2n Congrés

Qualitat de l'aire

14-15 d'octubre 2021

#CongresAire
#AireNet

SESIÓN: Emisiones 3
Contaminación y calidad del aire en entornos rurales

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Contaminantes críticos en entornos rurales: O_3 y PM

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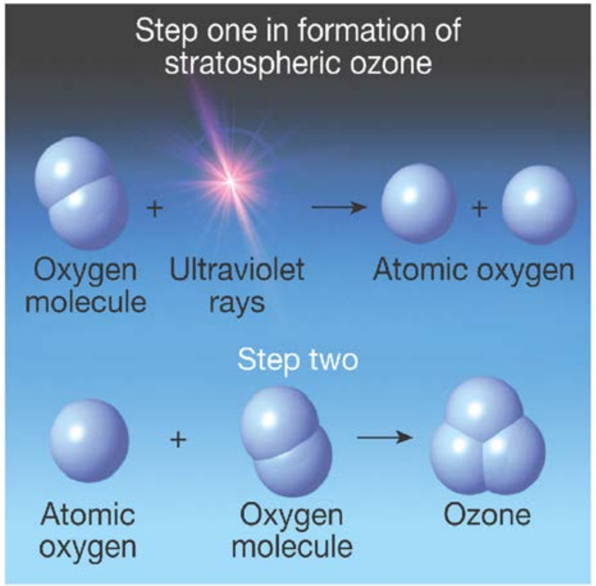
OUTLINE

