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Wet scavenging of nitrated and oxygenated aromatic hydrocarbons in urban and remote sites in Europe; levels and distribution in phase-segregated snow

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Introduction

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- Nitrated & oxygenated poly-aromatic hydrocarbons (N/O-PAHs):
  - Oxidation of PAHs during combustion process
  - Reactions with atmospheric oxidants e.g. hydroxyl and nitrate radicals
  - More mutagenic than parent PAHs
  - Classified as possible carcinogens

- Nitrated mono-aromatic compounds (NMACs):
  - Primarily, biomass burning or traffic exhaust
  - Secondarily, nitration of precursors – e.g. phenols
  - Might be toxic at high concentrations
  - Contribution to particulate matter (PM) light absorption

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Introduction

- Semi-volatile organic compound (SOC) wet scavenging mechanisms:
  - Gas scavenging (W_G) – relevant for substances in gas phase
  - Particle scavenging (W_P) – important for particle-bound species
  - $W_P > W_G$
- Scavenging linked to particulate mass fraction, $\Theta = c_{ip}/(c_{ip}+c_{ig})$
- SOC wet scavenging & concentration in precipitation:
  - Gas-particle partitioning (GPP)
  - SOC water solubility (WS)…
- SOC distribution in precipitation:
  - Gas-phase species predominant in dissolved phase
  - Particle-bound SOCs abundant in particulate phase

Introduction

- There is very little information about N/O-PAH & NMAC levels & distribution in precipitation in the literature

- **Objectives**
  - Investigate the presence of N/O-PAHs & NMACs in snow samples
  - Estimate their particulate mass fraction using a multiphase ppLFER model
  - Determine analyte fractions removed by particle or gas scavenging
  - Explore the effect of gas-particle partitioning vs. water solubility on scavenging processes

Methods: sample collection

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- Snow samples collected in Winter 2015 & 2016
- 3 locations in Germany: Mainz (residential), Winterberg & Altenberg (rural)
- 2 locations in Inn Valley, Austria: Götzens (residential), Kolsassberg (rural)
- 2 locations in Czech Republic: Ostrava (urban) & Pusta Polom (rural)
- Fresh snow collected using pre-cleaned polypropylene trays (0.25 m^2 each), placed on the ground prior to snowfall
- Surface snow transferred to amber glass bottles & kept frozen until laboratory analysis

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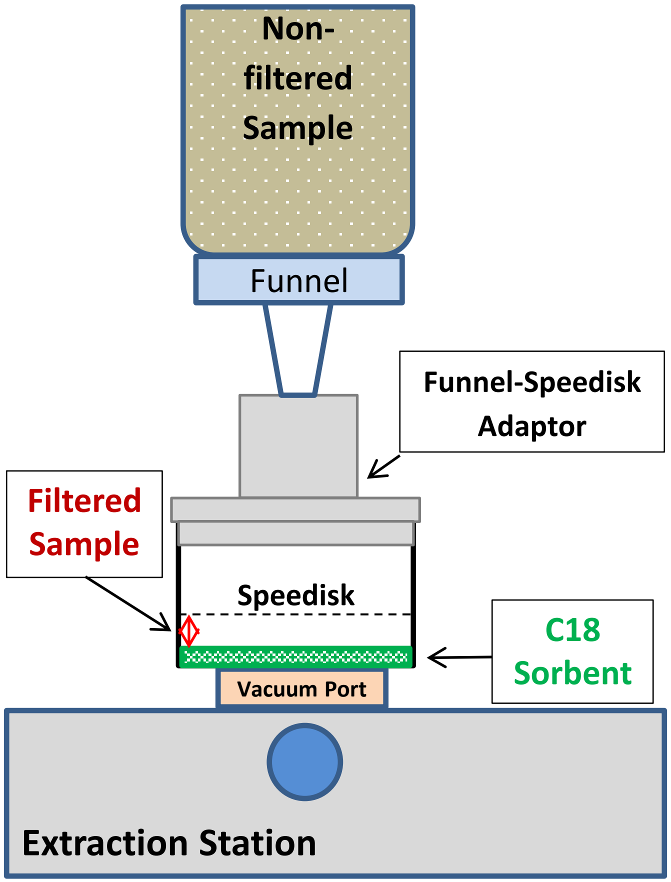
Methods: sample processing – N/O-PAHs

