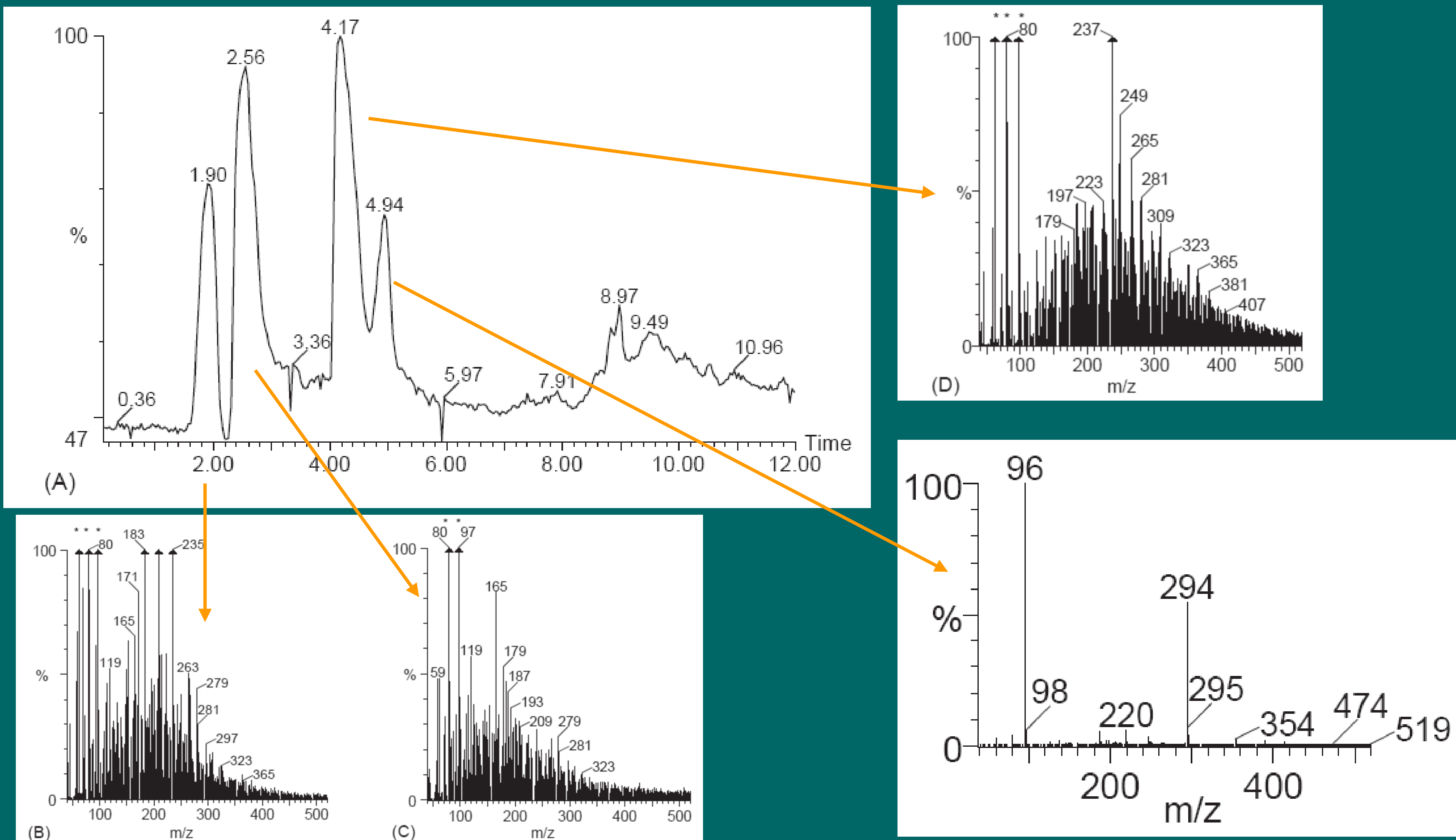
No aliphatic HA in aerosol!



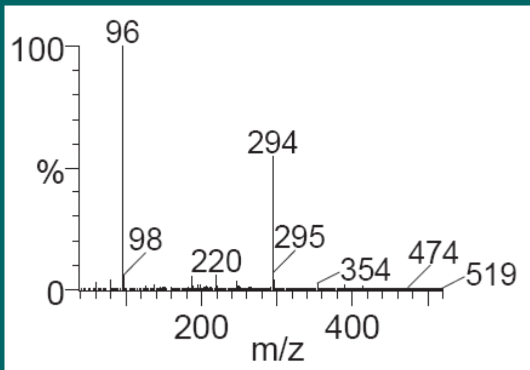

7% and 9% decrease ↔ 35-40% HULIS

# Another reason for ST depression?

HULIS operationally defined (isolated on HLB SPE column)
RP-LC-MS revealed the presence of other compounds:
*(Kiss et al., Atm. Env. 2003)*