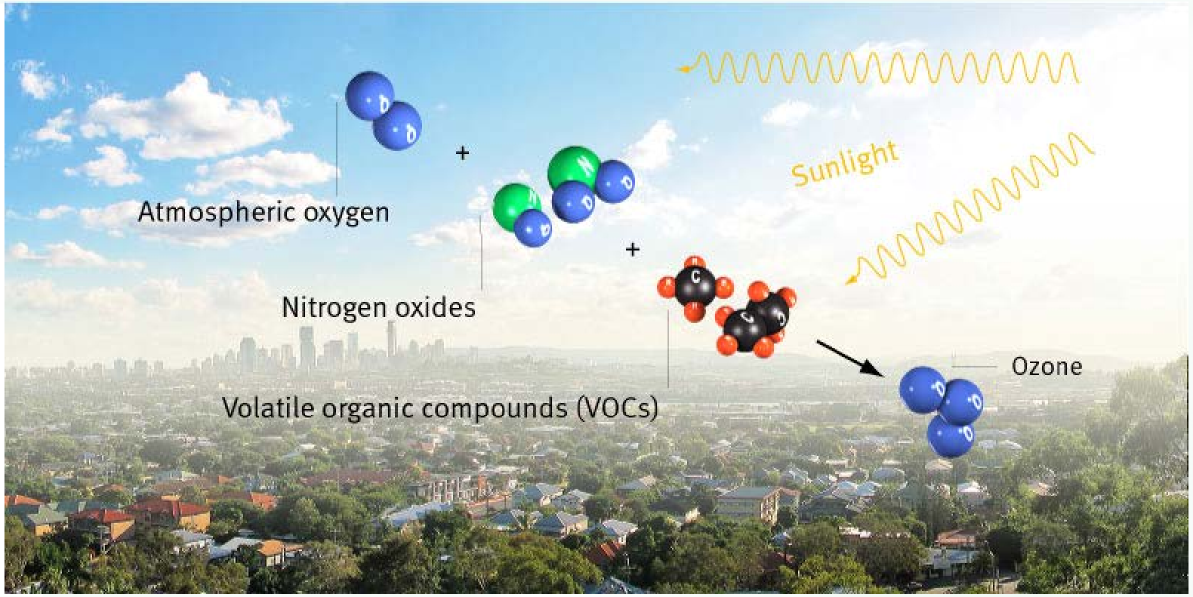
- O_3 in rural areas
- PM-BaP
- PM-NH_3

O_3 in the stratosphere



http://www.geo.hunter.cuny.edu

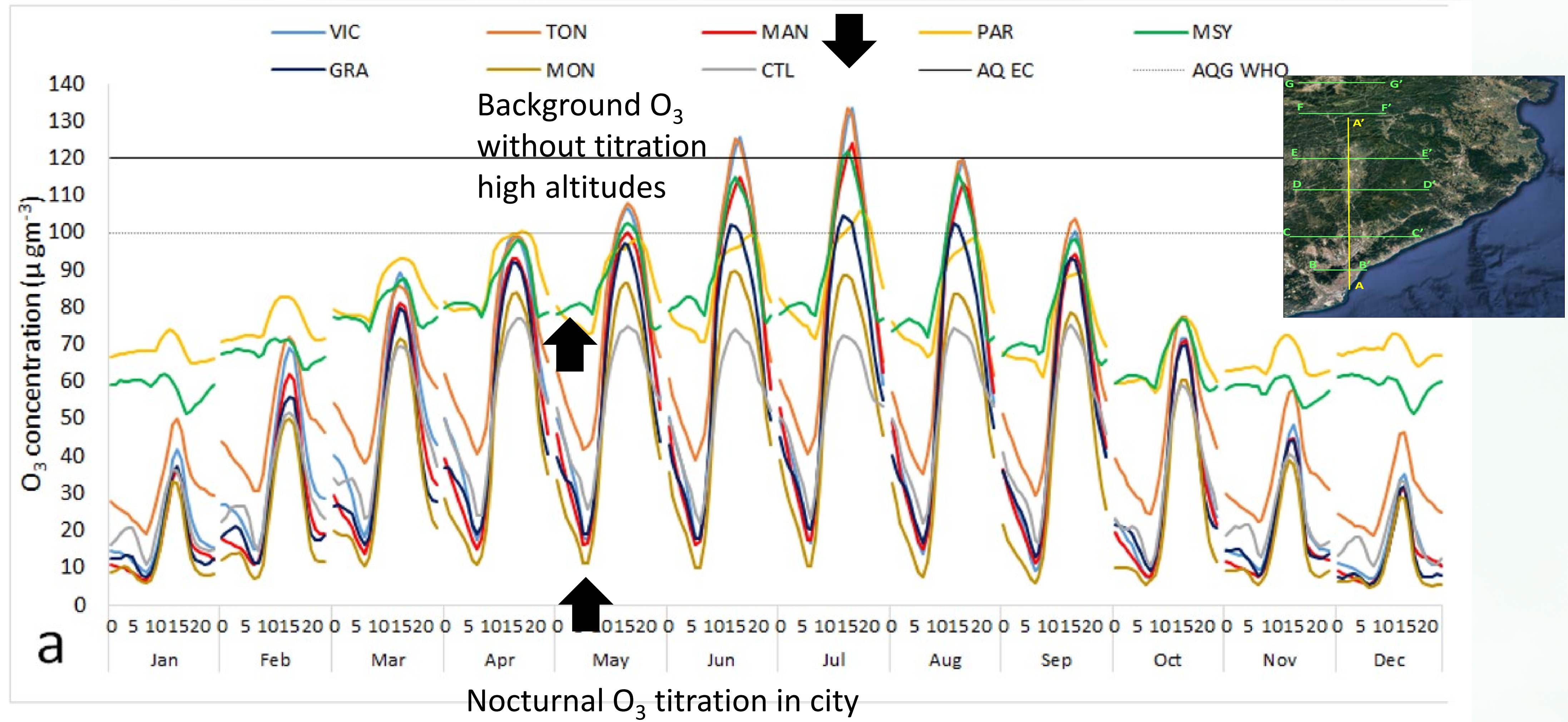
O_3 in the troposphere



https://www.qld.gov.au/environment/pollution/monitoring/air-pollution/ozone/
Queensland State Government, Australia

O_3 IN RURAL AREAS

O_3 formation during transport to rural areas



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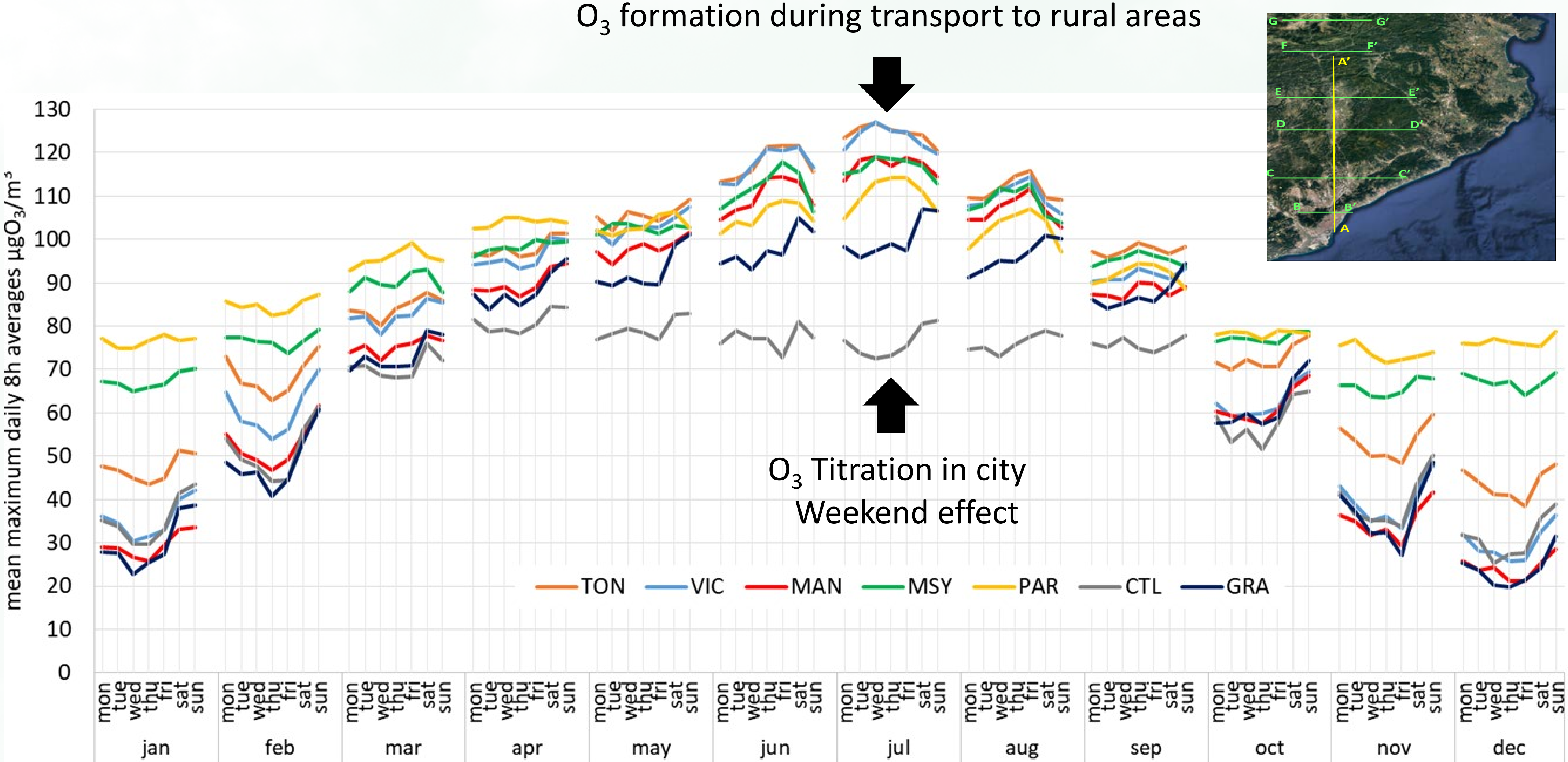
O_3 IN RURAL AREAS