1. Melted samples passed through filtration unit (0.2 micron, cellulose nitrate) & C18 Speedisks
2. Phase-separated samples spiked with surrogate standard mixture
3. Particulate phase vortexed with DCM & extracts purified using 500 mg silica cartridges
4. Dissolved phase from Speedisks eluted with 1:1 *n*-hexane:DCM
5. Analysis on Agilent 7000C & Thermo Scientific TSQ8000 GC-NCIMS/MS
6. Quantification in 1-1000 ppb range, using isotope dilution method
7. 9 OPAHs & 17 NPAHs were analyzed



Methods: sample processing - NMACs

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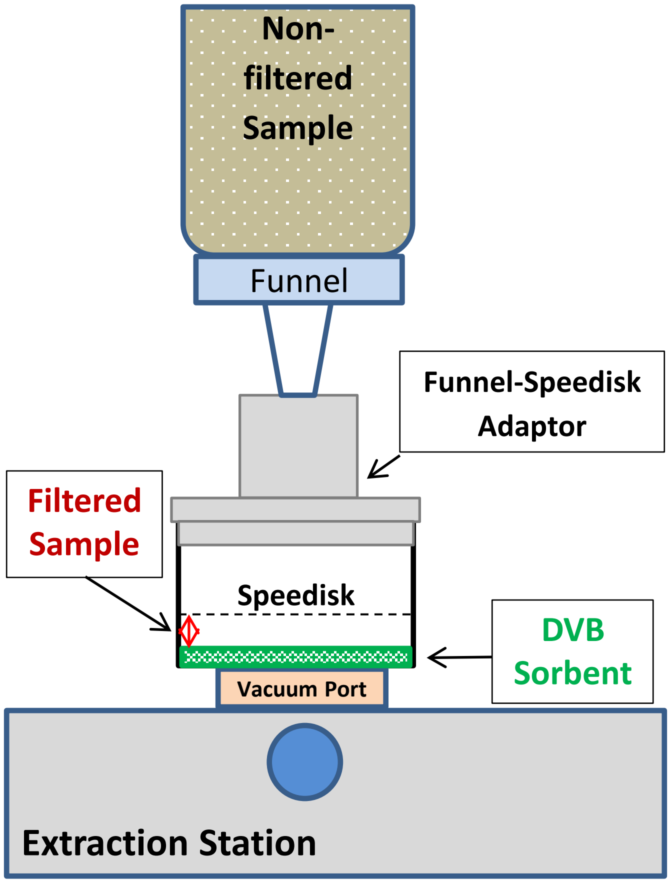
1. Melted samples passed through filtration unit (0.2 micron, cellulose acetate) & DVB Speedisks
2. Phase-separated samples spiked with a surrogates, 4-nitrophenol-d_4
3. Particulate phase ultrasonically extracted with MeOH (Kitanovski et al., 2012)
4. Dissolved phase eluted with acetonitrile-methanol
5. Samples analysed on Agilent HPLC (1200)-MS (6130) in negative ESI & SIM mode
6. Quantification in 1-500 ppb range using isotope dilution method
7. 10 NMACs were analysed



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Methods: estimation of Ɵ using multiphase ppLFER model