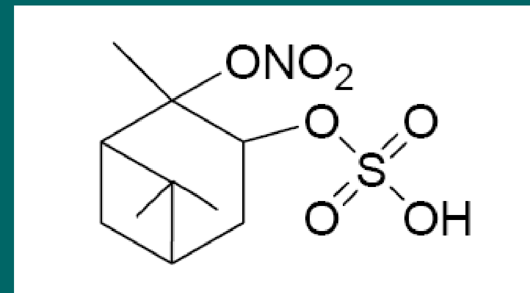


# Another reason for ST depression?




$C_{10}H_{17}NO_7S$

UHR-MS: OK

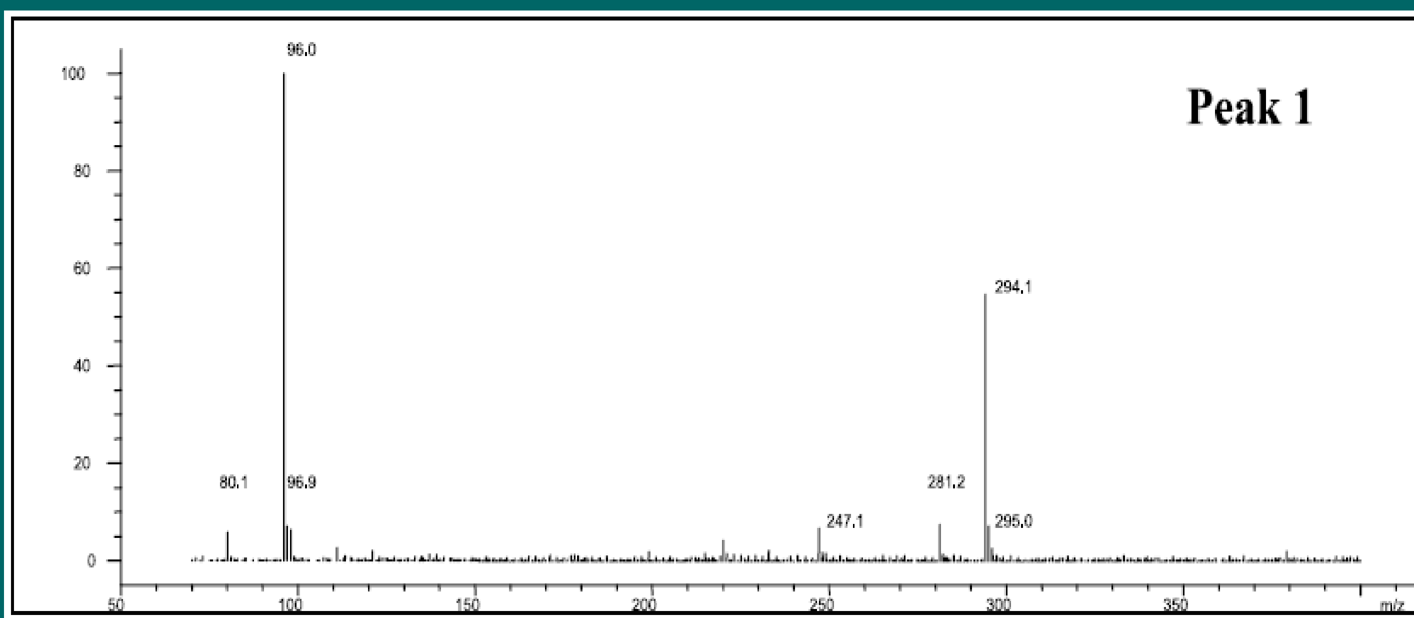



Surratt et al., EST 2007

Favored product

m/z =96 instead of 97!

96 is a fragment ion of 294




Gao et al., JGR 2006

# Organosulfates = HULIS?

HULIS: characteristic UV, fluorescence, FTIR, MS spectra, chromatographic behaviour

These have not been observed/examined for individual organosulfates (e.g. m/z=294)

Organosulfates individually identified so far ≠ HULIS

BUT!

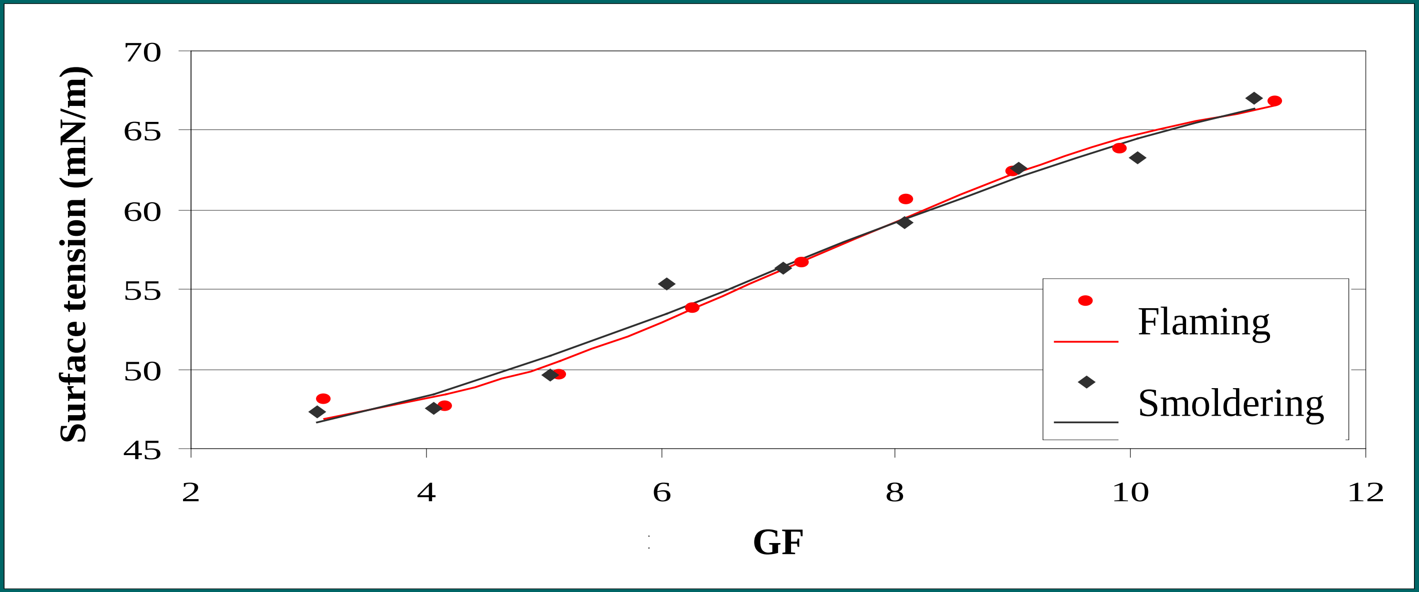
There can be sulfur-containing organics in the unresolved HULIS fraction.

