

# Bulk characterization of organosulfates in continental fine aerosol

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# Sulfate esters (organosulfates) are important components of SOA—chamber studies

## First observations:

- Acidic seeds significantly enhance SOA yield in smog chambers (*Jang, Science 2002*)

## Smog-chamber studies

$\alpha$ -pinene (*Czoschke, AE 2003; Gao, EST 2004; Iinuma AE 2004; Kleindienst, EST 2006; Jang, EST, 2006*)

$\beta$ -pinene (*Iinuma EST, 2007; Northcross AE, 2007*)

Isoprene (*Czoschke AE 2003; Edney AE 2005; Surratt JPC, 2006; Surratt EST, 2007*)

Limonene (*Iinuma AE 2007; Northcross AE, 2007*)

Pinonaldehyde (*Liggio GRL, 2006*)

Glyoxal (*Kroll AE, 2005; Liggio JGR 2005*)

# Sulfate esters (organosulfates) are important components of SOA—field studies

Sulfate esters have been identified

In urban and rural aerosol by

- **LC-ESI-MS** (Gao JGR 2006; Surratt EST, 2007; Iinuma EST, 2007, Gómez-González, JMS 2008)
- **FTIR** (Blando EST 1998; Gilardoni JGR, 2007)

In water-soluble HULIS by

- **ESI-ITMS and ESI-TOF** (Romero and Oehme, JAC 2005)

# Suggested mechanisms of sulfate esters formation

## In the presence of acidic seed aerosols

Reactive uptake of semi-volatile BVOC photooxidation products

Hydroxy compounds: esterification with sulfuric acid

Carbonyl compounds: esterification after gem-diol formation

Direct uptake of BVOC (Liggio GRL, 2005)

## In the absence of seed aerosols

Photooxidation of BVOC ( $\alpha$ -pinene or isoprene) and  $\text{SO}_2$  (Surratt EST, 2007)

*High  $\text{NO}_x$  strongly suppresses organosulfate formation (organic acid formation vs. esterification)*

# Open questions

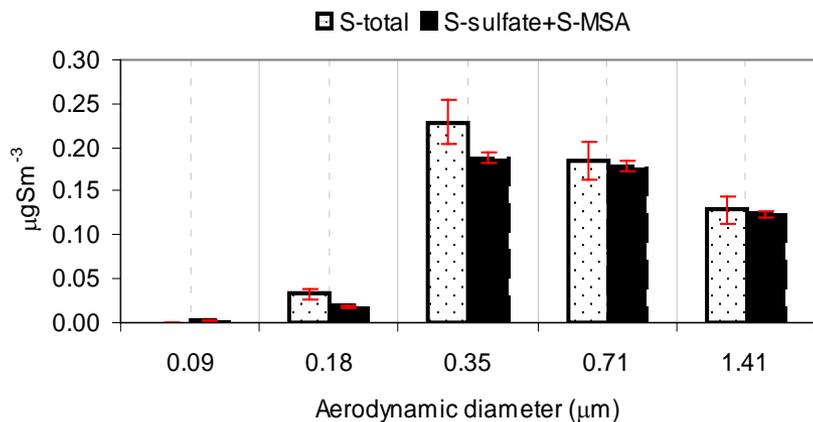
- 1) Could organosulfate formation be a quantitatively important SOA formation mechanism in ambient aerosol?
- 2) In which particle size fraction do organosulfates occur?
- 3) How is sulfur distributed between organic compounds?
- 4) Which formation mechanism could be operative in the atmosphere?