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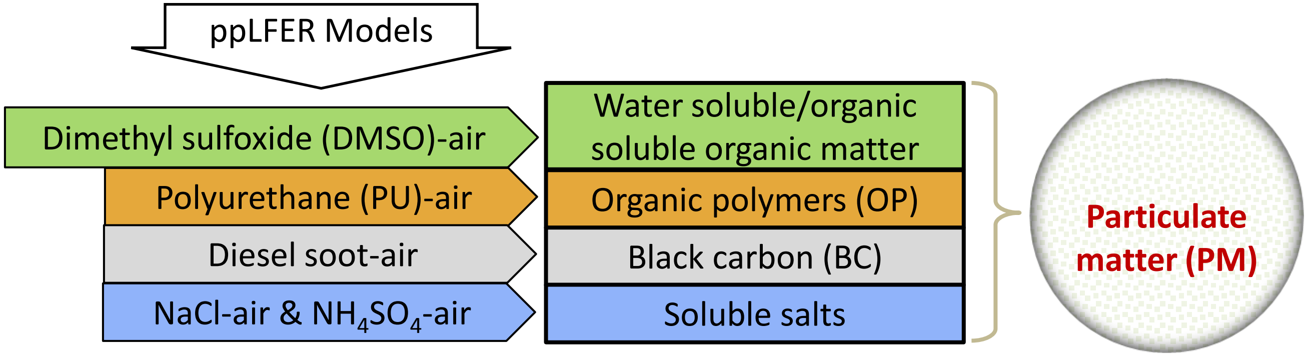


1) Abraham *et al* (2010), *J. Pharm. Sci.* 99, 500-1515
2) Kamprad & Goss (2007), *Anal. Chem.* 79, 4222-4227
3) Roth *et al* (2005), *Environ. Sci. Technol.* 39, 6638-6643
4) Goss *et al (2003), Environ. Toxicol. Chem.* 22, 2667-2672

Abs.

$K_{P,DMSO}/\rho_{DMSO} \times f_{OM,A}$ +

$K_{P,PU} \times f_{OM,B}$ +

Ads.

$K_{P,soot} \times a_{soot} \times f_{BC}$ +

$K_{P,(NH_4)_2SO_4} \times a_{(NH_4)_2SO_4} \times f_{(NH_4)_2SO_4}$ +

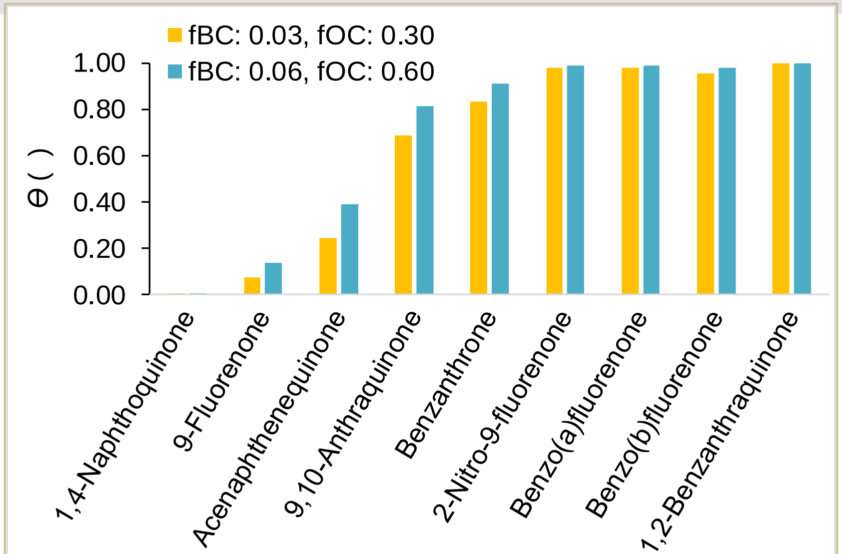
$K_{P,NaCl} \times a_{NaCl} \times f_{NaCl}$

