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

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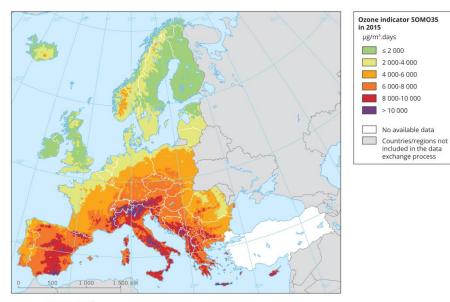


# **Ozone** $(O_3)$

#### 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)

Pollutant	EU reference value (ª)	Exposure estimate (%)	WHO AQG (°)	Exposure estimate (%)
PM <sub>2.5</sub>	Year (25)	6-8	Year (10)	74-85
PM <sub>10</sub>	Day (50)	13-19	Year (20)	
O <sub>3</sub>	8-hour (120)	7-30	8-hour (100)	95-98
NO <sub>2</sub>	Year (40)	7-8	Year (40)	7-8
BaP	Year (1)	20-24	Year (0.12) RL	
SO <sub>2</sub>	Day (125)	< 1	Day (20)	21-38

Source: EEA (2018)



	c	) <sub>3</sub>	
Country	SOM035 (°)	Premature deaths ( <sup>b</sup> )	
Austria	6 170	380	
Belgium	2 790	220	
Bulgaria	4 180	350	
Croatia	6 240	230	
Cyprus	6 390	40	
Czechia	5 560	460	
Denmark	2 200	90	
Estonia	1 780	20	
Finland	1 360	50	
France	4 250	1 800	
Germany	4 300	3 000	
Greece	6 910	610	
Hungary	5 550	530	
Ireland	860	20	
Italy	6 860	3 200	
Latvia	2 560	50	
Lithuania	2 800	90	
Luxembourg	3 460	10	
Malta	5 790	10	
Netherlands	2 680	290	
Poland	4 530	1 300	
Portugal	3 990	300	
Romania	2 950	580	
Slovakia	5 460	210	
Slovenia	6 650	100	
Spain	5 820	1 800	
Consider	2 000	4.40	

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

Total	4 310	17 700
EU-28	4 250	16 400
Switzerland	6 170	300
Serbia	5 280	420
San Marino	7 180	< 5
Norway	1 760	50
Montenegro	6 790	30
Monaco	8 020	< 5
Liechtenstein	5 800	< 5
Kosovo under UNSCR 1244/99	6 130	120
Iceland	260	< 1
Former Yugoslav Republic of Macedonia	6 200	90
Bosnia and Herzegovina	6 050	170

Source: ETC/ACM, 2018b.



- \* Maximum concentrations in the southern regions (Mediterranean)
- \* Local formation and depletion (daily cycles)
- \* Long-range transport (European and hemispheric)

## **Ultrafine Particles (UFP)**

 $\ensuremath{N}$  : Particle number concentration

N1 : Contribution of vehicle exhaust to N

(Reche et al., 2011)

N2 = N - N1: Contribution of new particle formation or primary particles excluding vehicle exhaust (e.g., biomass burning, biogenic emissions, residential emissions)

%	BCN	LUG	NK	Bern	MR	HU	SCO
N1	46	39	54	45	78	38	47
N2	54	61	46	55	22	62	53
N1 (11:00–14:00 h UTC)	31	41	45	49	91	15	36
N2 (11:00–14:00 h UTC)	69	59	55	51	9	85	64

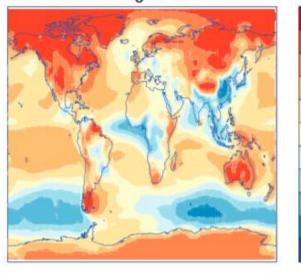
1.0 0.9 0.8 0.7

0.6

0.5 0.4 0.3 0.2 0.1 0.0



PD frac N<sub>3</sub> from NPF

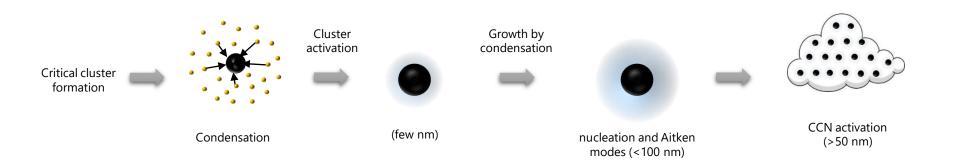


Secondary particles dominate UFP number concentration in the global troposphere

(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).