## Sampling and analysis methods

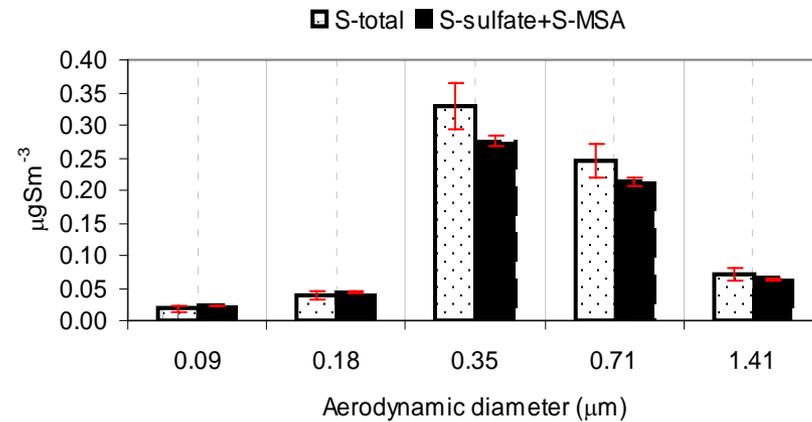
- 48-h aerosol samples were collected with 8-stage Berner impactor at K-pusztá (rural site) in summer 2006
- Samples were ***extracted in water*** and analyzed for
  - total sulfur by XRFS
  - sulfate and methanesulfonate by IC
- Organic S = Total S – sulfate – methanesulfonate
- Uncertainties were minimized and carefully evaluated
- TC mass concentrations were also measured by thermal analysis

# Size-distributions of total S and S<sub>sulfate+MSA</sub>

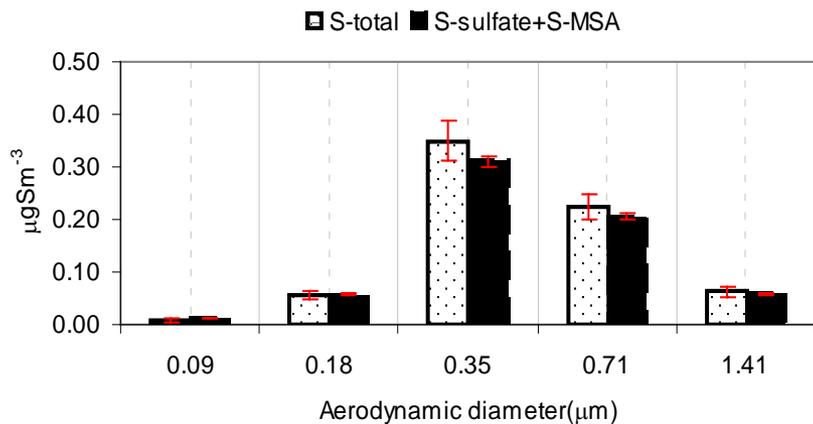
29 - 31 May 2006



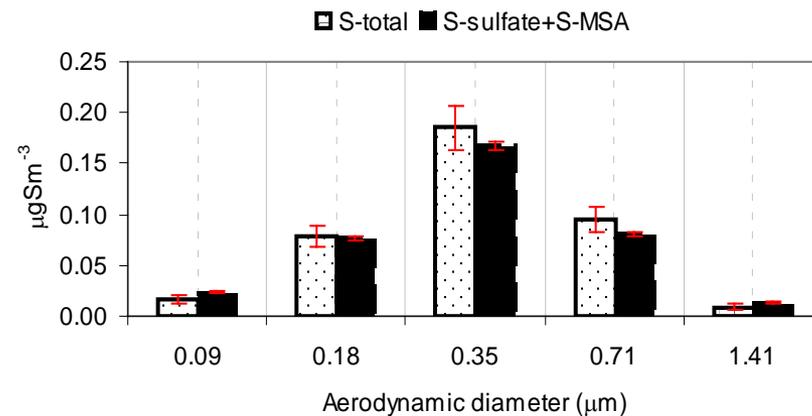
04 - 06 June 2006



06 - 08 June 2006



14 - 16 June 2006



## Mass concentrations of major sulfur species in water extract of PM2.5 aerosols

Sample	$S_{\text{total}}$	$S_{\text{sulfate}}$	$S_{\text{org}}$	$S_{\text{org}}/S_{\text{sulfate}}$	
	$\mu\text{gSm}^{-3}$	$\mu\text{gSm}^{-3}$	$\mu\text{gSm}^{-3}$	%	RSD
29-31 May 2006	0.57	0.50	0.06	13	63
04-06 June 2006	0.70	0.60	0.09	14	58
06-08 June 2006	0.70	0.63	0.05	9	96
14-16 June 2006	0.38	0.35	0.02	6	129