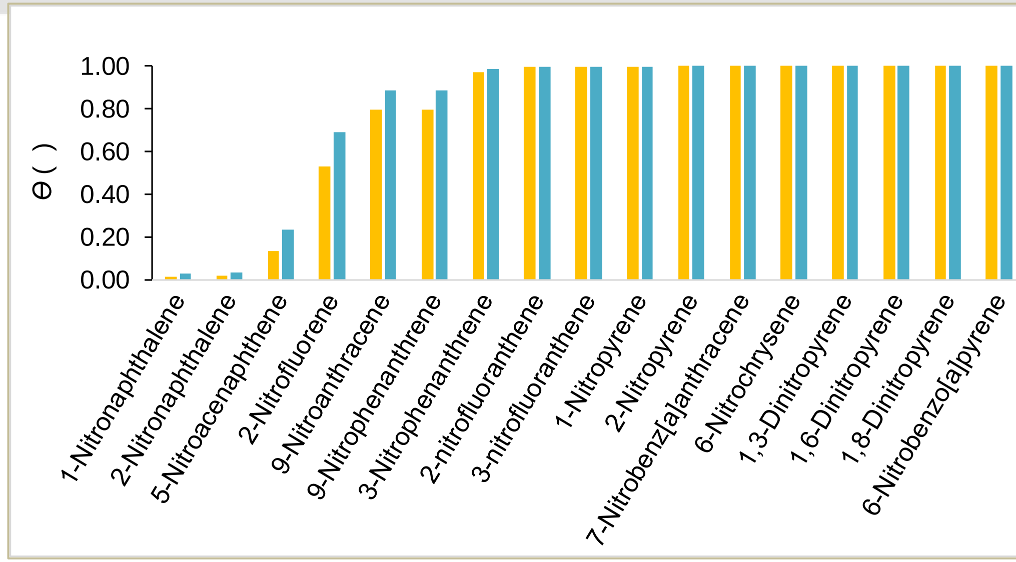
- a_X: Sorbent specific surface area
- f_X: Sorbent mass mixing ratio in PM;
- $f_{OM,A}$: 0.6 f_{OM}, $f_{OM,B}$: 0.4 f_{OM}
- ρ_X: Sorbent density

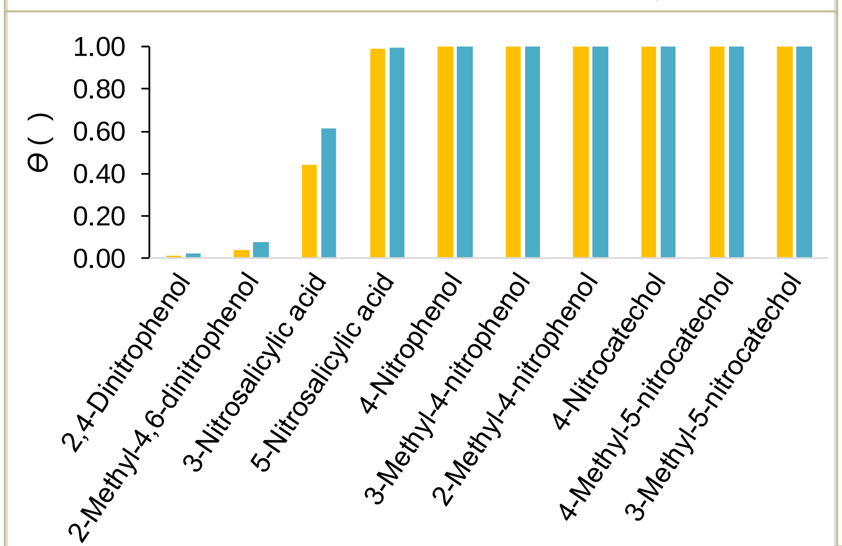
- Ɵ estimated using K_P at 273 K, default PM_{10} concentrations (25 µg m^{-3}), f_{BC} (0.03 and 0.06), and f_{OM} (0.30 and 0.60)

Shahpoury et al., (2016) Environmental Science & Technology, 50, 12312–12319

Results: estimated particulate mass fractions at 273 K







- Θ ~ 1 found for most analytes, regardless of f_{BC} and f_{OC}, indicating high particle scavenging potential
- Exceptions: 3 OPAHs, 4 NPAHs, 4 NMACs