# Samples from BB and K-puszta

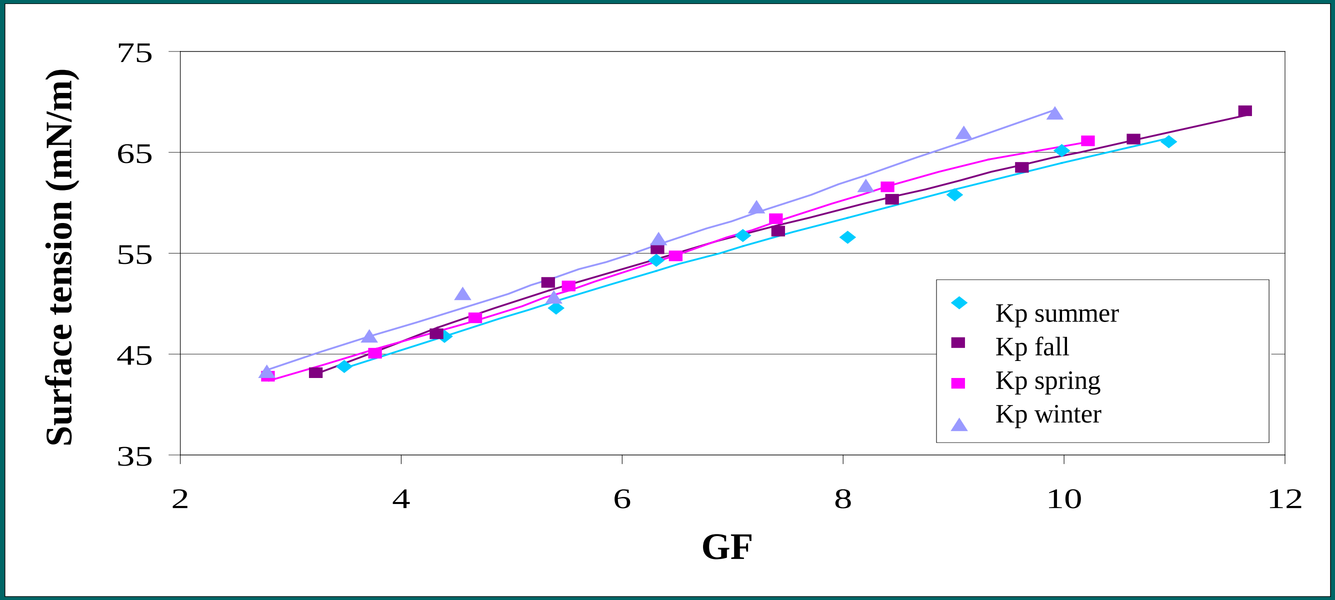
Main difference: the whole WS fraction is involved (organics and inorganics)

| Sample | Inorganic mass/Total mass (%) |
|---|---|
| BB flaming | 2.4 |
| BB smoldering | 0.1 |
| K-puszta spring | 57 |
| K-puszta summer | 42 |
| K-puszta fall | 45 |
| K-puszta winter | 56 |

