Observation-based method to evaluate nocturnal ozone destruction due to dry deposition and NO titration in southern Taiwan

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Objectives

- Our objective is to present an observation-based method to determine the overall nocturnal degradations of $O_3$ and $Ox$ and their individual losses caused by dry deposition and chemical losses in a polluted environment.

- The method is based on some assumptions and the surface measurements of $NO_2$ and $O_3$ and vertical $O_3$ profiles at nights.
Nocturnal $O_3$/Ox destruction by dry deposition process

Constant flux assumption

$$F(z) = -V_d C_3$$

$$V_d = \frac{1}{R_a + R_b + R_c} = \frac{1}{R_t}$$

$$V_d = -\frac{F(z)}{C}$$

Notably, $C$ is a function of height $z$ above the ground, $V_d$ is also a function of $z$ and must be related to a reference height at which $C$ is specified.
## Nocturnal O₃/Ox destruction due to chemical losses

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃ loss no Ox loss</td>
<td>( \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 )</td>
</tr>
<tr>
<td>O₃ loss no Ox loss</td>
<td>( \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 )</td>
</tr>
<tr>
<td>Ox losses</td>
<td>( \text{NO}_3 + \text{VOCs} \rightarrow \text{Organic nitrate} )</td>
</tr>
<tr>
<td>No O₃/Ox loss</td>
<td>( \text{NO}_2 + \text{NO}_3 \leftrightarrow \text{N}_2\text{O}_5 )</td>
</tr>
<tr>
<td>Ox loss</td>
<td>( \text{N}_2\text{O}_5 + \text{H}_2\text{O(het)} \rightarrow 2\text{HNO}_3 )</td>
</tr>
<tr>
<td>Total oxidant, Ox</td>
<td>( \text{O}_x = \text{O}_3 + \text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5 )</td>
</tr>
</tbody>
</table>

In a polluted environment \( \text{NO}_3 \) and \( \text{N}_2\text{O}_5 \) are not important
Model development – Estimating total destruction of nocturnal Ox

Basic assumptions:
1. Horizontal transport and subsidence are not important
2. Complete mixing at t1 (sunset); NO\textsubscript{2} above the NBL is invariant.
3. NO\textsubscript{2} distribution is linear in the NBL
Estimating total destruction of nocturnal Ox

\[
DOx_{\text{tot}} = \int_{t_1}^{t_2} \int_0^h \frac{d[O_x]_z}{dt} \, dz \, dt = \int_0^h [O_x]_{z_1} \, dz - \int_0^h [O_x]_{z_2} \, dz
\]

\[
DOx_{\text{tot}} = h[O_x]_{z_1} - h[O_x]_{z_2}
\]

\[
= h([O_3]_{z_1} + [NO_2]_{z_1}) - h([O_3]_{z_2} + [NO_2]_{z_2})
\]

**Diagram:**

- **NO₂, O₃, Ox**
- **Aloft**
- **Ground measurement**
Estimating total destruction of nocturnal Ox

\[ [\text{NO}_2]_{t2} = \frac{[\text{NO}_2]_{h}^t + [\text{NO}_2]_{0}^t}{2} \]

\[ = \frac{[\text{NO}_2]_{h}^t + [\text{NO}_2]_{0}^t}{2} \]

\[ = \frac{[\text{NO}_2]_{h}^t + [\text{NO}_2]_{0}^t}{2} \]

\[ DO_{\text{tot}} = h\left([\text{O}_3]_{0}^t + [\text{NO}_2]_{0}^t \right) \]

\[ - h\left([\text{O}_3]_{Z}^t + 0.5[\text{NO}_2]_{0}^t + 0.5[\text{NO}_2]_{0}^t \right) \]
Estimating total destruction of nocturnal O$_3$

$$DO3_{\text{tot}} = \int_{t_1}^{t_2} \int_{0}^{h} - \frac{d [O_3]^t}{dt} dz dt$$