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Results: N/O-PAH concentrations in snow

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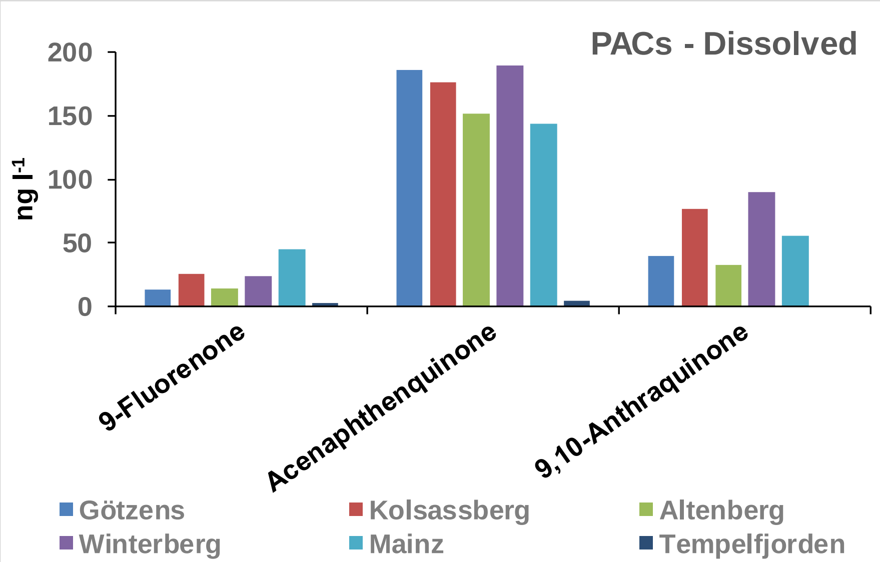