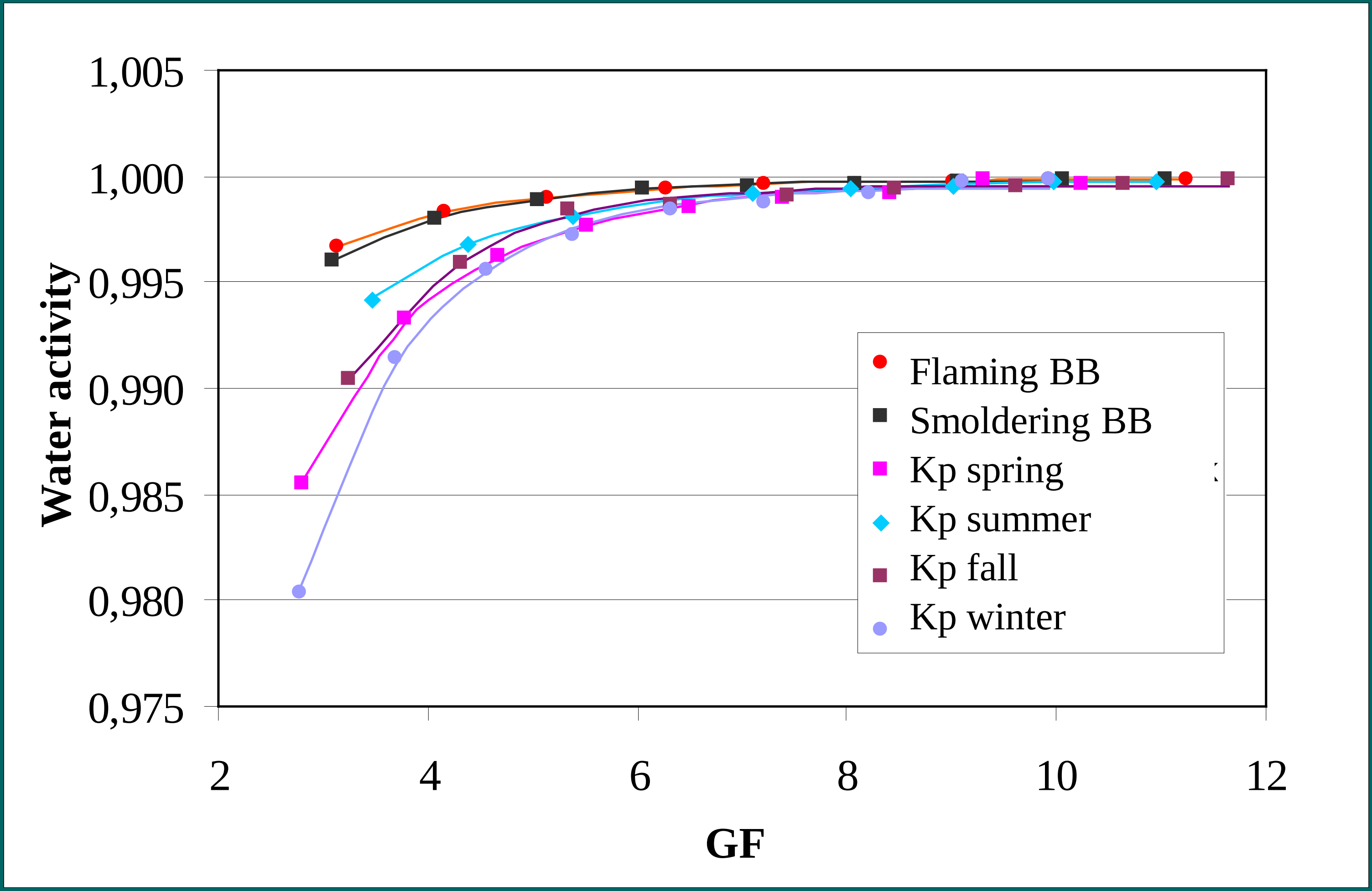
# Surface tension of BB and K-puszta samples




Significant decrease in ST!

