Relating high ozone, ultrafine particles and new particle formation episodes using cluster analysis

7th EFCA International Symposium on Ultrafine Particles – Brussels, 15 May 2019

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Ozone ($O_3$)

Table ES.1 Percentage of the urban population in the EU-28 exposed to air pollutant concentrations above certain EU and WHO reference concentrations (minimum and maximum observed between 2014 and 2016)

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>EU reference value (°)</th>
<th>Exposure estimate (%)</th>
<th>WHO AQG (°)</th>
<th>Exposure estimate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{2.5}$</td>
<td>Year (25)</td>
<td>6-8</td>
<td>Year (10)</td>
<td>74-85</td>
</tr>
<tr>
<td>PM$_{10}$</td>
<td>Day (50)</td>
<td>13-19</td>
<td>Year (20)</td>
<td>42-52</td>
</tr>
<tr>
<td>$O_3$</td>
<td>8-hour (120)</td>
<td>7-30</td>
<td>8-hour (100)</td>
<td>95-98</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>Year (40)</td>
<td>7-8</td>
<td>Year (40)</td>
<td>7-8</td>
</tr>
<tr>
<td>BaP</td>
<td>Year (1)</td>
<td>20-24</td>
<td>Year (0.12) RL</td>
<td>85-90</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>Day (125)</td>
<td>&lt; 1</td>
<td>Day (20)</td>
<td>21-38</td>
</tr>
</tbody>
</table>

Source: EEA (2018)

17 700 premature deaths per year in Europe (excl. Ukraine, Belarus, Moldova, Turkey and Russia)

Source: EEA (2018)
* Maximum concentrations in the southern regions (Mediterranean)
* Local formation and depletion (daily cycles)
* Long-range transport (European and hemispheric)
Ultrafine Particles (UFP)

\[ N : \text{Particle number concentration} \]
\[ N_1: \text{Contribution of vehicle exhaust to } N \]
\[ N_2 = N - N_1 : \text{Contribution of new particle formation or primary particles excluding vehicle exhaust (e.g., biomass burning, biogenic emissions, residential emissions)} \]

(Reche et al., 2011)

<table>
<thead>
<tr>
<th>%</th>
<th>BCN</th>
<th>LUG</th>
<th>NK</th>
<th>Bern</th>
<th>MR</th>
<th>HU</th>
<th>SCO</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_1 )</td>
<td>46</td>
<td>39</td>
<td>54</td>
<td>45</td>
<td>78</td>
<td>38</td>
<td>47</td>
</tr>
<tr>
<td>( N_2 )</td>
<td>54</td>
<td>61</td>
<td>46</td>
<td>55</td>
<td>22</td>
<td>62</td>
<td>53</td>
</tr>
<tr>
<td>( N_1 ) (11:00–14:00 h UTC)</td>
<td>31</td>
<td>41</td>
<td>45</td>
<td>49</td>
<td>91</td>
<td>15</td>
<td>36</td>
</tr>
<tr>
<td>( N_2 ) (11:00–14:00 h UTC)</td>
<td>69</td>
<td>59</td>
<td>55</td>
<td>51</td>
<td>9</td>
<td>85</td>
<td>64</td>
</tr>
</tbody>
</table>

Secondary particles dominate UFP number concentration in the global troposphere

(Gordon et al., 2017)
New Particle Formation (NPF)

Atmospheric new particle formation and growth involves the formation of molecular clusters and their subsequent growth from gaseous precursors to larger sizes, up to sizes at which these particles may act as cloud condensation nuclei (CCN).

The interest in NPF lies in its potential ability to increase – even dominate – UFP number concentration and CCN concentration.
Simultaneity of $O_3$, NPF and UFP

Previous studies on particle number size distribution in high insolation urban areas reveal the frequent simultaneous occurrence of NPF and $O_3$ episodes in spring and summer

(e.g., Fernández-Camacho et al., 2010; Minoura and Takekawa, 2005; Park et al., 2008; Pey et al., 2009; Brines et al., 2015; Wonaschütz et al., 2015; Wang et al., 2016)
Area of study

Montseny (MSY; Barcelona, Spain)
41°46′45.63″N, 02°21′28.92″E
720 m a.s.l.
Instrumentation

2014 – 2018 (April – Sept)