Inverse to weekend effect
O_3 formation during transport to rural areas



O_3 Titration in city
Weekend effect

O_3 IN RURAL AREAS

THE HIGHEST O_3 AQ MONITORING SITE IN EACH AUTONOMOUS REGION 2025-2019

AUTONOMOUS REGION	O_3 Apr.-Sep. ($\mu g\ m^{-3}$)	AOT40 veg. ($\mu g\ m^{-3}$ hour)	SOMO35 ($\mu g\ m^{-3}$ day)	Exc. TV-HP (days year^{-1})	p93.2 ($\mu g\ m^{-3}$)	4th higehst 8hDM ($\mu g\ m^{-3}$)	Exc. Inf. T. (hours year^{-1})
Andalucía	99	31633	10776	59	131	145	2.4
Aragón	92	22902	8336	26	121	134	0.4
Asturias	75	6367	5091	5	106	124	1.0
Islas Baleares	91	25110	8648	27	122	133	0.2
Comunidad Valenciana	102	33420	10875	64	131	144	1.2
Islas Canarias	75	6397	5096	7	105	116	0.2
Cantabria	67	5096	4392	3	103	119	0.2
Cataluña	101	29800	10434	54	135	161	17.6
Castilla La Mancha	99	24332	9664	47	127	153	10.4
Castilla y León	88	21964	8537	32	123	138	0.4
Extremadura	84	19465	7182	40	125	147	3.6
Galicia	73	7626	5191	14	111	136	4.2
Madrid	95	27597	10607	72	141	163	9.8
Murcia	84	21911	8236	25	119	134	0.3
Navarra	82	18902	6677	24	120	136	0
País Vasco	81	16151	8034	30	122	140	0.8
La Rioja	73	15256	5365	15	114	127	0

PM FROM BIOMASS BURNING

Agricultural biomass burning
- Burning biomass wastes
- Burning fields to fertilize or to prevent infections

Peak PM concentrations in short periods
& elevated winter-autumn PM
(mostly BB PM)



Preventive bush fires

Peak PM concentrations in short periods
(mostly BB PM)

Forest fires


Peak PM concentrations in short periods
(mostly BB PM)

Biomass burning as an energy source
- Domestic-residential
- Commercial-industrial

(PM mixed)

Elevated winter-autumn PM

PM FROM BIOMASS BURNING

- In EU-28, 37% BC, 54% PM2.5, 73% BaP arise from solid fuel domestic , institutional & commercial heating
- Primary PM of this source: soot and ash
- Most PM falls in PM2.5
- Soot is mainly EC (=BC) and OC, including PAHs
- PAH in PM is mostly semi-volatile: Formed instantaneously from flue gas or exhaust
- The condensable fraction is difficult to measure and it can be largely reduced by an improvement of the combustion conditions
- Denier van der Gon et al. (2015, ACP): Revised residential wood combustion emissions were by a factor of 2-3 higher