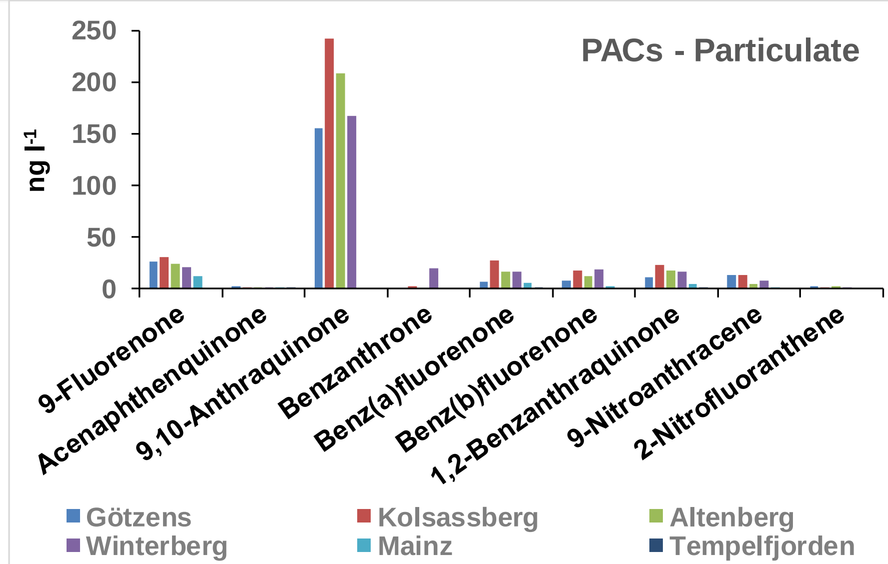

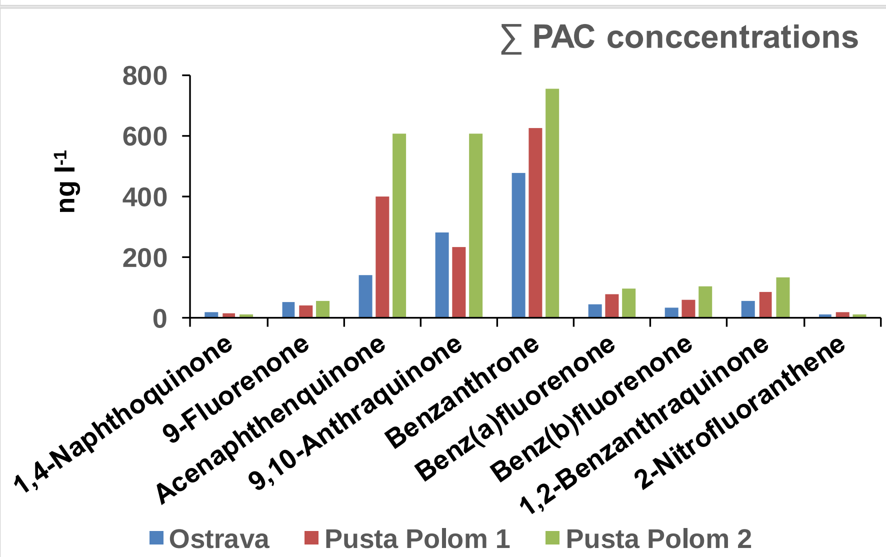

- Dissolved benzanthrone, benz(a)fluorenone, 1,2-benzanthraquinone found < 1 ng l^{-1}
- NPAHs not found in dissolved phase
- Particulate 1- and 2-nitronaphthalene found ≤ 1 ng l^{-1}
- Similar analyte set but higher abundance for samples from Czech Republic