$$= \int_{0}^{h} [O_3]_{z}^{t_1} dz - \int_{0}^{h} [O_3]_{z}^{t_2} dz = h ([O_3]_{z}^{t_1} - [O_3]_{z}^{t_2})$$

$$DO3_{\text{tot}} = h ([O_3]_{0}^{t_1} - [O_3]_{z}^{t_2})$$
Estimating nocturnal $O_3$ dry deposition velocity

$$DO_{x\text{ tot}} = DO_{3\text{ dry}} + DNO_{2\text{ dry}} + DO_{x\text{ chem}}$$

$$DO_{3\text{ dry}} = \int_{t_1}^{t_2} F_{O_3} dt = \int_{t_1}^{t_2} V_{O_3} \cdot [O_3]^t_0 dt = V_{O_3}[O_3]^t_0 \Delta t$$

$$DNO_{2\text{ dry}} = \int_{t_1}^{t_2} F_{NO_2} dt = \int_{t_1}^{t_2} V_{NO_2} \cdot [NO_2]^t_0 dt = V_{NO_2}[NO_2]^t_0 \Delta t$$
Estimating nocturnal $O_3$ dry deposition velocity

$$D_{NO_2}^{\text{dry}} = V_{NO_2}[NO_2]^t_0 \Delta t = \alpha \cdot V_{O_3}[NO_2]^t_0 \Delta t$$

Both dry deposition models (Wesely, 1989; Zang et al., 2002) and experimental investigation (Pilegaard et al., 1998) indicate that the $V_{NO_2}$ are well correlated with to $V_{O_3}$; their ratio is typically from 0.5 to 0.8.

$$DOx_{\text{chem}} = \beta \cdot D_{NO_2}^{\text{dry}} = \alpha \cdot \beta \cdot V_{O_3}[NO_2]^t_0 \Delta t$$

For simplicity sake, the ratio of $DOx_{\text{chem}}$ to $D_{NO_2}^{\text{dry}}$ is approximately at 0.8-1.2 in a typical polluted NBL (Geyer and Stutz, 2004).
Estimating nocturnal O$_3$ dry deposition velocity

\[
\text{DOx}_{\text{tot}} = \text{DO}3_{\text{dry}} + \text{DNO2}_{\text{dry}} + \text{DOx}_{\text{chem}}
\]

\[
\text{DO}3_{\text{dry}} = \nu_{\text{O}3} [\text{O}_3]_0^\dagger \Delta t
\]

\[
\text{DNO2}_{\text{dry}} = \alpha \cdot \nu_{\text{O}3} [\text{NO}_2]_0^\dagger \Delta t
\]

\[
\text{DOx}_{\text{chem}} = \alpha \cdot \beta \cdot \nu_{\text{O}3} [\text{NO}_2]_0^\dagger \Delta t
\]

\[
\nu_{\text{O}3} = \frac{h([\text{O}_3]_{0}^{t_1} + [\text{NO}_2]_{0}^{t_1}) - h([\text{O}_3]_{z}^{t_2} + 0.5[\text{NO}_2]_{0}^{t_1} + 0.5[\text{NO}_2]_{0}^{t_2})}{\Delta t([\text{O}_3]_{0}^{t_1} + \alpha[\text{NO}_2]_{0}^{t_1} + \alpha\beta[\text{NO}_2]_{0}^{t_1})}
\]
Estimating individual destructions of Nocturnal Ox and O₃

\[
\begin{align*}
\text{DOx}_{\text{tot}} &= \text{DO}3_{\text{dry}} + \text{DNO2}_{\text{dry}} + \text{DOx}_{\text{chem}} \\
\text{DO}3_{\text{tot}} &= \text{DO}3_{\text{dry}} + \text{DO}3_{\text{chem}}
\end{align*}
\]

\[
\begin{align*}
\text{DO}3_{\text{dry}} &= V_{O3}[O_3]_0 \tilde{t} \Delta t \\
\text{DNO2}_{\text{dry}} &= \alpha \cdot V_{O3}[NO_2]_0 \tilde{t} \Delta t \\
\text{DOx}_{\text{chem}} &= \alpha \cdot \beta \cdot V_{O3}[NO_2]_0 \tilde{t} \Delta t \\
\text{DO}3_{\text{chem}} &= \text{DO}3_{\text{tot}} - \text{DO}3_{\text{dry}}
\end{align*}
\]
Measurement of ozone profiles