PM FROM BIOMASS BURNING

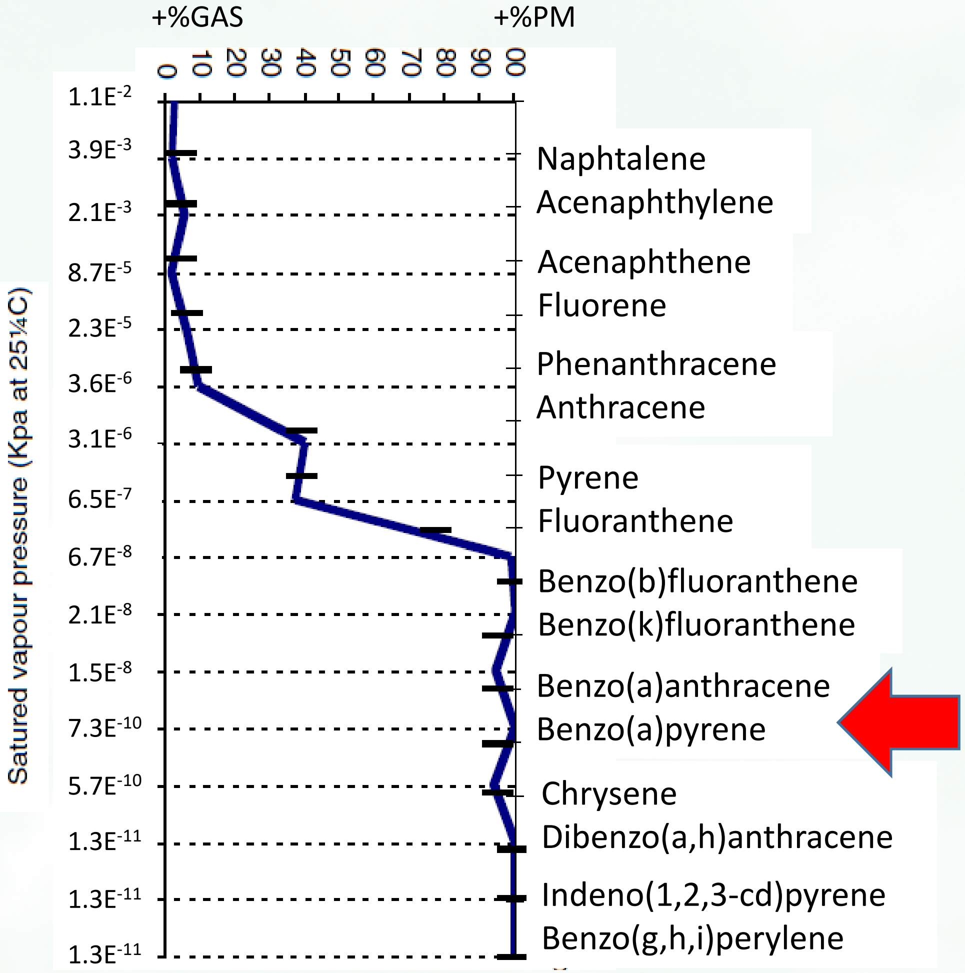
BaP carcinogenic activity

BaP % contribution to total PAHs carcinogenic activity (37-70%, most 44-63%) in ambient air reported in the literature. Modified from Delgado-Saborit et al. (2011)

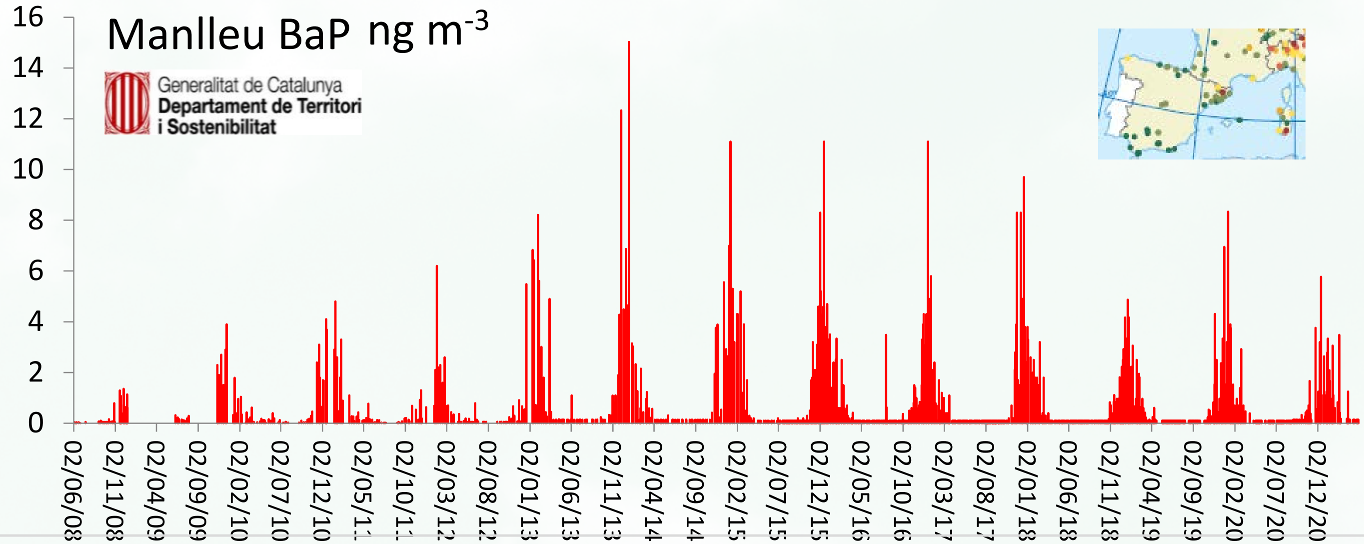
Site	Period	BaP % contribution to total PAHs carcinogenic activity	Reference
UK (Traffic Roadside, Parks)	2006–2007	54-56	Delgado-Saborit et al. (2011)
London (UK)	1991–1995	44	EPAQS (1999)
Middlesborough (UK)	1993–1995	37	EPAQS (1999)
Florence (Italy)	1992–2001	40	Lodovici et al. (2003)
Zurich (Switzerland)	1992	57	Petry et al. (1996)
Bangkok (Thailand)	2002–2003	63	Norramit et al. (2005)
Nagasaki (Japan)	1997–1998	55	Wada et al. (2000)
Copenhagen (Denmark)	1992	70	Nielsen et al. (1996)
Rome (Italy)	1996–1997	49	Menichini et al. (1999)
Bangkok (Thailand)	1996–1997	60	Norramit et al. (2005)
Turkey	Winter 2007	70	Akyuz and Cabuk (2008)
Turkey	Summer 2007	54	Akyuz and Cabuk (2008)