# Estimated mass contribution of water-soluble organosulfates to WSOC

Can only be estimated with a high level of uncertainty:  
mass-weighted average C-to-S molar ratio would be needed

C:S ratio 2:1 in sulfate ester of glyoxal

10:1 in sulfate esters of monoterpene derivatives

15:1 in sulfate esters of sesquiterpenes derivatives



**16–57% of WSOC (SOA) are bound in organosulfates**

## Analysis of organosulfates in water-soluble sub-fraction of rural PM2.5 aerosols

- PM2.5 aerosol samples were collected on quartz filters at rural sites of K-pusztá (Hungary) and St. Anicet and Canterbury (Canada) in summer 2004 and 2005
- Samples were extracted in water
- *Extracts were isolated on a C18 column, eluted with methanol and brought to dryness*
- Samples were analyzed with an ultra high resolution Bruker (Bremen, Germany) APEX 12 Qe Fourier transform ion cyclotron resonance mass spectrometer (FTICR-MS) coupled to an APOLLO II microelectrospray source
- Mass range  $m/z$  100-2000, Resolution  $\gg$  100,000
- Peak assignment with software using theoretical isotope scoring

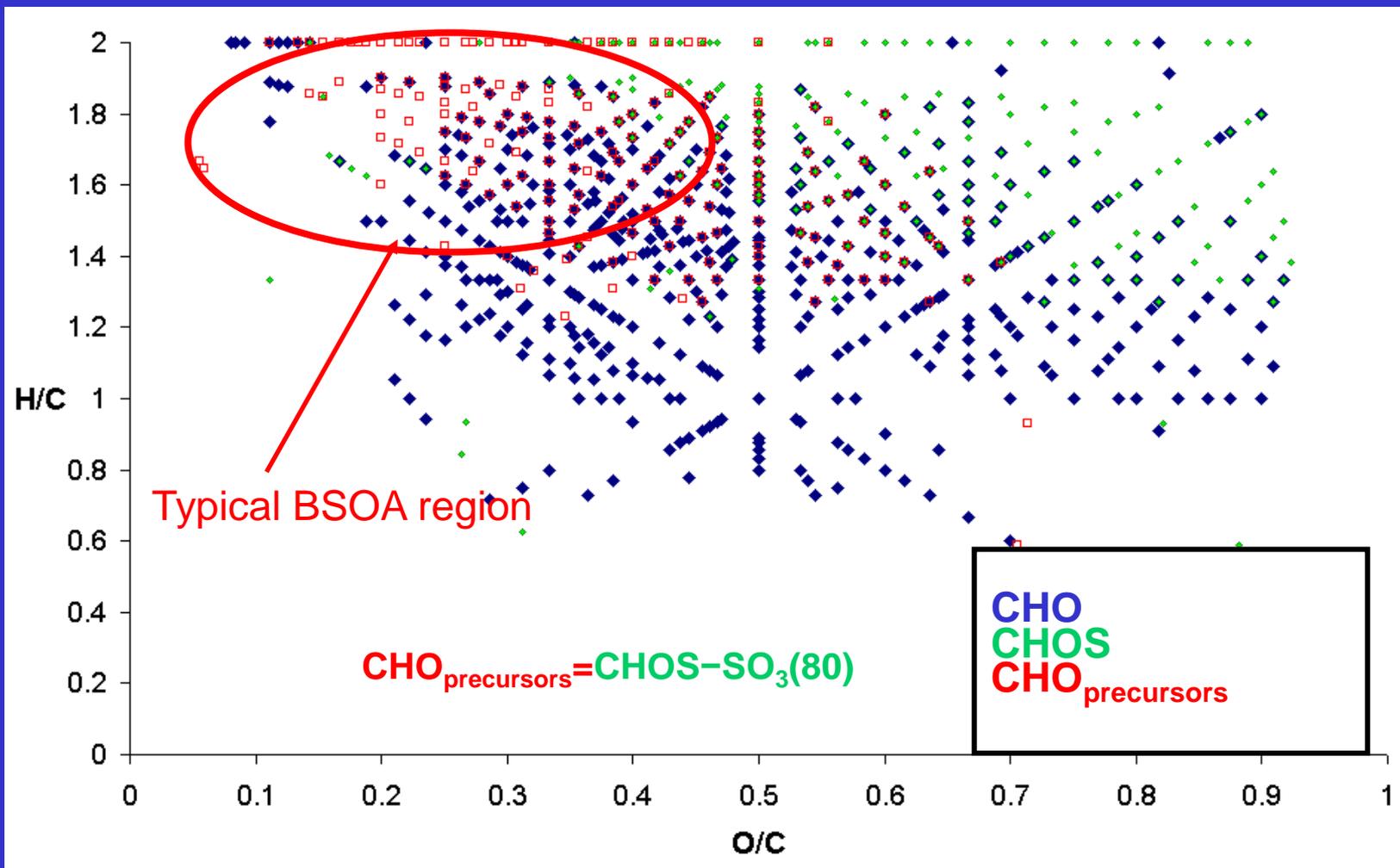
## Peak number statistics by elemental composition in water-soluble sub-fraction of rural PM<sub>2.5</sub> aerosols