- The required surface concentrations of $\text{NO}_2$ and $\text{O}_3$ and the vertical $\text{O}_3$ profiles were measured during an ozone field study conducted in southern Taiwan in 2006 (Lin et al., 2010)
- $\text{O}_3$ profiles were measured by tethered ozonesondes
Diurnal variations of surface NO$_2$ and O$_3$
Vertical ozone profiles

(a) Nov. 8 23:01 LST

(b) Nov. 9 02:04 LST
Vertical ozone profiles

Potential temperature (PT) (°K)

Altitude (m)

Ozone concentration (ppb)

(c) Nov. 9 23:02 LST

(d) Nov. 10 02:08 LST

RL

O₃

PT

NBL
Vertical ozone profiles

Potential temperature (PT) (°K)

Altitude (m)

Ozone concentration (ppb)

(e) Nov. 10 22:58 LST

(e) Nov. 11 02:10 LST

RL

PT

O₃

NBL

RT

NBL

Altitude (m)

Ozone concentration (ppb)
Ozone dry deposition velocity

Table 1 Parameters used to calculate $O_3$ dry deposition velocity, $V_{O3}$, in the six selected cases. $H$ represents depth of NBL; $[O_3]_0^t$ and $[NO_2]_0^t$ are surface $O_3$ and $NO_2$ concentrations at $t_1$; $[O_3]_x^2$ is average of $O_3$ concentration within NBL at $t_2$; $[NO_2]_x^2$ is surface $NO_2$ concentration at $t_2$; $[O_3]_0^t$ and $[NO_2]_0^t$ are average surface concentrations of $O_3$ and $NO_2$ from $t_1$ to $t_2$, and $t_1$ is set to 17:00 LST.

<table>
<thead>
<tr>
<th>Case no.</th>
<th>t$_2$, Ozone sounding time</th>
<th>H (m)</th>
<th>$[O_3]_0^t$ (ppb)</th>
<th>$[NO_2]_0^t$ (ppb)</th>
<th>$[O_3]_x^2$ (ppb)</th>
<th>$[NO_2]_x^2$ (ppb)</th>
<th>$[O_3]_0^t$ (ppb)</th>
<th>$[NO_2]_0^t$ (ppb)</th>
<th>$V_{O3}$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nov.8 23:01</td>
<td>100</td>
<td>68.1</td>
<td>35.0</td>
<td>56.1</td>
<td>18.1</td>
<td>42.7</td>
<td>28.3</td>
<td>0.13</td>
</tr>
<tr>
<td>2</td>
<td>Nov.9 02:04</td>
<td>100</td>
<td>64.6</td>
<td>35.0</td>
<td>37.2</td>
<td>15.4</td>
<td>31.9</td>
<td>24.1</td>
<td>0.19</td>
</tr>
<tr>
<td>3</td>
<td>Nov.9 23:02</td>
<td>140</td>
<td>80.9</td>
<td>28.1</td>
<td>60.9</td>
<td>19.1</td>
<td>55.0</td>
<td>25.9</td>
<td>0.19</td>
</tr>
<tr>
<td>4</td>
<td>Nov.10 02:08</td>
<td>200</td>
<td>83.1</td>
<td>28.1</td>
<td>64.4</td>
<td>15.1</td>
<td>40.2</td>
<td>22.7</td>
<td>0.23</td>
</tr>
<tr>
<td>5</td>
<td>Nov.10 22:58</td>
<td>150</td>
<td>85.3</td>
<td>26.7</td>
<td>69.7</td>
<td>18.7</td>
<td>51.5</td>
<td>27.9</td>
<td>0.17</td>
</tr>
<tr>
<td>6</td>
<td>Nov.11 02:10</td>
<td>150</td>
<td>75.0</td>
<td>26.7</td>
<td>46.6</td>
<td>15.4</td>
<td>38.2</td>
<td>23.6</td>
<td>0.24</td>
</tr>
<tr>
<td>Ave.</td>
<td></td>
<td>150</td>
<td>76.2</td>
<td>29.9</td>
<td>55.8</td>
<td>17.0</td>
<td>43.2</td>
<td>25.4</td>
<td>0.19</td>
</tr>
</tbody>
</table>
Sensitivity analysis