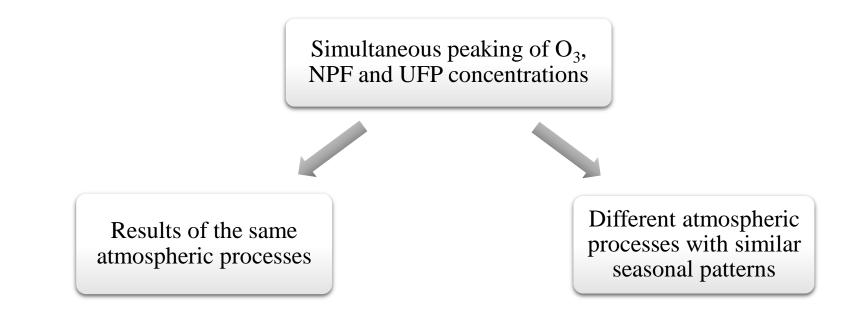


The interest in NPF lies in its potential ability to increase – even dominate – UFP number concentration and CCN concentration.

# Simultaneity of O<sub>3</sub>, NPF and UFP

Previous studies on particle number size distribution in high insolation urban areas reveal the **frequent simultaneous occurrence of NPF and O<sub>3</sub> 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)

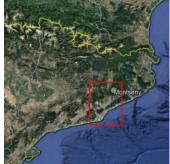
41°46'45.63"N, 02°21'28.92"E

720 m a.s.l.



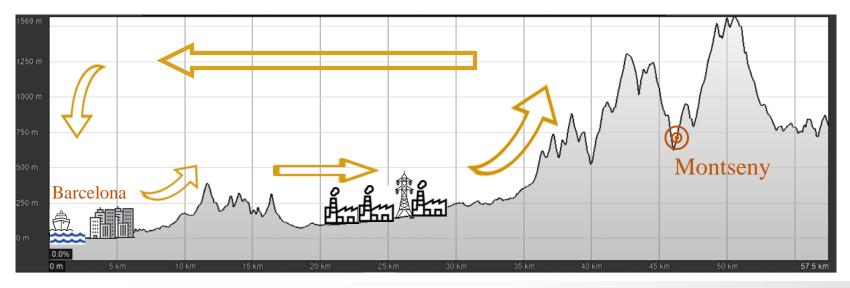








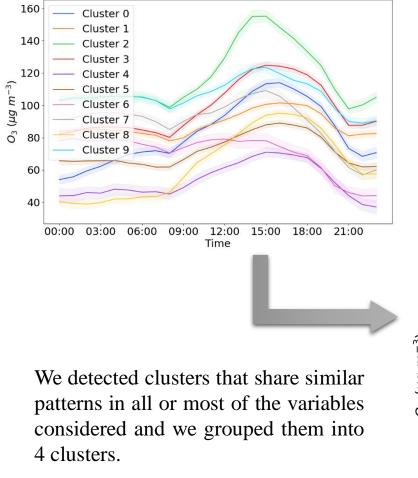




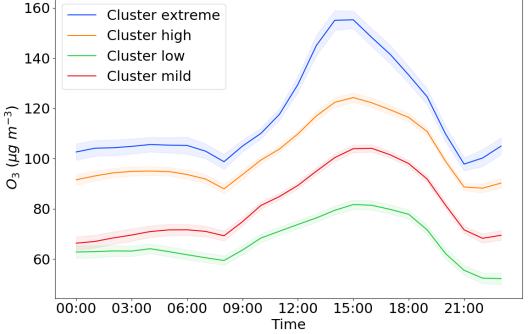
#### Instrumentation

2014 – 2018 (April – Sept)	<ul> <li>O<sub>3</sub>: Photometry-based analyzer (MCV 48AV)</li> <li>N<sub>9-856 nm</sub>: SMPS (TROPOS) + CPC (TSI 3772)</li> <li>NOx: Chemiluminiscence-based analyzer (Thermo Scientific 42i-TL)</li> <li>SO<sub>2</sub>: UV fluorescence analyzer (Teledyne T100)</li> <li>BC: MAAP</li> <li>Meteorological data: Davis Vantage Pro Plus</li> </ul>			
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 $N_{8-245 nm}$ : Hy-SMPS $N_{>3 nm}$ : Hy-CPC $O_3$ : POM (2B Technologies)BC: microAethalometerMeteorological data: T, RH, P, WS, WD			