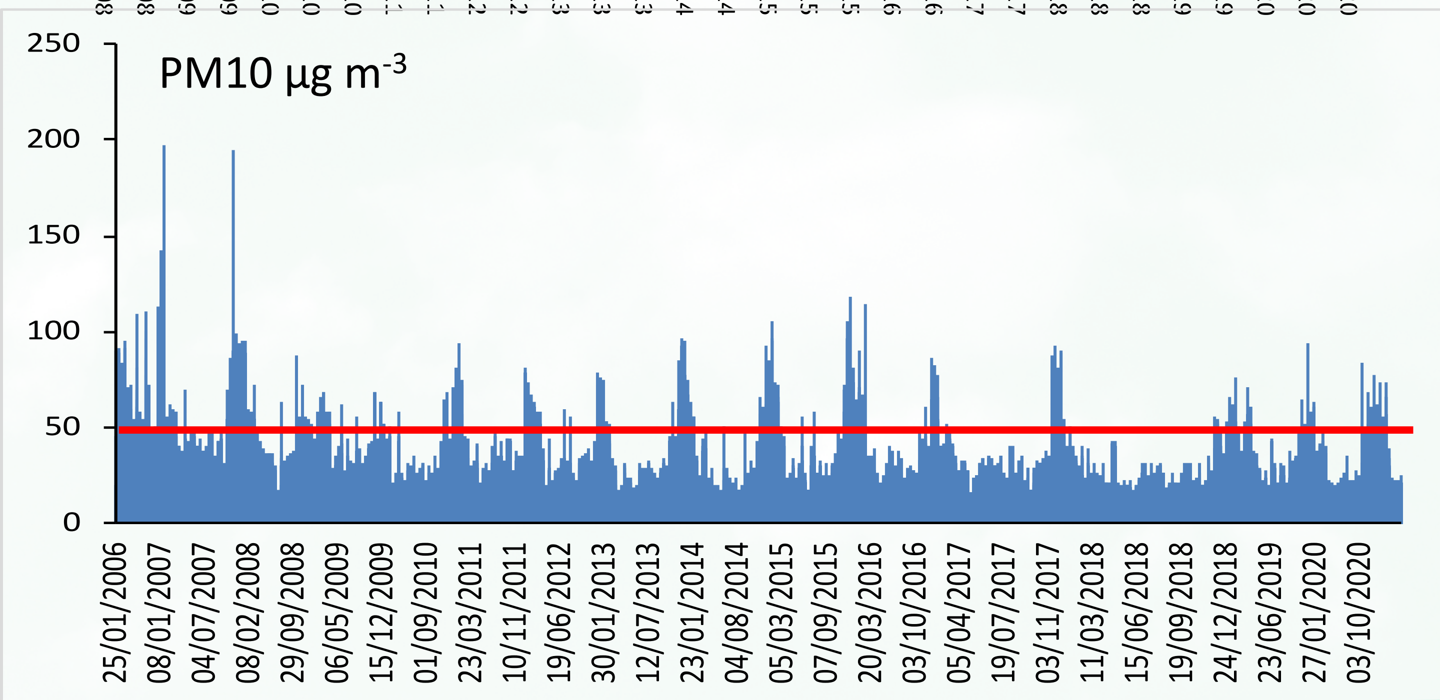
Gas to particle partitioning

De Pieri S., et al., 2014. Env. Mon. Assess.



PM FROM BIOMASS BURNING





PM FROM BIOMASS BURNING

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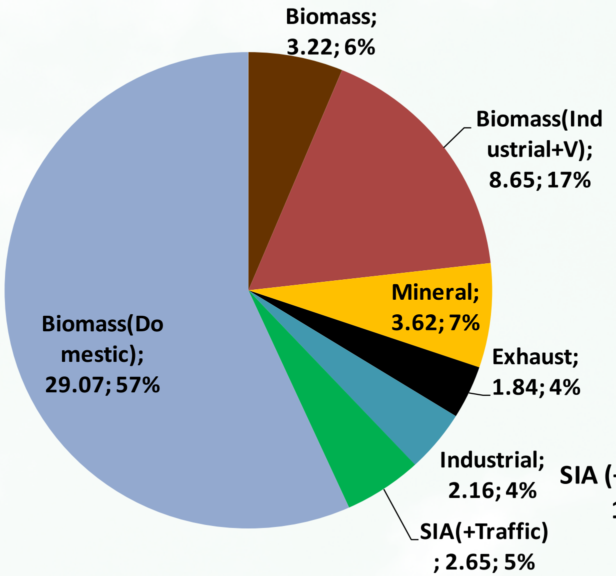
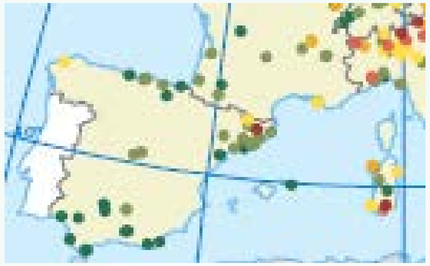
Source mean contributions

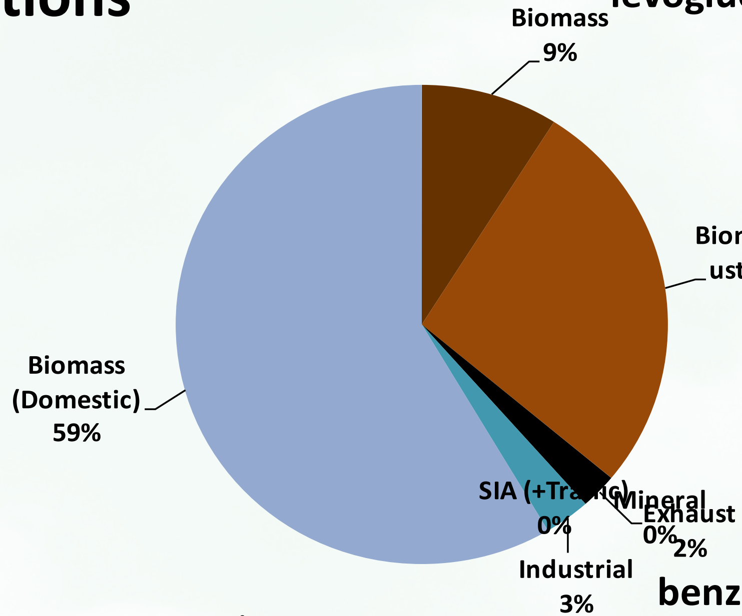
Source mean contributions to $PM_{2.5}$ (only $PM_{2.5}$ > 35 µg/m³)



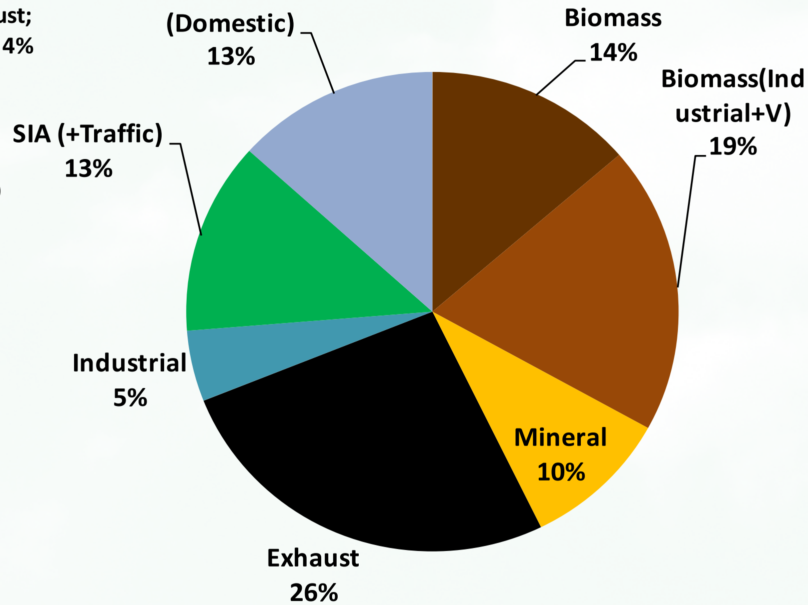
Manlleu (Spain)



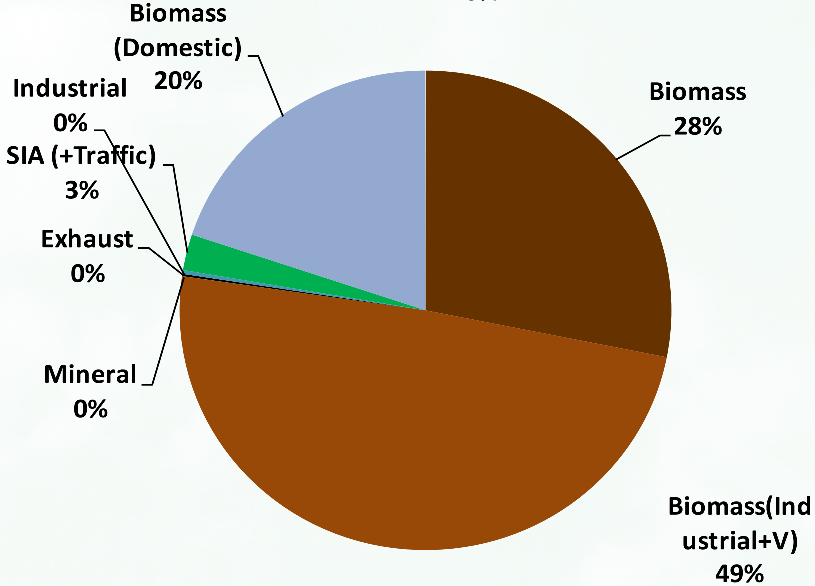
levoglucosan



EC



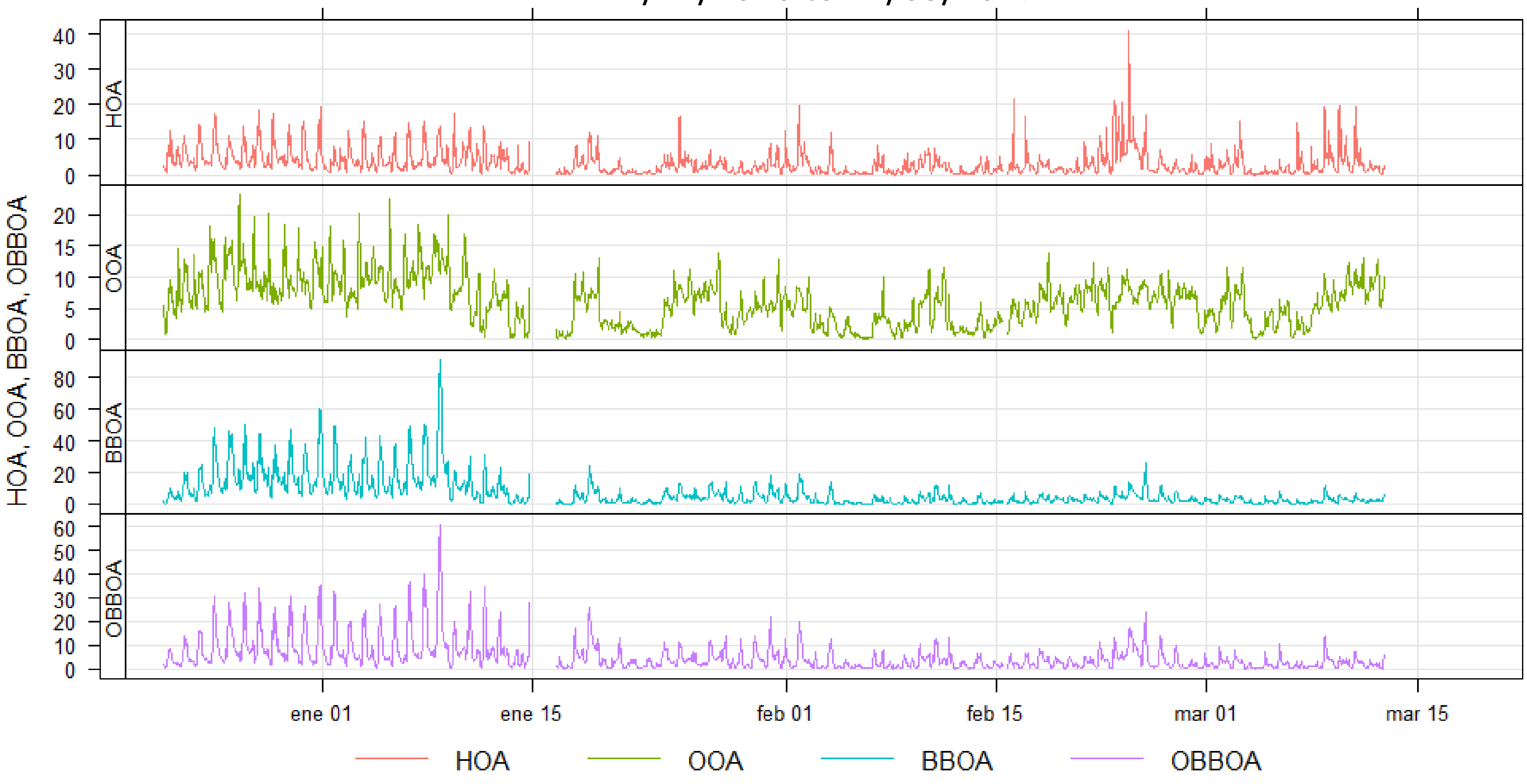
benzo[a]pyrene



PM FROM BIOMASS BURNING

Manlleu, measurements with ACSM

21/12/2016 to 12/03/2017



PM FROM BIOMASS BURNING

Health outcomes of biomass burning

•Only studies on short term effects were found

•A few studies meet requirements for meta-analysis

•**All-causes and cardiovascular** seems to increase with statistical significance during **forest fire** days (Yes/No) approach, and also associated with PM10 increases, as **respiratory morbidity is**

•Most studies on **morbidity** suggest that PM from wildland fires mainly cause short-term respiratory impacts, but results are contradictory for cardiovascular impacts

•It is uncertain if the increased mortality in fires is exclusively due to smoke and not to the combination of PM sources and/or meteorology (temperature?)

•In summer wildfires the combination of high T and PM10 has to be taken into account

•For source apportionment studies in urban areas **domestic BB** are studied together with other sources. Studies only available for US, and **no significant association of BB emissions and mortality was found**, while it was for vehicles derived PM

•**Studies are needed for Europe for health outcomes of domestic heating**

Karanasiou A. et al., 2021

PM AND NH_3

Dry oxidation (homogeneous)

Generation of oxidant radicals

O_3+hν (solar) → O*   O*+H_2O → 2OH

Oxidation

SO_2+OH+m → $HOSO_2$+m $HOSO_2$+O_2 → HO_2+SO_3

SO_3+H_2O → H_2SO_4

NO+O_3 → NO_2+O_2 NO_2+OH+m → HNO_3+m

Maximal velocities (summer, max hν):
6%SO_2h^{-1}, 18%NO_2h^{-1}
34%SO_2day^{-1}, 98%NO_2day^{-1}

Wet oxidation (dissolution of gases, mainly SO_2)
(condensation nuclei, fog, precipitation,
'wet aerosol films')

Oxidants: H_2O_2 (pH<5), O_3 (pH>5),
O_2 (catalysers, Cl, m)

Oxidation

HCOH+hν *(solar)* → H+HCO*   HCO*+O_2 → HO_2+ CO*
(formaldehyde)

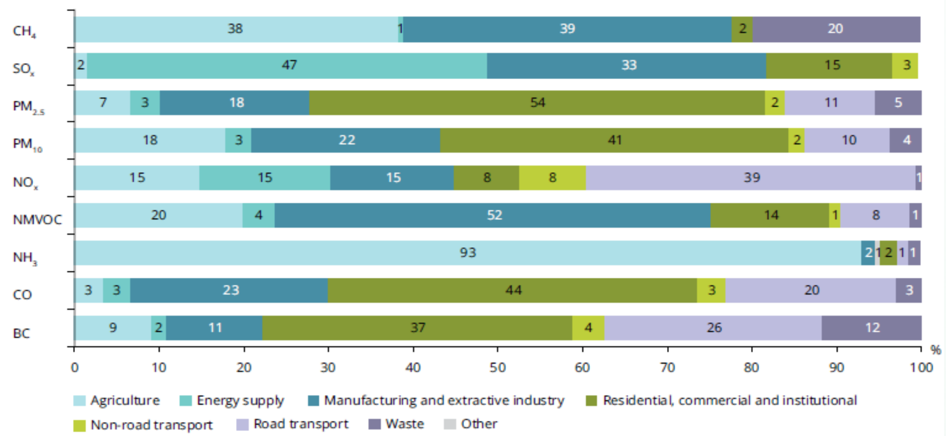
HO_2+ HO_2 → H_2O_2+O_2

$2SO_2$ + $2H_2O$ → SO_3^{2-}+HSO_3^-+$3H^+$

HSO_3^-+ H_2O_2 → HSO_4^-+H_2O

Maximal velocities (summer, max hν):
270%SO_2h^{-1} (H_2O_2) 410%SO_2h^{-1} (O_3)

Figure 3.4 Contribution to EU-28 emissions from the main source sectors in 2018 of CH_4, SO_x, NO_x, primary PM_{10}, primary $PM_{2.5}$, NH_3, NMVOCs, CO and BC