Elemental formula	Occurrence %
CHO	67–75
CHOS	17–23
CHON	4–6
CHONS	4–5

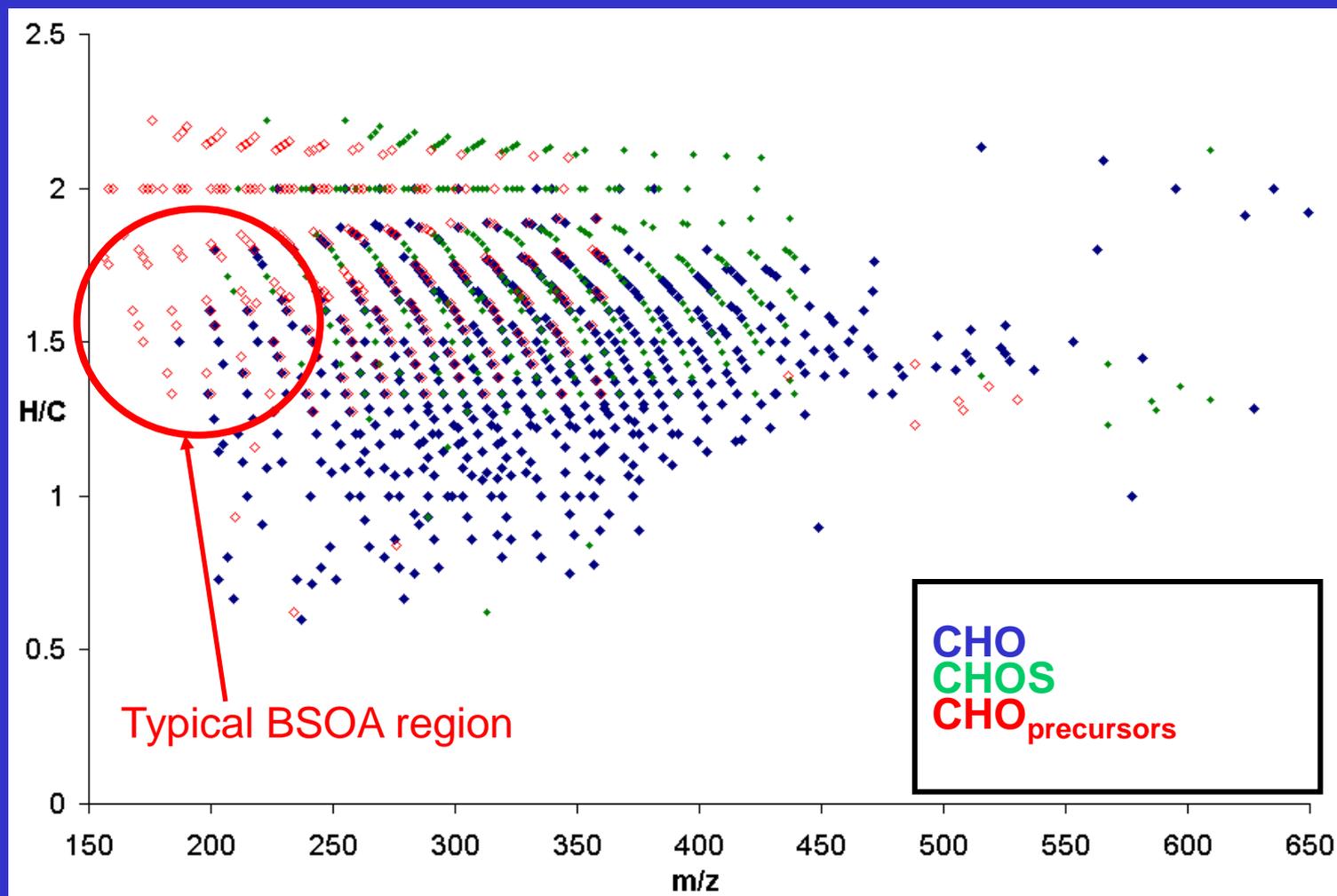
Based on 770–1000 assigned peaks of four PM<sub>2.5</sub> samples each

**Number of compounds can be substantially larger since a single elemental formula may belong to several compounds**

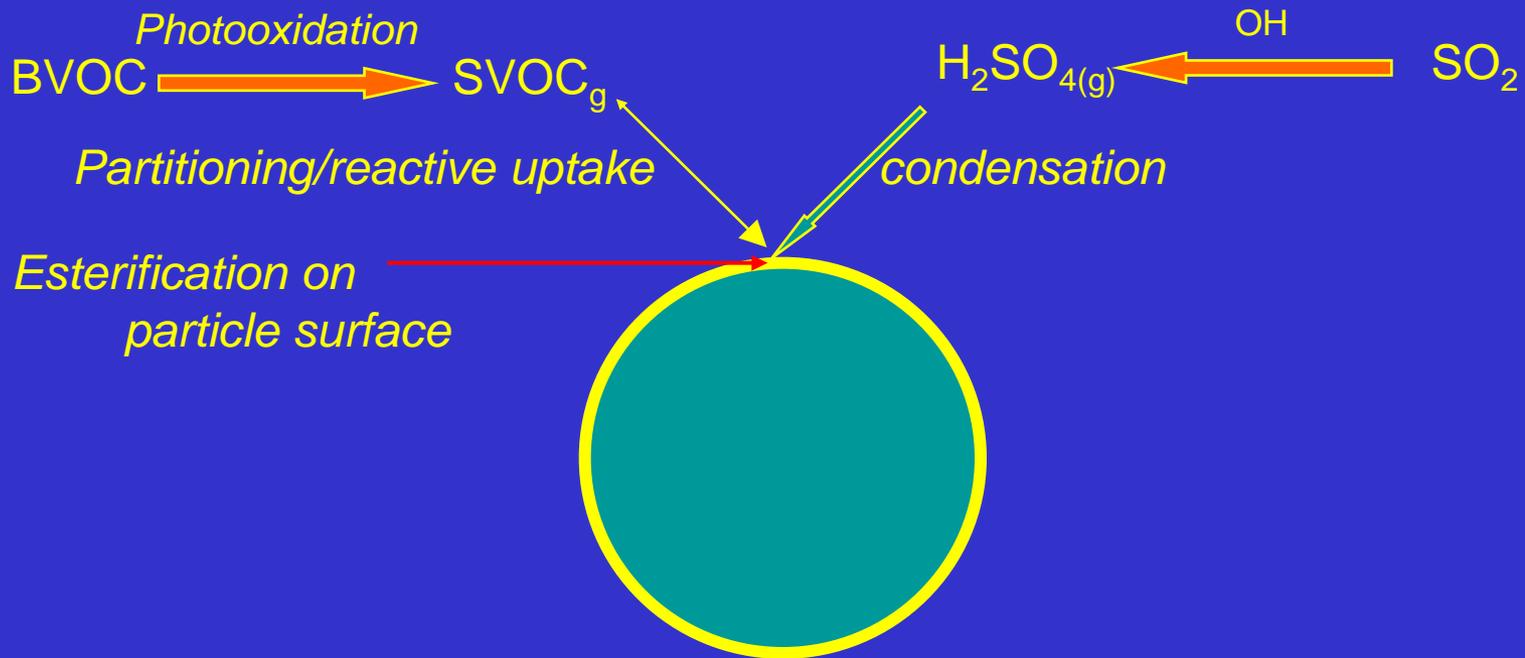
# Van Krevelen diagram of assigned peaks