## Clustering O<sub>3</sub> daily cycles

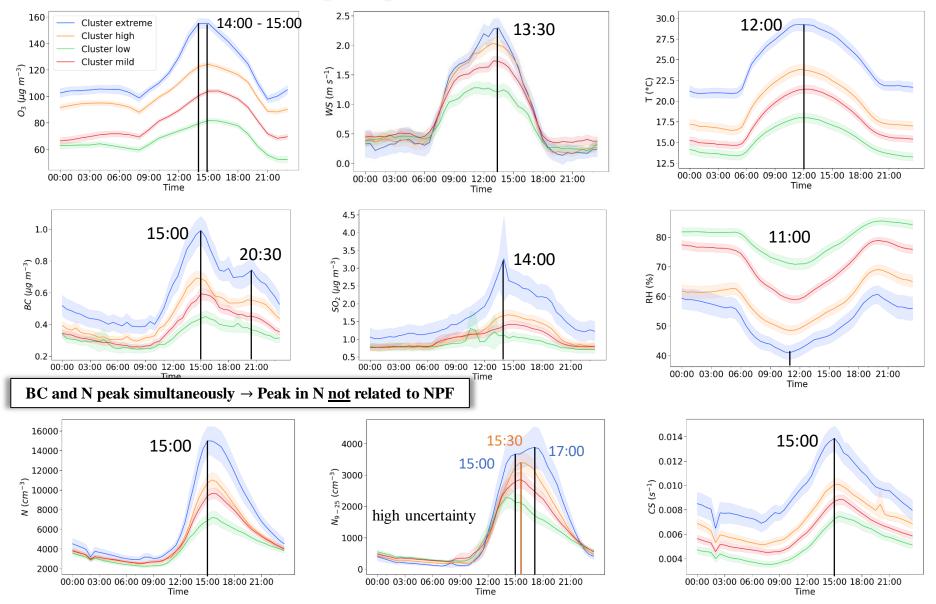


The number of clusters was chosen manually so that only 1 cluster contained exceedances of the EU hourly target value (180  $\mu$ g m<sup>-3</sup> h<sup>-1</sup>), using the minimum number of clusters.



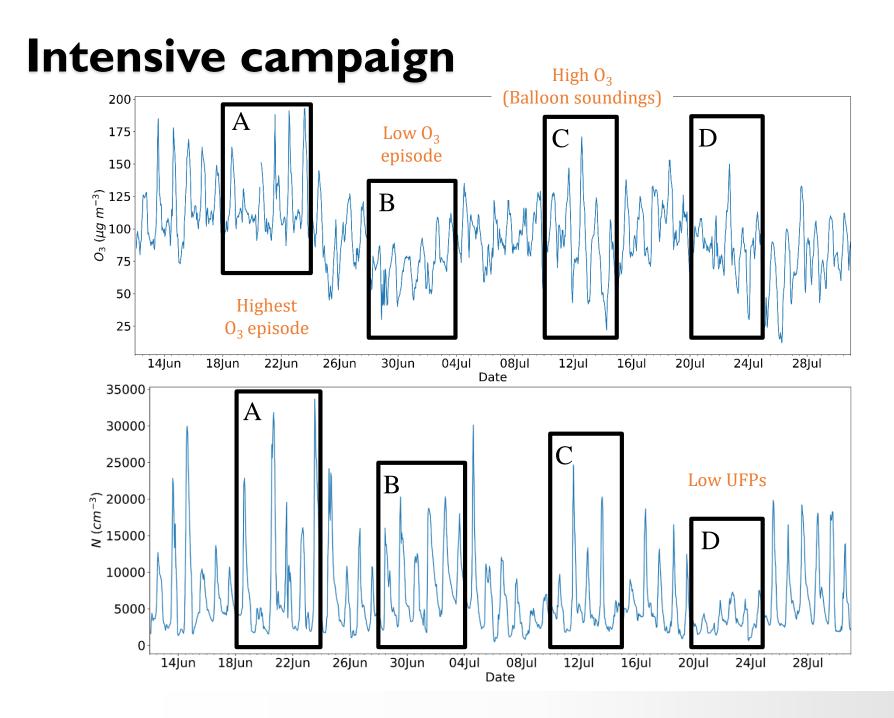
<sup>\*</sup> Shaded areas show 95% confidence intervals

#### Average daily cycles

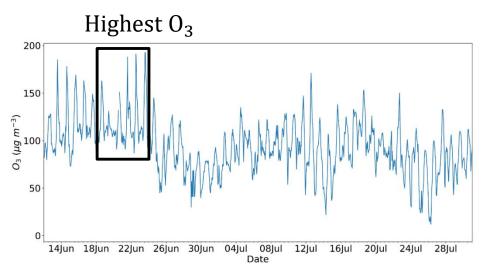


### **O**<sub>3</sub> and New Particle Formation

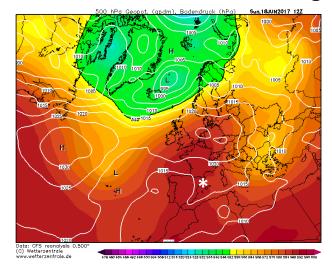
NPF category		Extreme O <sub>3</sub>	High O <sub>3</sub>	Mild O <sub>3</sub>	Low O <sub>3</sub>
No data		11.9%	14.2%	16.2%	21.8%
Non-event	A an and a stand of a	72.9%	66.1%	60.8%	56.4%
Undefined	YD # P	3.49 NP	he 1.3%		
Bursts		10.2%	10.1%	8.8%	8.5%
Class II event		1.7 %	3.2 %	2.8 %	3.4 %
Class I event		0.0 %	3.7 %	8.5 %	8.6 %

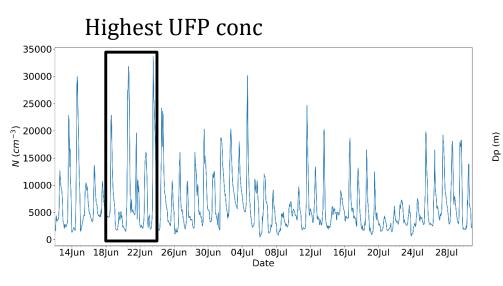


### Case A: Highest O<sub>3</sub> episode

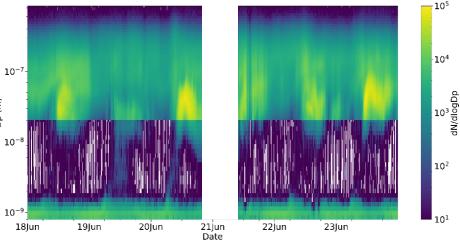


#### Heat wave, stagnation



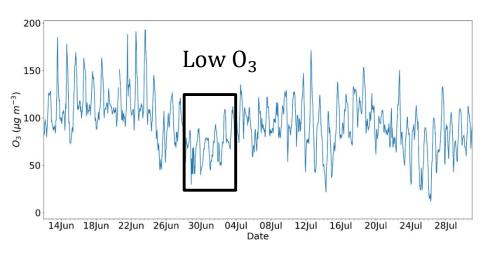


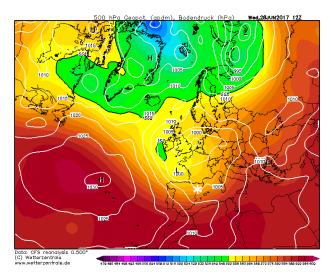
#### NPF not favoured

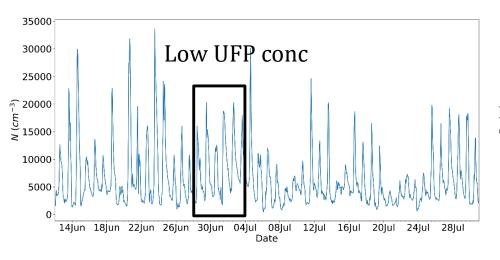


### **Case B: Low O<sub>3</sub> episode**

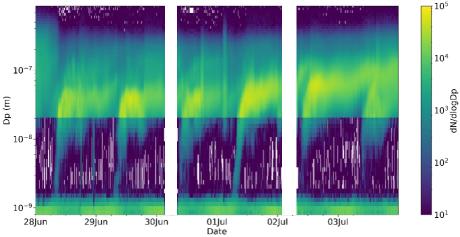
Front





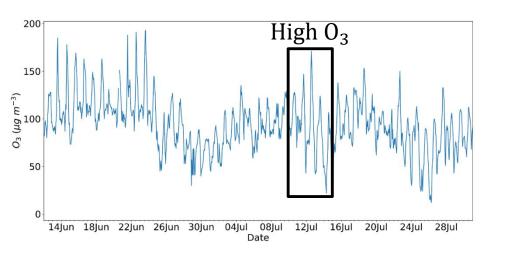


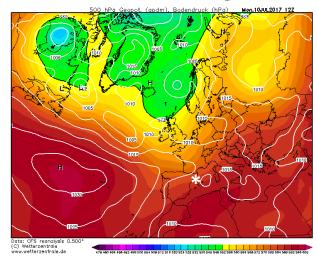
#### **Regional NPF**

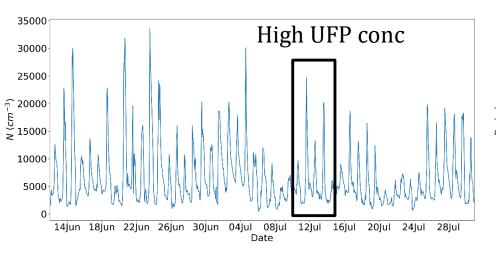


# Case C: High O<sub>3</sub> (Balloon soundings)

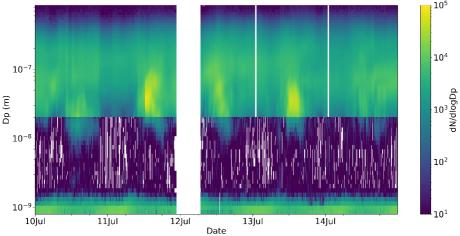
#### **Stagnation starting**



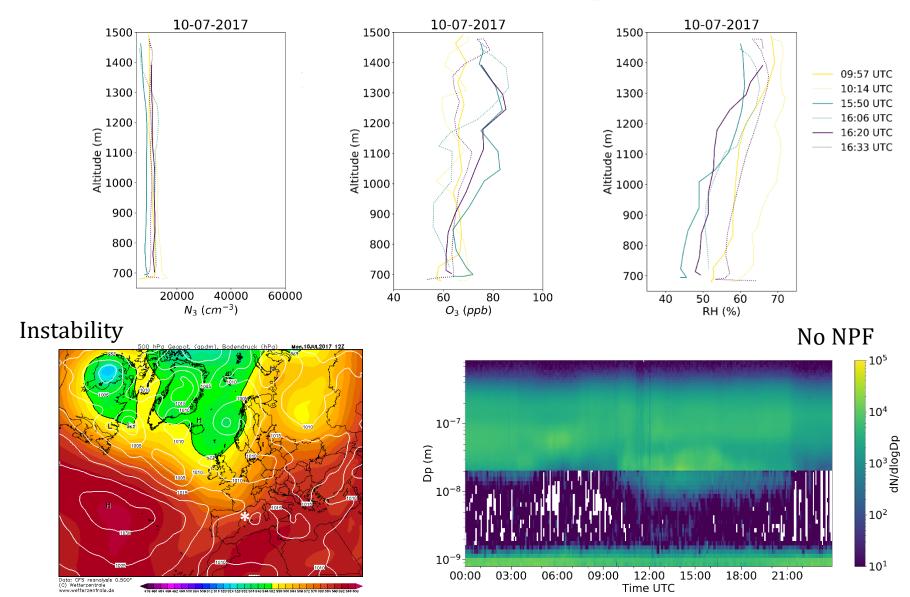




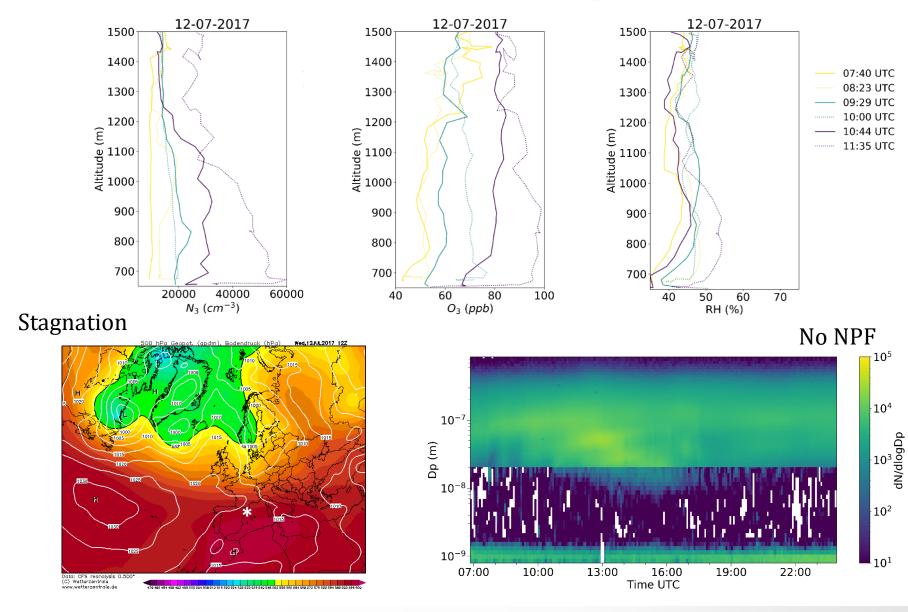
No NPF



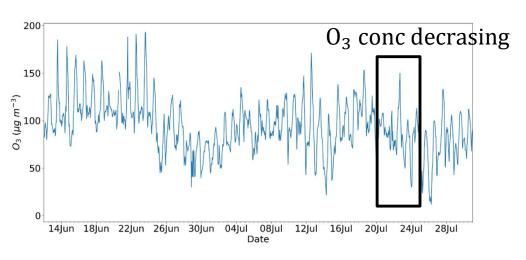
### **Case C: Balloon soundings**



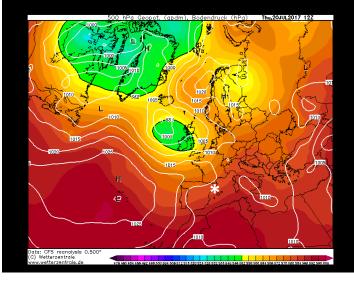
#### **Case C: Balloon soundings**



### **Case D: Low UFPs episode**

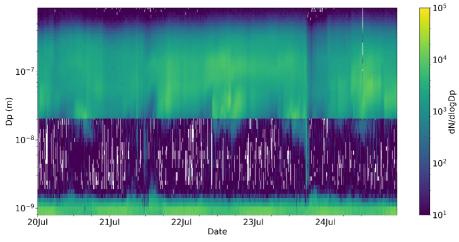


Storms high Temp.



35000 30000 Lowest UFP conc 25000 ( 20000 E-E) S 15000 10000 5000 0 14Jun 18Jun 22Jun 26Jun 30Jun 04Jul 20jul 24jul 28Jul 08Jul 12Jul 16Jul Date

No NPF



#### Conclusions

- \* During vertical recirculation of air masses in the W Mediterranean the main cause of regional O<sub>3</sub> episodes high levels of UFP are recorded in parallel with high O<sub>3</sub> 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 NH<sub>3</sub>. This is an **optimal scenario for NPF** in air masses with relatively **low O<sub>3</sub> 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 O<sub>3</sub> levels can still be relatively high because of typically high background levels in summer, but UFP concentrations are low.
- \* The fact that the highest O<sub>3</sub> episodes were recorded together with the highest UFPs may enhance the health impact of the episodes. During the lowest O<sub>3</sub> 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.