EEA, 2020

SECONDARY INORGANIC PM

H_2SO_4(aq) → $2H^+$+SO_4^{2-}

SO_4^{2-}(aq) + $2NH_4^+$(aq) → $(NH_4)_2SO_4$(s)

HNO_3(g) + NH_3(g) → NH_4NO_3(s)

T>20-25°C (summer) NH_4NO_3(g) + → HNO_3(g) + NH_3(g)

H_2SO_4(aq) + 2NaCl(s) → Na_2SO_4(s) + 2HCl(g)

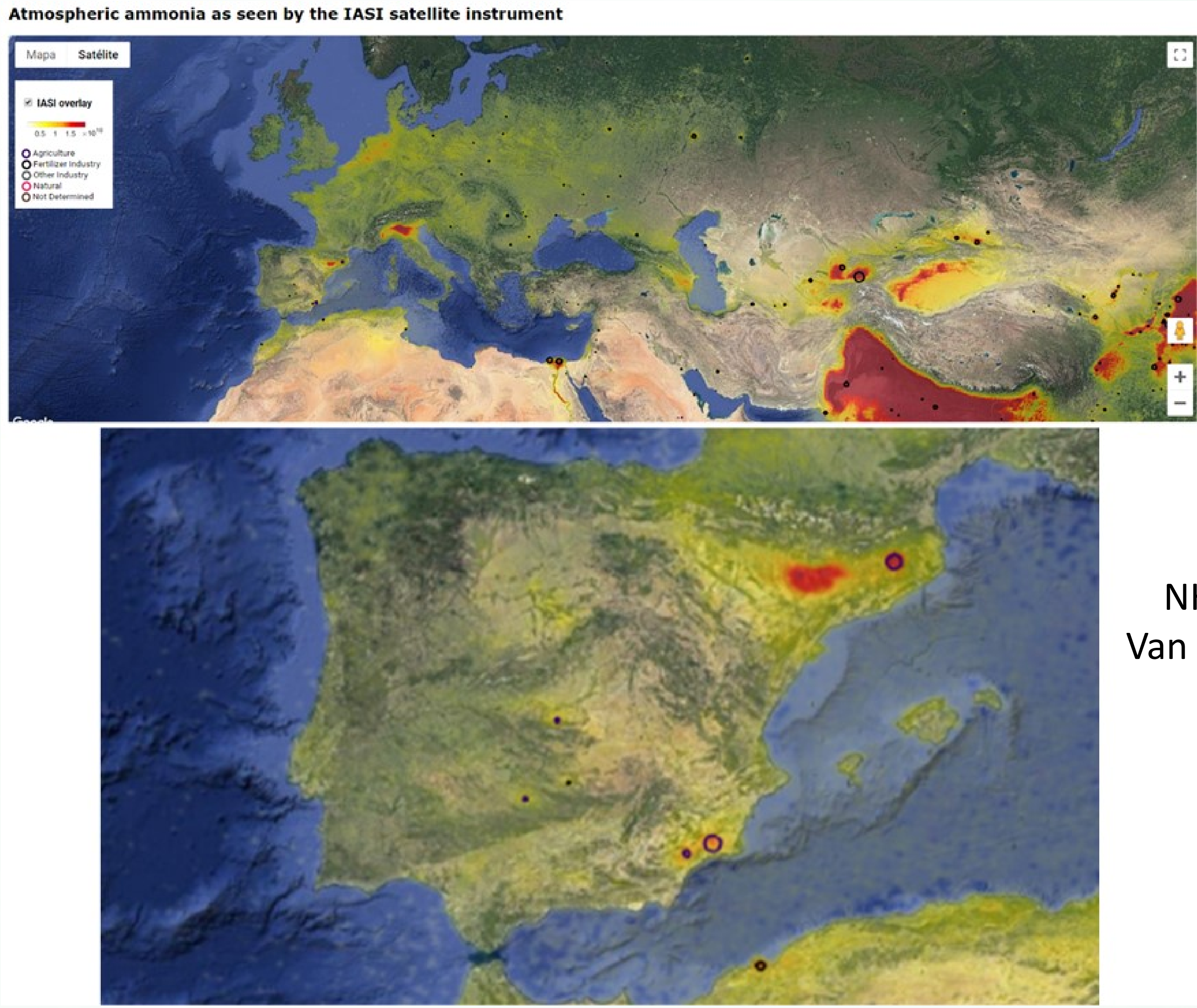
H_2SO_4(aq) + $CaCO_3$(s) → $CaSO_4$(s) + H_2CO_3(g)

NH_4NO_3(s) + NaCl(s) → $NaNO_3$(s) + NH_4Cl(g)

HNO_3(g) + NaCl(s) → $NaNO_3$(s) + HCl(g)

$2HNO_3$(g) + $CaCO_3$(s) → $Ca(NO_3)_2$(s) + H_2CO_3(g)

PM AND NH_3



NH_3 concentrations
Van Damme et al., 2018, Nature

MAJOR LESSONS LEARNT

- Rural areas are receptors of O_3 from urban/industrial ones and keep higher nocturnal O_3 because the lower titration
- COVID19 lockdown effects showed that O_3 can be reduced in receptor areas by reducing emissions in the rural/industrial sources, although the effect is not proportional

- We should abate emissions from domestic-comercial burning, but also agricultural burning, industrial combustion and forest fires might contribute to BaP
- The condensable fraction is very important and it is not always measured
- Low emission boilers and certified fuels should be mandatory in rural areas
- Burning bans in agricultural areas should be implemented

- To abate PM2.5 to meet the forthcoming AQ limit values it is crucial abating NH_3, SO_2, NO_X and VOCs: NH_3 from rural areas is very relevant

MOLTES GRÀCIES !

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