**O₃**: Photometry-based analyzer (MCV 48AV)

**N₉.₈₅₆ nm**: SMPS (TROPOS) + CPC (TSI 3772)

**NOx**: Chemiluminescence-based analyzer (Thermo Scientific 42i-TL)

**SO₂**: UV fluorescence analyzer (Teledyne T100)

**BC**: MAAP

**Meteorological data**: Davis Vantage Pro Plus

12 June – 1 August 2017

**AIS** (Air Ion Spectrometer; Airel Ltd.): ion spectra 0.8 – 40 nm

**PSM** (Particle Size Magnifier; Airmodus): number size distribution 1.15 – 2.6 nm

10 – 14 July 2017

**Balloon soundings 0 – 2 km a.g.l.**

Resolution: 45 s, ~25 m

**N₈.₂₄₅ nm**: Hy-SMPS

**N₉.₃ nm**: Hy-CPC

**O₃**: POM (2B Technologies)

**BC**: microAethalometer

**Meteorological data**: T, RH, P, WS, WD
Clustering O₃ daily cycles

We detected clusters that share similar patterns in all or most of the variables considered and we grouped them into 4 clusters.

The number of clusters was chosen manually so that only 1 cluster contained exceedances of the EU hourly target value (180 µg m⁻³ h⁻¹), using the minimum number of clusters.

* Shaded areas show 95% confidence intervals
Average daily cycles

BC and N peak simultaneously → Peak in N not related to NPF
# O₃ and New Particle Formation

<table>
<thead>
<tr>
<th>NPF category</th>
<th>Extreme O₃</th>
<th>High O₃</th>
<th>Mild O₃</th>
<th>Low O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>No data</td>
<td>11.9%</td>
<td>14.2%</td>
<td>16.2%</td>
<td>21.8%</td>
</tr>
<tr>
<td>Non-event</td>
<td>72.9%</td>
<td>66.1%</td>
<td>60.8%</td>
<td>56.4%</td>
</tr>
<tr>
<td>Undefined</td>
<td>3.4%</td>
<td></td>
<td></td>
<td>1.3%</td>
</tr>
<tr>
<td>Bursts</td>
<td>10.2%</td>
<td>10.1%</td>
<td>8.8%</td>
<td>8.5%</td>
</tr>
<tr>
<td>Class II event</td>
<td>1.7%</td>
<td>3.2%</td>
<td>2.8%</td>
<td>3.4%</td>
</tr>
<tr>
<td>Class I event</td>
<td>0.0%</td>
<td>3.7%</td>
<td>8.5%</td>
<td>8.6%</td>
</tr>
</tbody>
</table>

NPF is less frequent the higher the O₃.
Intensive campaign

Highest O₃ episode

Low O₃ episode

High O₃
(Balloon soundings)

Low UFPs
Case A: Highest O$_3$ episode

Highest O$_3$

Heat wave, stagnation

Highest UFP conc

NPF not favoured
Case B: Low O$_3$ episode

[Graph showing Low O$_3$ concentration over time]

[Map showing regional NPF]

[Graph showing Low UFP concentration over time]

Front

Regional NPF
Case C: High O₃ (Balloon soundings)

Stagnation starting

High O₃

High UFP conc

No NPF
Case C: Balloon soundings

10-07-2017

Instability

No NPF
Case C: Balloon soundings

Stagnation

No NPF
Case D: Low UFPs episode

Storms, high Temp.

O_3 conc decreasing

Lowest UFP conc

No NPF
Conclusions

* During vertical recirculation of air masses in the W Mediterranean – the main cause of regional O₃ episodes – high levels of UFP are recorded in parallel with high O₃ concentrations. This causes the increase of the condensation sink to the point that NPF is inhibited.

* In the absence of recirculation and during its initial stages, humid air masses with NPF precursors are transported inland and diluted into dryer and warmer rural air masses, enriched with biogenic VOCs and NH₃. This is an optimal scenario for NPF in air masses with relatively low O₃ background concentrations.

* It might also be the case that, when the atmosphere is too clean, e.g. during the passage of a cold front, the concentrations of NPF precursors is too low, and NPF is not detected. In this case O₃ levels can still be relatively high because of typically high background levels in summer, but UFP concentrations are low.

* The fact that the highest O₃ episodes were recorded together with the highest UFPs may enhance the health impact of the episodes. During the lowest O₃ episodes, the contribution of primary UFPs is very low; UFPs are mainly secondary resulting from NPF, and the total number of particles is the lowest. The health impact of UFPs in these two types of episodes is probably different.
THANK YOU

Acknowledgements: