EMEP NMVOC - model and observations

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EMEP MSC-W model: NMVOC

Recent developments:

- New species: EmChem19a chemistry has toluene, benzene as “pure” species.

- New NMVOC speciations added (2020):
  - Country specific profiles
  - Accounting for diesel, gasoline, LPG, non-exhaust
  - Data from TNO/CAMS databases (not national reporting)
  - Hopefully big improvement compared to earlier pan-European and old profiles
NMVOC measurements in EMEP

“Inhomogeneous” data:

➢ Different methods

➢ Different time resolution
  ○ Continuous, hourly
  ○ Canister samples (1-2 per week)
  ○ 4-h samples

➢ Changing network

But:

➢ ACTRIS project: Major improvement in QA/QC for NMVOC measurements
Status of monitoring of VOCs

- C2-C5 NMHC have been measured for several decades
- Very few sites measure OVOCs
- Methanol and terpenes reported for the first time in 2018

<table>
<thead>
<tr>
<th></th>
<th>EMEP required</th>
<th>EMEP desirable</th>
<th>Number of sites in 2018</th>
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<td>Alkanes</td>
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<td>C₆-C₈</td>
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<td>X</td>
<td>5-13</td>
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<tr>
<td>C₂-C₃</td>
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<tr>
<td>C₄-C₅</td>
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<td>X</td>
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<td>Isoprene</td>
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<tr>
<td>Styrene</td>
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<td>X</td>
<td>0</td>
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<td>Carbonyls</td>
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<td>DMS</td>
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</table>
Can we model toluene? (Prelim results, 2018!)

Yes, pretty well!
Can we model isoprene? (Prelim results, 2018!)

Hmm, trickier! (but no surprise)
Issues with NMVOC comparisons

➢ Model issues:
  ○ NMVOC speciation is coming from CAMS - unclear origin
  ○ Some model species are surrogates, e.g. n-butane represents all heavier alkanes, and o-xylene represents many aromatics.
  ○ Some species are “pure” and can be directly compared to observations - isoprene, toluene, benzene
  ○ Biogenic emissions are very tricky - many super-emitters!

➢ Observation issues:
  ○ Many sites are in mountains (e.g. > 500m) - creates difficulties when comparing to model
  ○ Are data representative for grids? Many biogenic VOC have very short lifetimes and can come from those super-emitters!
An aside: do BVOC matter?

At first sight, not so much? Zero isoprene over Europe affected annual daily-max by ~ 1-3 ppb

EMEP model results (very old!)
Do BVOC matter? Yes!

- On particular days O₃ changes can be 10-40 ppb!
- Because ... VOC needs NOx to make ozone. Only when BVOC passes over high NOx regions do we get much O₃ production.

EMEP model results
Sources of BVOC: many, complex and uncertain!

Fig: European isoprene emissions from four CTMs, Langner et al., ACP, 2012

Loreto & Fares, 2013
NMVOC - final comments

1. A proper model-measurement comparison is long overdue

2. New VOC in EMEP model (e.g. toluene, benzene), and updated speciations, allow for more realistic testing

3. Information comes from TNO - need national evaluation?

4. Even surrogate species (e.g. n-butane) can be used to test overall ppbC levels

5. We can add “tracer” species to track other NMVOC if this is useful
The end... thank you!
Do AVOC matter? Yes! Contrast impacts of 50% emission control on NOx and AVOC:

- As AVOC are usually located near NOx sources, good ozone production conditions more likely than with BVOC. The higher the Nox, the more impact the AVOC!

Simpson, JGR, 1995  EMEP model results

NOTE: different legends!
Can we model Ozone? Examples, EMEP model

- Daily max O3 (ppb) vs GAW data
EMEP 3-D CTM performance – global (GAW)

- Daily max O3, M7, 2012
- (From Mills et al 2018, SI)
## Lifetimes of VOC

<table>
<thead>
<tr>
<th></th>
<th>OH</th>
<th>O$_3$</th>
<th>NO$_3$</th>
<th>$h\nu$</th>
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<tbody>
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<td>n-butane</td>
<td>5.7 days</td>
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<td>2.8 yr</td>
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<td>propene</td>
<td>6.6 h</td>
<td>1.6 days</td>
<td>4.9 days</td>
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<tr>
<td>toluene</td>
<td>2.4 days</td>
<td>-</td>
<td>1.9 yr</td>
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<td>HCHO</td>
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<td>-</td>
<td>80 days</td>
<td>4 h</td>
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<td>C5H8</td>
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<td>1.3 days</td>
<td>0.8 h</td>
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<tr>
<td>$\alpha$-pinene</td>
<td>3.4 h</td>
<td>4.6 h</td>
<td>2.0 h</td>
<td></td>
</tr>
<tr>
<td>$\beta$-pinene</td>
<td>2.3 h</td>
<td>1.1 days</td>
<td>4.9 h</td>
<td></td>
</tr>
<tr>
<td>d-limonene</td>
<td>1.1 h</td>
<td>1.9 days</td>
<td>53 min</td>
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<tr>
<td>terpinolene</td>
<td>49 mins</td>
<td>17 min</td>
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<td>$\beta$-caryophyllene</td>
<td>56 min</td>
<td>1.8 min</td>
<td>5.4 min</td>
<td></td>
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</tbody>
</table>

Notes: most values from Seinfeld & Pandis (1998), assuming OH of 1.5e(6) molecules cm$^{-3}$, 30 ppb O$_3$, 1 ppt NO$_3$. $\beta$-caryophyllene estimated for same settings.
Sources of VOC

Global non-methane VOC emissions

- Biogenic: ~1000 TgC yr⁻¹
- Isoprene (C₅H₈): 475 TgC
- Monoterpenes (C₁₀H₁₆): 212 TgC
- Other VOCs: 242 TgC
- Sesquiterpenes (C₁₅H₂₄): 34 TgC

Anthropogenic: ~100 TgC yr⁻¹
- Alkanes
- Alkenes
- Aromatics
- Acids
- Carbonyls
- RETRO inventory

Biomass Burning: ~500 Tg yr⁻¹

Yokelson et al., ACP 8:3509 (2008)

MEGAN 2.1, Year 2000
Guenther et al., GMDD 5:1503, 2012