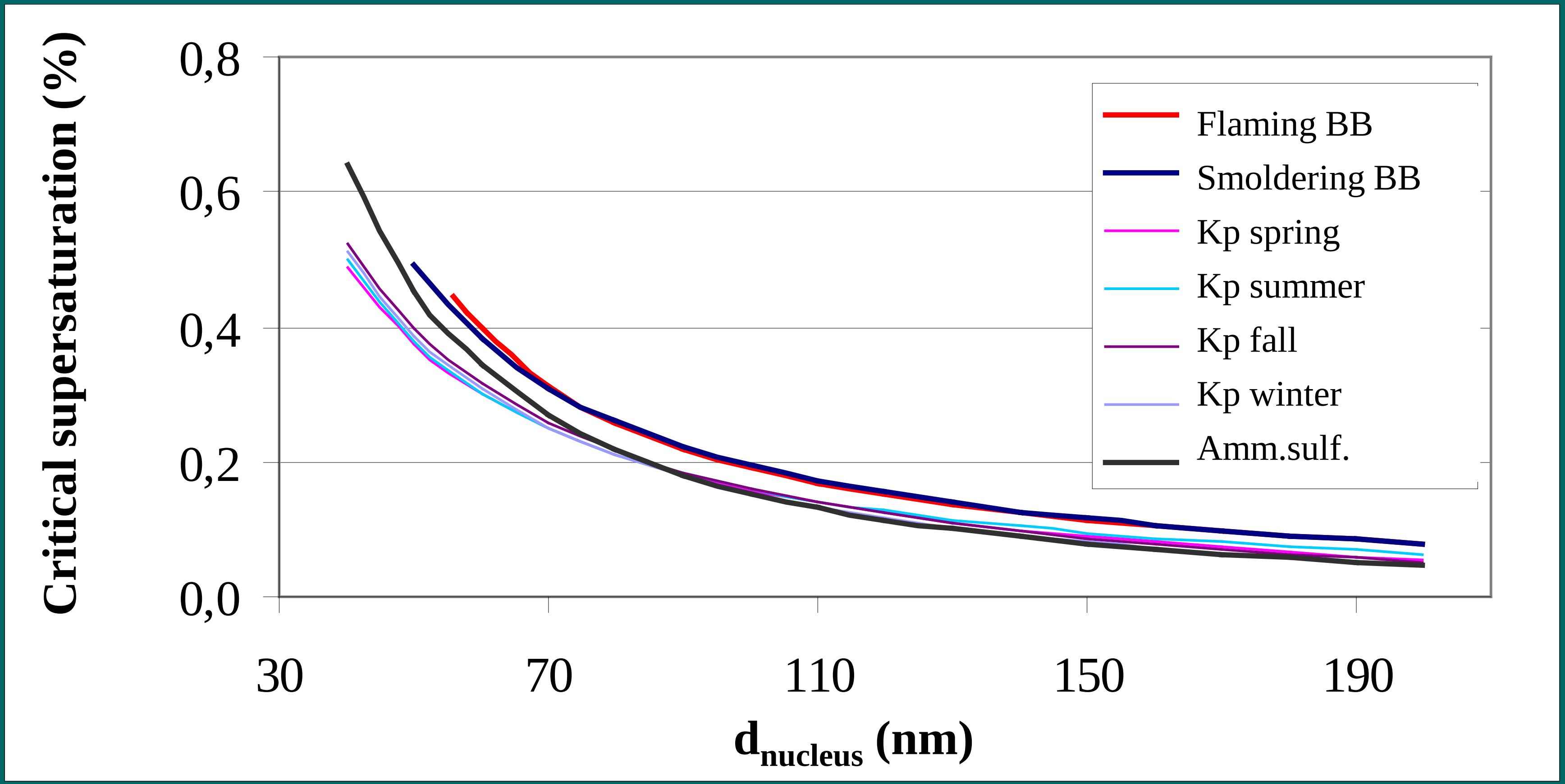


# Water activity of BB and K-puszta samples




Lower $a_w$ for K-puszta samples (esp. winter and spring) as a consequence of higher inorganic content.

# Activation of aerosol particles




BB aerosol activate at higher $S_c$ (lack of inorganics!) than rural aerosol from K-puszta

No difference in $S_c$ between seasons at K-puszta (ST counterbalanced by water activity)

Mixed aerosol (org.+inorg.) from K-puszta activate at similar $S_c$ as ammonium sulfate.

# Summary

**Model compounds (organic acids)**

Surface tension (Kelvin effect) and dissociation (Raoult effect) of organic components are not influenced by inorganic salts in droplets relevant for cloud droplet activation.
Mixtures activate at lower $S_c$ than pure organics studied.

**HULIS**

The HULIS fraction isolated from *ambient aerosol* samples have stronger surface active effect than *model compounds* examined so far. Organosulphates may play a role in it.

**Aerosol samples from BB and K-puszta**

Mixed (organic+inorganic) aerosol from K-puszta activates at similar $S_c$ as AS. Water-soluble organics do not decrease $S_c$ necessary for cloud droplet activation but increase CCN mass/size/number considerably thus playing a role in radiative forcing.

# Acknowledgements

Thanks to:

A. Hoffer (BB samples from MPIC)

H-C. Hansson (VPO and FTA 125)

János Bolyai Research Fellowship of Hungarian Academy of Sciences

BACCI

**Special thanks to the organizers of the 9th ICCPA!**

# Overview of samples

**Model compounds**

oxalic acid, NaCl (1:1, 4:1), AS (1:1, 4:1)

malonic acid

succinic acid, AS (1:1)

glutaric acid

adipic acid, AS (1:1)

malic acid

maleic acid

citric acid, AS (1:1)

*cis*-pinonic acid, AS (1:1)

