Ozone, peroxyacetyl nitrate, and biogenic volatile organic compounds observed at peri-urban Taewha Research Forest in Korea

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Motivation: What do BVOCs do for O3 and aerosols in Seoul Metropolis Areas

Taehwa Research Forest • Measurements overview
Site Characterization • BVOCs & Ozone

• Established by NIER (Government institute of the Ministry of Environment) with a support of NCAR folks
AVOC 723,000 ton/yr

BVOC 431,000 ton/yr

BVOCs is 40% of Total VOCs
[NIER, 2005]

Forest is 65% of Korea territory
[KFRI, 2010]

72% of urban areas
Simplified Atmospheric Chemistry

- **Emission**
  - BVOCs 1150 Tg C/yr
  - AVOCs 142 Tg C/yr
  - NOx, CO, SO2
  - CO2 + CO + CH4 ~ 1000 Tg C/yr

- **Transport**
  - O3 ~ 1 cm s⁻¹
  - Vd

- **Deposition**
Taehwa Research Forest
• 170 m asl
• planted forest (300 ha) Korean Pine (Pinus koraiensis Siebold et Zucc.).
• natural forest: deciduous trees Murray (Quercus serrata Murray) Blume (Quercus aliena Blume)

• VOCs : PTR-QMS
• PAN : GC-luminol (2 min)  HONO : Diffusion scrubber-IC  
H₂O₂ : HPLC
• O₃, NOₓ, NOᵧ, CO, SO₂
• 3d anemometer & Met. data
• OC/EC, SMPS, composition
Measurement Overview (2011-2014)

Seasonal & annual variations
Variations of reactive Gases during 2011-2014
Light & Temperature 2013

NPP of Coniferous trees

NPP of Deciduous trees

[Kim et al., 2015]
Chemical regime of Taehwa Site

Gosan: Background site

[Annual Report, NIER 2011~2014]
Chemical regime of Taehwa Site

- Background
- Outflow
- Near-source
- Near-urban

Cold season
Warm season

June

[Month]

[O3/NOx]

[CO/NOx]

[Month]

[Morgan et al., 2013]
Isoprene maximum in the very late afternoon

Emission or loss ($\tau \sim 1$ hr against OH)

• Typical trend?
**BVOCs Profiles (warm seasons)**

**Isoprene**

**Monoterpenes**

**MVK+MACR**
BVOCs Profiles (warm seasons)

- **O₃**, **NO**, **NO₂**
- **isoprene**, **monoterpene**
- **MVK+MACR**
- **MVK+MACR / isoprene**

Wind direction:
- Easterly in the morning
- Calm

Wind speed:
- Null

Pollutants:
- Toluene
- Benzene
- MEK

NO₂/NOₓ
Meteorological Condition (stagnation)

Figure 5. Patterns in the distribution of tropospheric NO$_2$ correspond closely to large population centers. (taken from http://www.temis.nl/airpollution/no2.html)

[MAPS-Seoul While Paper, 2015]
Ozone increase in the morning

Rapid increase under high NOx condition

• What initiates Hox-NOx radical cycle?
Hourly increase in O₃ concentrations in June
HONO photolysis

[Kim et al., 2015]
The 2\textsuperscript{nd} peak of PAN & O\textsubscript{3} ~ 17:00

@ 5 PM with Isoprene Maximum

• PAN from isoprene oxidation?
PAN & O₃ (95 percentile) diurnal variations in May and June, 2012~2013

\[ O_3 = 20 [\text{PAN}] + 4.3 \quad R^2 = 0.81 \]

O₃ concentration patterns:
- \(~14\) h

PAN concentration patterns:
- \(~18\) h
June: Stagnant condition compared to May with similar BVOCs levels
O3 difference between the above and below canopy

Deposition of O3 deposition expected to be the maximum when boundary layer expands

- Reaction of O3 with MT
Diurnal Variations of MT and O$_3$ at 6 heights in June

The graph shows the diurnal variations of monoterpenes (MT) and ozone (O$_3$) at six different heights (39m, 31m, 20m, 15m, 9.5m, 4.1m) in June. The x-axis represents the hour of the day, and the y-axis represents the concentration of monoterpenes (0.0 to 1.0) and ozone (0.0 to 60). The graph illustrates the fluctuations in concentration levels throughout the day.
Vertical profiles of selected species in different time zones in June.
Based on measurement data using the method of Shepson et al. (1992).
Hourly difference of MT and O3 concentrations between 39 m and 9.6 m in June.
• Taehwa Research Forest is relevant site to examine the role of BVOCs being mixed with urban emissions
• O₃ and BVOCs concentrations highest in June at Taehwa Research Forest near Seoul metropolitan areas (SMA), when PAR (photosynthetically active radiation) and NPP (net primary production) were the highest.
• Isoprene and monoterpenes concentrations were evidently higher below canopy (< 20 m) than above canopy (> 20 m) with a maximum in late afternoon (17 H) and before sunset (6 h), respectively.
• In June when O₃ concentrations were the highest under stagnant condition, BVOCs were likely to play a critical role in elevating O₃ levels, particularly in late afternoon.
• BVOCs are intimately linked with oxidants chemistry of the atmosphere.
  Isoprene variation coupled with OH
  MT variation coupled with O₃
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