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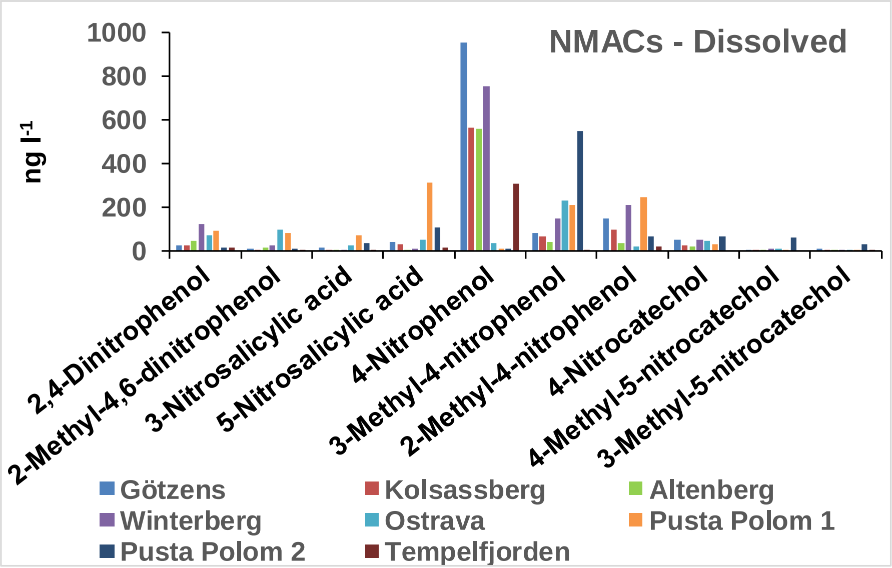
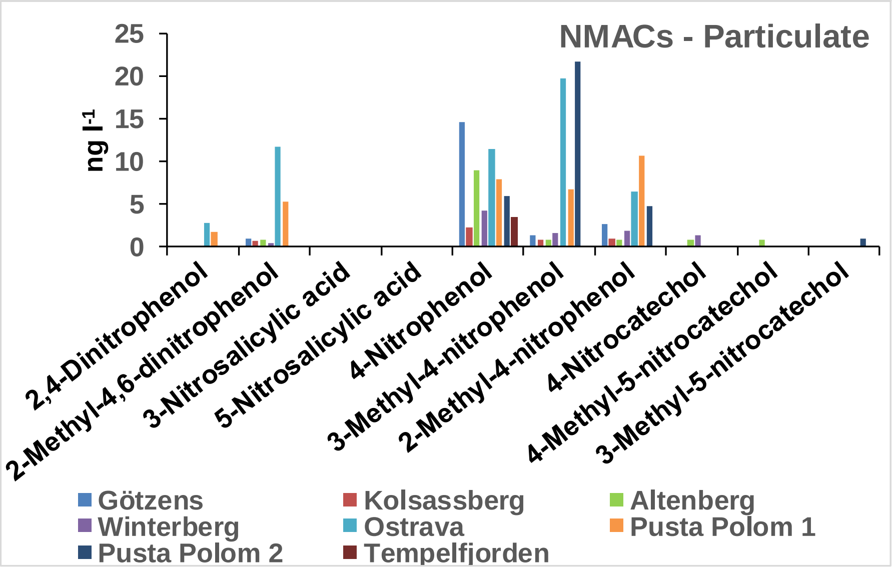
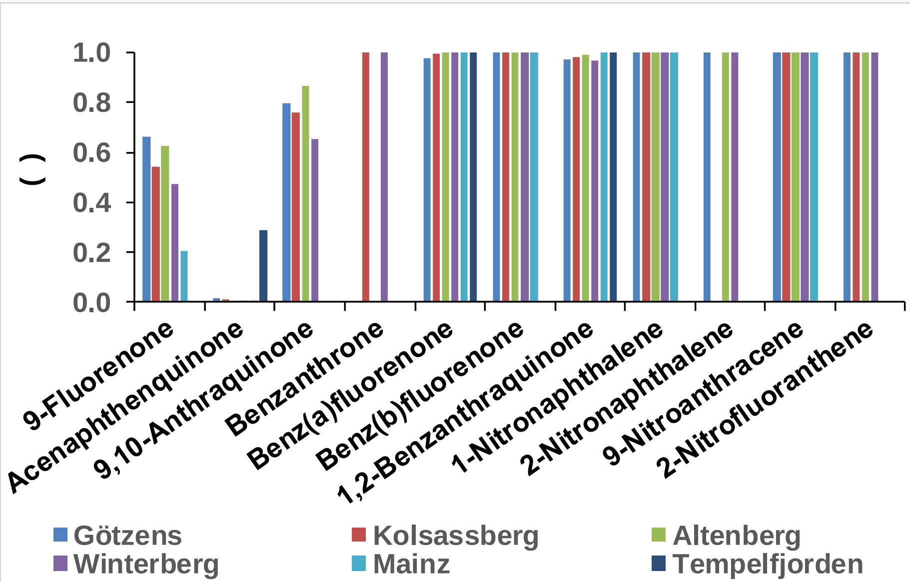
Results: NMAC concentrations in snow