NRFA, AS (1:1), SRFA, alHA, arHA

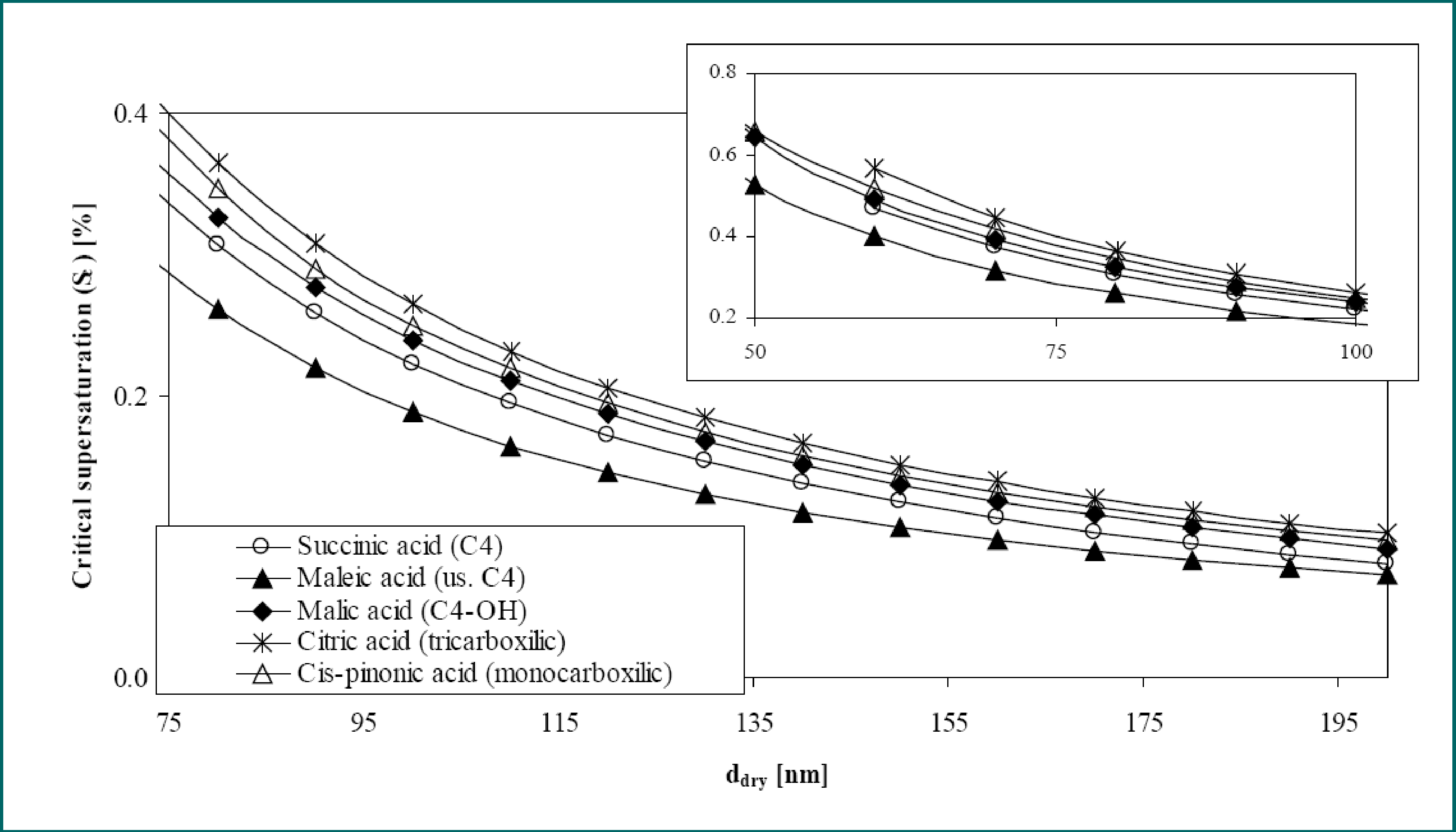
**Aerosol samples**

K-puszta (rural site, 4 seasons)

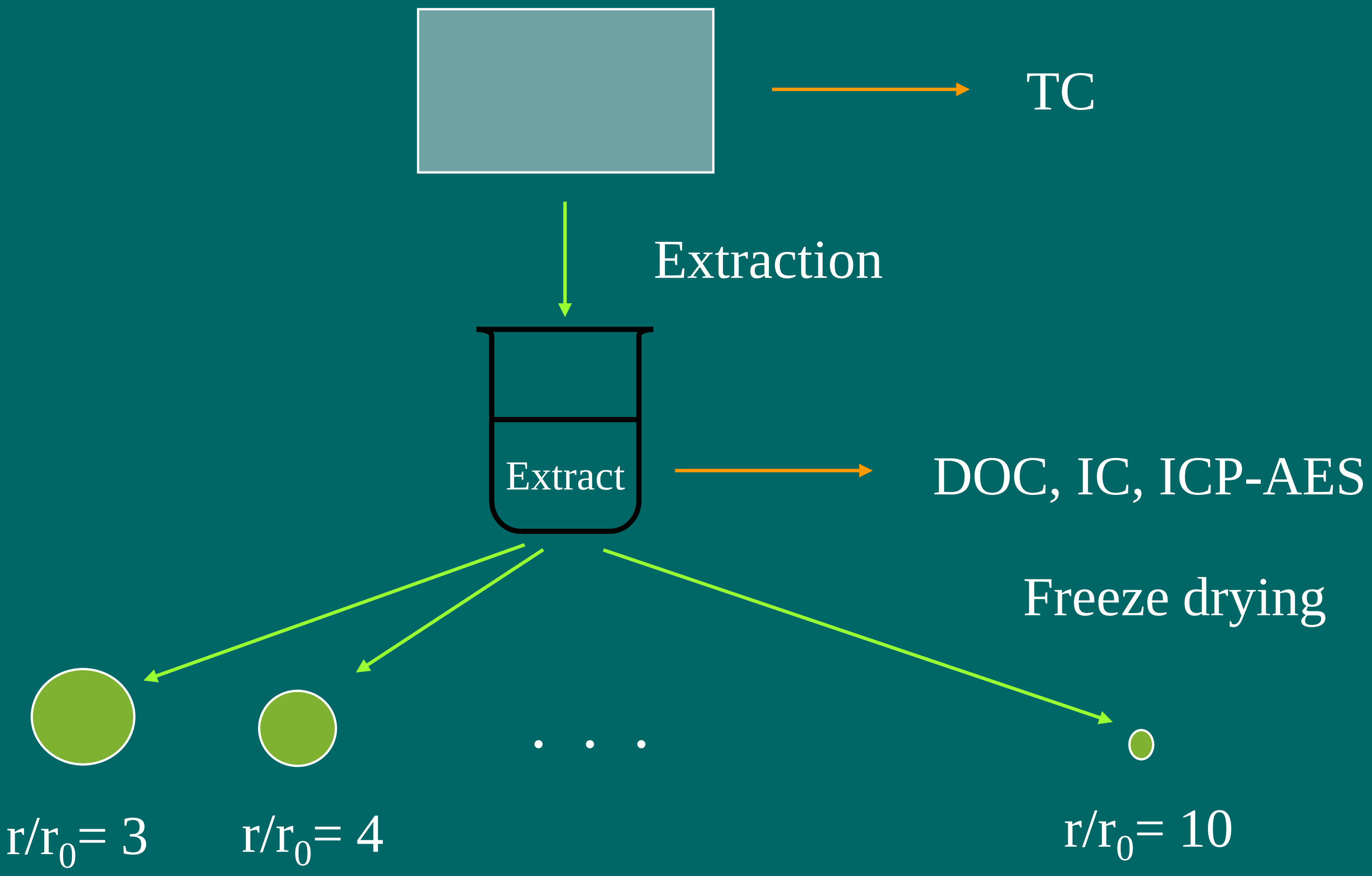
Biomass burnining (oak)