# Mass resolved van Krevelen in H/C of assigned peaks



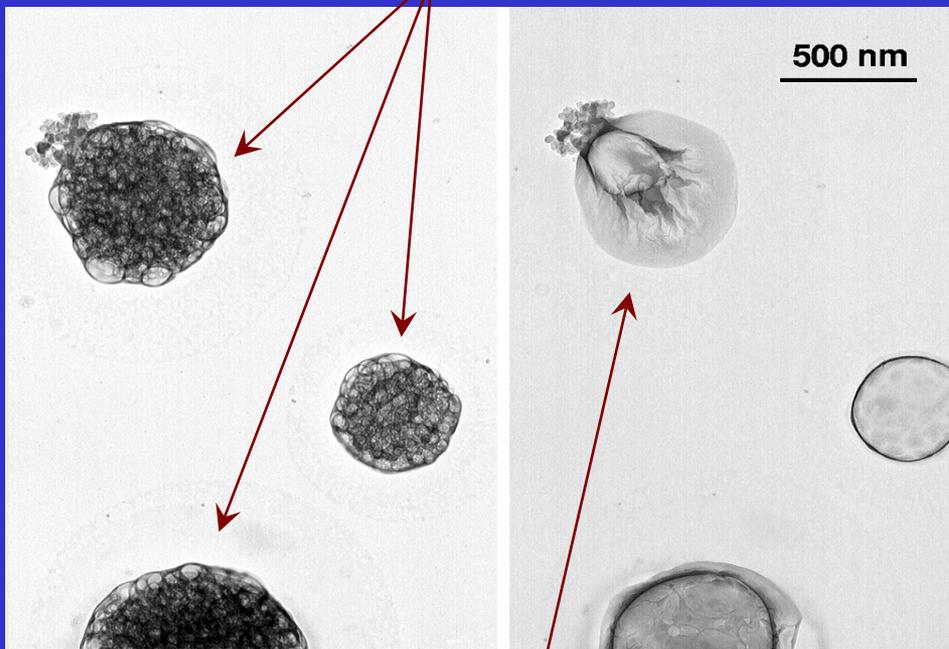
# Conceptual model of organosulfate formation in the atmosphere