Table 2 Effect of the variations of parameters $\alpha$ and $\beta$, defined in Eqs. (20) and (21), respectively, on predicted $O_3$ dry deposition velocities.

<table>
<thead>
<tr>
<th>$\alpha$ \ $\beta$</th>
<th>0.80</th>
<th>0.90</th>
<th>1.00</th>
<th>1.10</th>
<th>1.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.22</td>
<td>0.22</td>
<td>0.21</td>
<td>0.21</td>
<td>0.21</td>
</tr>
<tr>
<td>0.6</td>
<td>0.21</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
<td>0.19</td>
</tr>
<tr>
<td>0.7</td>
<td>0.20</td>
<td>0.19</td>
<td>0.19</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>0.8</td>
<td>0.18</td>
<td>0.18</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
</tr>
</tbody>
</table>
Comparisons with previous studies

Table 3 Comparison of nocturnal ozone dry deposition velocities from various studies.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Location</th>
<th>surface</th>
<th>$V_{O_3}(cm/s)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wesely et al. (1982)</td>
<td>Pennsylvania, U.S.A.</td>
<td>Soyabean</td>
<td>0.29</td>
</tr>
<tr>
<td>Galbally and Roy (1980)</td>
<td>Australia</td>
<td>Grass</td>
<td>0.24</td>
</tr>
<tr>
<td>Van Dop et al. (1977)</td>
<td>Cabauw, Netherlands</td>
<td>Grass</td>
<td>0.13</td>
</tr>
<tr>
<td>Pilegaard et al. (1988)</td>
<td>Scherzheim, Germany</td>
<td>Harvested wheat</td>
<td>0.18</td>
</tr>
<tr>
<td>Gusten et al. (1988)</td>
<td>Gamsgurst, Germany</td>
<td>Valley floor</td>
<td>0.12-0.14</td>
</tr>
<tr>
<td>Wesely and Hicks (2000)</td>
<td>Review work</td>
<td>Agricultural land</td>
<td>0.2</td>
</tr>
<tr>
<td>This work</td>
<td>Southern Taiwan</td>
<td>Agricultural land</td>
<td>0.17-0.22</td>
</tr>
</tbody>
</table>
This work develops an observation-based method that accounts for the overall nocturnal destructions of O$_3$ and Ox and their individual losses caused by dry deposition and chemical losses in a polluted environment.

The method adopts data that are typically obtained in an ozone field study, including surface measurements of O$_3$, and NO$_2$ and O$_3$ profiles.

The usefulness of the model is demonstrated by its application to the data obtained in an ozone field study in southern Taiwan in 2006.
Conclusions

- The model should be carefully used. First, the model should be applied to cases in which horizontal transport and/or subsidence are not important.
- Second, sensitivity analysis of the two parameters, alfa and beta, to predicted $O_3$ dry deposition velocities and the various destruction terms of $O_3$ and Ox should always be performed.
- Third, the model should always be applied to a polluted environment to ensure that the Ox can be reasonably estimated from the sum of $O_3$ and NO$_2$. 
Thank you for your attendance!