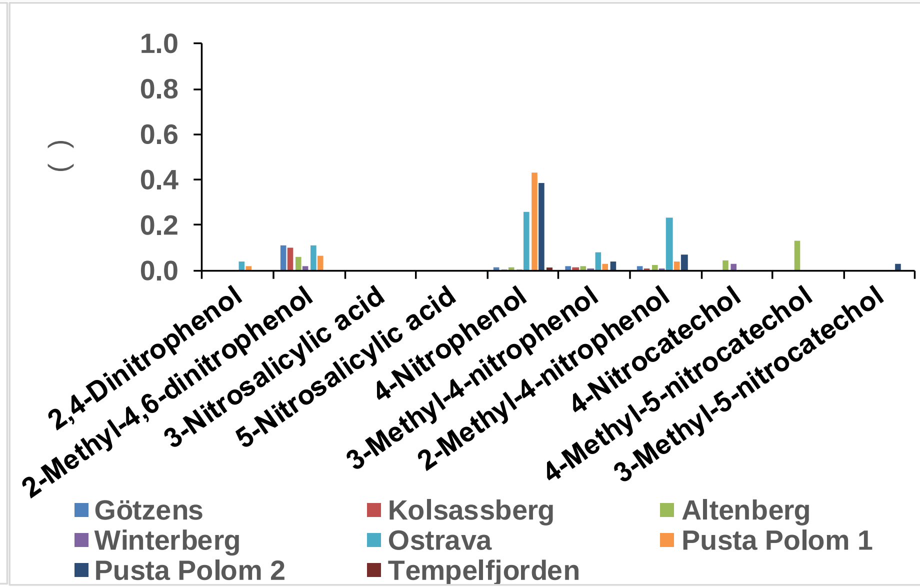




- Target analytes found in 100% dissolved phase samples, but showed lower detection frequencies in particulate phase
- 4-nitrophenol & its methylated derivatives most abundant in both dissolved & particulate phases, suggesting biomass burning sources in winter
- Analytes considerably more abundant in dissolved phase

Results: Fractions removed by particle scavenging





- N/O-PAHs with relatively low WS (log K_{OW} ~ 3-6), GPP (i.e. magnitude of Θ) controls scavenging >> Particle scavenging becomes dominant
  - Exception, acenaphthenquinone log K_{OW} 1.95 >> gas scavenging dominant
- Water soluble SOCs, both GPP & WS play role, with WS dominating the process >> gas scavenging becomes important

Conclusions

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- Higher detection frequency & abundance of O-PAHs in snow could be due to their higher stability in atmosphere
- Most N/O-PAHs are affected by particle scavenging
- 100% detection frequency & considerably higher abundance of NMACs in dissolved phase highlight the importance of gas scavenging
- *ϴ* should be used with caution when estimating SOC wet scavenging potential >> it is a good indicator for relatively water-insoluble SOCs
- Scavenging of water soluble SOCs controlled only partly by GPP, but dominated by WS, suggesting:
  - Dissolution of particle-bound NMACs in cloud droplets prior to snow formation
  - Partitioning of gaseous NMACs into the droplets or onto snowflakes during snowfall

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Thank you for your attention

ppLFER models

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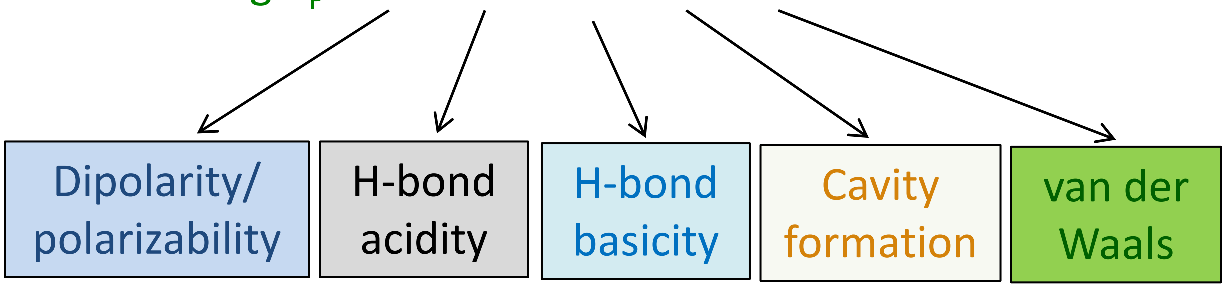
- ppLFER model relates SVOC partitioning to several physico-chemical properties & accounts for significant molecular interactions between solute and sorbent

$$\log K_{\mathrm{P}} = sS + aA + bB + vV + lL + c$$



1) Abraham (1993), *Chem. Soc. Rev.* 22, 73-83
2) Goss (2005), *Fluid Phase Equilib.* 233,19-22
3) Endo & Goss (2014), *Environ. Sci. Technol.* 48, 12477–12491

- ***Capital letters***: Abraham solute descriptors; ***Small letters***: system parameters
- Developed for various organic/inorganic partitioning systems & are available in the literature