Humic-like substances (HULIS) isolated from ambient aerosol + AS

# $S_{crit}$ of organic acids as a function of dry diameter

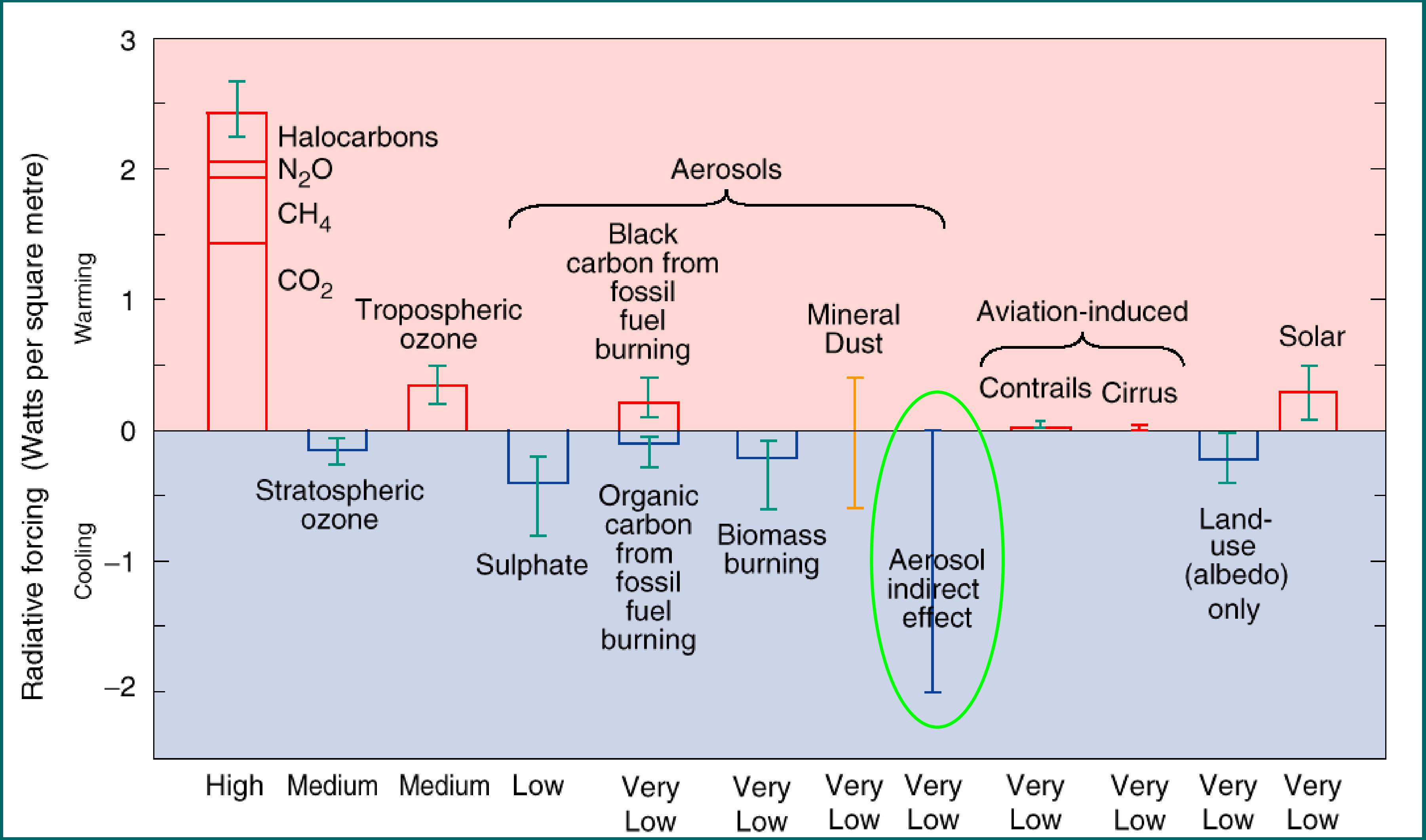


# Sample preparation




ST and VPO of the re-dissolved fractions

# IPCC 2001



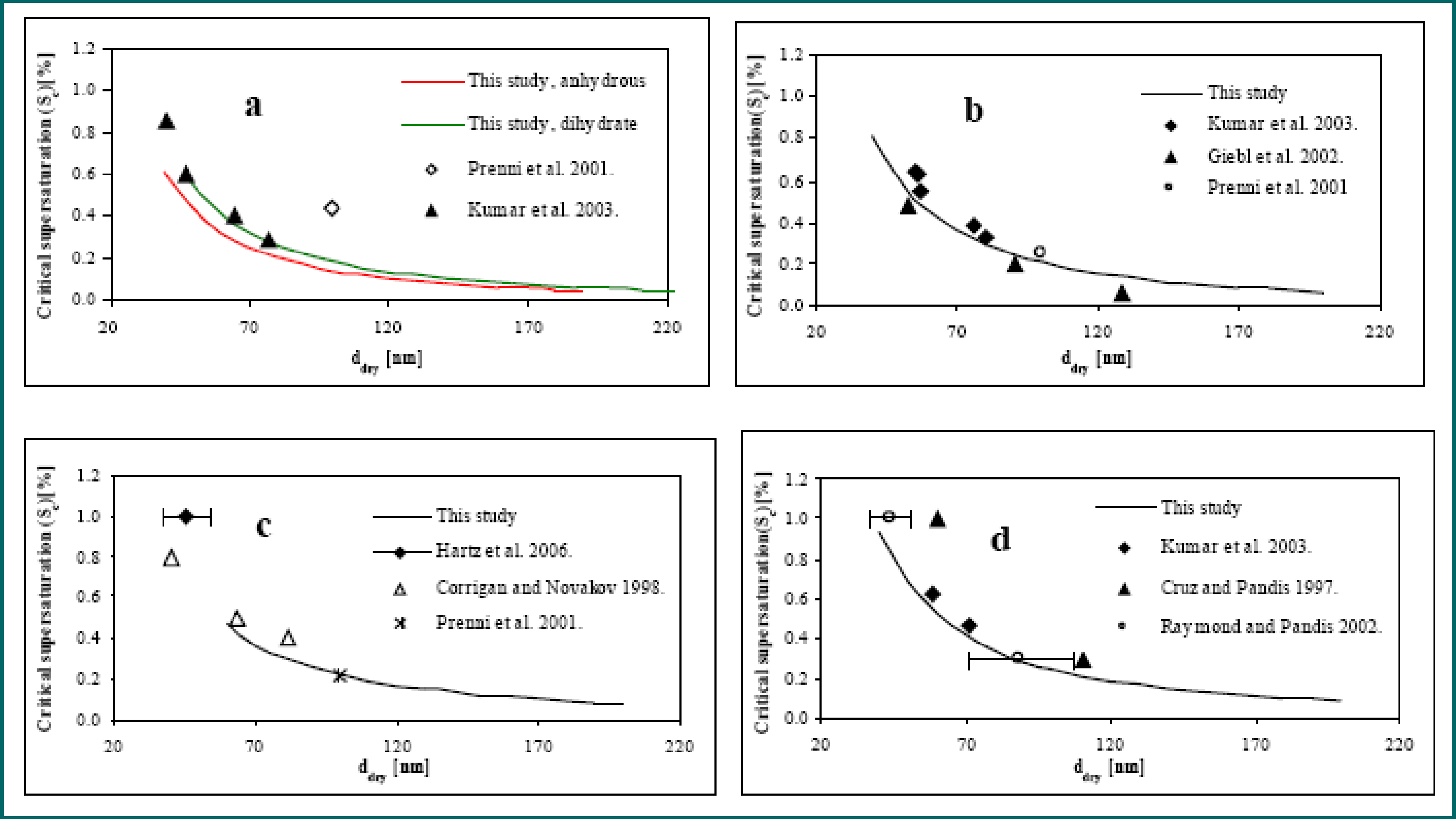
Radiative forcing (Watts per square metre)
Warming
Cooling
3
2
1
0
−1
−2
Halocarbons
$N_2O$
$CH_4$
$CO_2$
Tropospheric ozone
Stratospheric ozone
Aerosols
Black carbon from fossil fuel burning
Sulphate
Organic carbon from fossil fuel burning
Biomass burning
Mineral Dust
Aerosol indirect effect
Aviation-induced
Contrails
Cirrus
Land-use (albedo) only
Solar
High
Medium
Medium
Low
Very Low
Very Low
Very Low
Very Low
Very Low
Very Low
Very Low
Very Low

# The carbonaceous fraction in the samples

| Sample name | 4F | 16S |
|---|---|---|
| Burning conditions | flaming | smoldering |
| Colour of the filter | homogenous | homogenous |
| TC (mg/m3) | 14.0 (11.8 on average) | 7.1 (10.2 on average) |
| WSOC (% of TC) | 70 (77 on average) | 99 (96 on average) |
| EC* | 20 | 0 |
| WINSOC* | 10 | 1 |

# The inorganic fraction in the samples

| | | |
|---|---|---|
| Sample name | 4F | 16S |
| Burning conditions | flaming | smoldering |
| Sulphate (µg/m3) | 330 | 7.7 |
| Nirate (µg/m3) | 91 | 6.4 |
| Chloride (µg/m3) | 18 | < 3 |
| Potassium (µg/m3) | 87 | < 0.3 |
| Ammonium (µg/m3) | 2.9 | 2.0 |
| Zn, Fe, Mg, Ca, Al, Na (µg/m3) | < 0.3 | < 0.3 |




a.) oxalic b.) malonic c.) succinic d.) glutaric