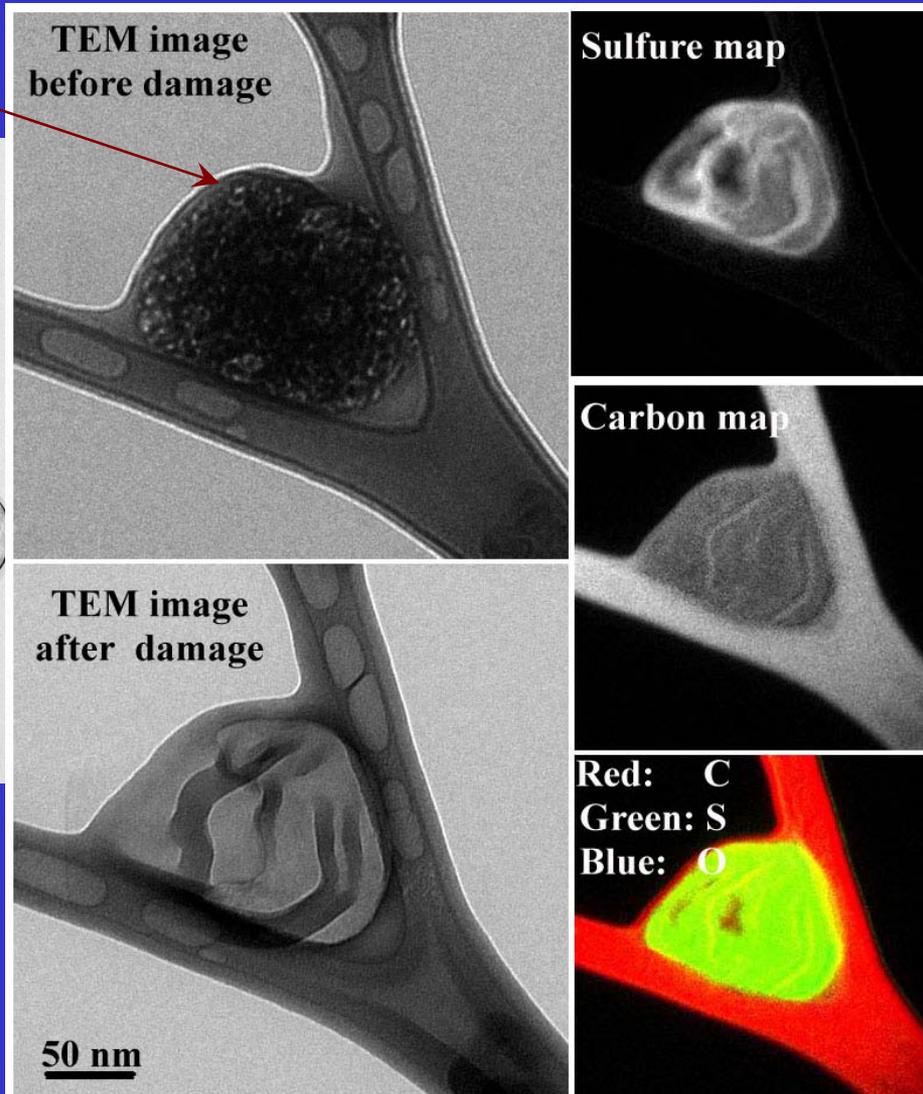
No acidic aerosols are needed

# TEM-EELS studies on individual particles from K-pusztá

ammonium sulfate particles



S-containing organic residue remains after irradiation



# Conclusions

- 1) Organosulfates seem to be quite significant SOA components at least in summer rural aerosols;
- 2) Total sulfur in organosulfates may not be negligible even related to sulfate S;
- 3) They tend to be overwhelmingly in (on) accumulation (condensation) mode particles;
- 4) There are several hundreds of S-containing organic peaks even in a subfraction of WSOC;
- 5) These compounds span a wide range of MW and O/C-H/C ratios;
- 6) Likely formation mechanism is reactive uptake of BSOA powered by heterogeneous reactions with gaseous sulfuric acid.

**Thanks for your attention!**