Origin of urban ammonia as deduced from air quality measurements in Spain



Addressing unexpected impacts of structural changes on European air quality. Warsaw 11-12/02/2019

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OUTLINE

1. Why it matters?

3. Challenges

4. Urban ammonia measurements: Our experience

5. Final remarks and recommendations

Why it matters?

Fundamental properties

-Only gaseous base in the atmosphere

-Major role in biogeochemical cycles of N

-Produces particles & cloud condensation nuclei

- ·Haze/Visibility
- ·Radiative balance; direct & indirect cooling
- ·Stability wrt vertical mixing
- ·Precipitation and hydrological cycle

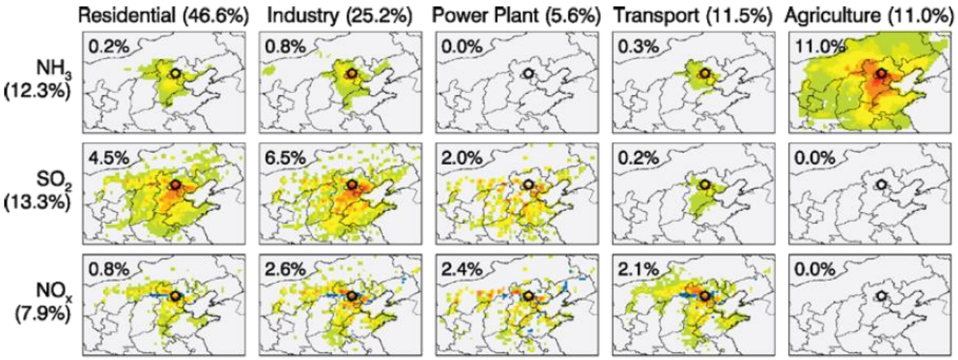
- Potential source of NO and N_2O

WHY IT MATTERS?

Formation of aerosols

Ammonia plays a major role in the chemistry of the atmosphere. Atmospheric ammonia (NH_3) reacts with nitric and sulfuric acids to form nitrate and sulfate aerosols, a key component of fine particulate matter ($PM_{2.5}$)

Source attribution of Jan. PM2.5 event
(Zhang et al., ERL, 2015)



Nucleation – the transformation from the gaseous to condensed phase; the generation of new particles.

H_2SO_4/H_2O system does not nucleate easily.

$NH_3/H_2SO_4/H_2O$ system does (e.g., Coffman & Hegg, 1995).

$NH_3(g) + H_2SO_4(l) \rightarrow NH_4HSO_4(s, l)$ (ammonium bisulfate)
$NH_3(g) + NH_4HSO_4(l) \rightarrow (NH_4)_2SO_4(s, l)$ (ammonium sulfate)

WHY IT MATTERS?

Formation of aerosols

$NH_3(g) + HNO_3(g) \leftrightarrow NH_4NO_3(s)$

$\Delta G°rxn = -22.17$ kcal $mole^{-1}$

$$Keq = \frac{[NH_4NO_3]}{[NH_3][HNO_3]} = \exp(-\Delta G/RT)$$

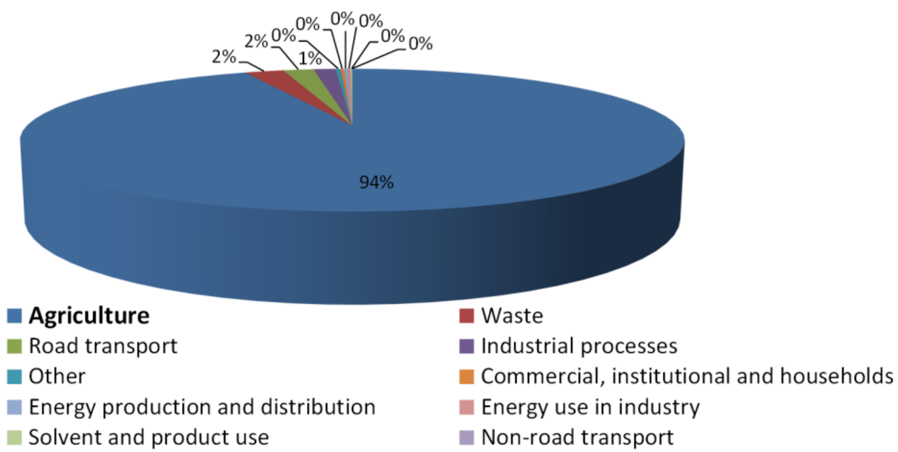
Keq = 1.4x1016 at 25°C; = 1.2x1019 at 0°C

Solid ammonium nitrate (NH_4NO_3) is unstable except at high [NH_3] or at low temperatures. More NH_4NO_3 in winter.

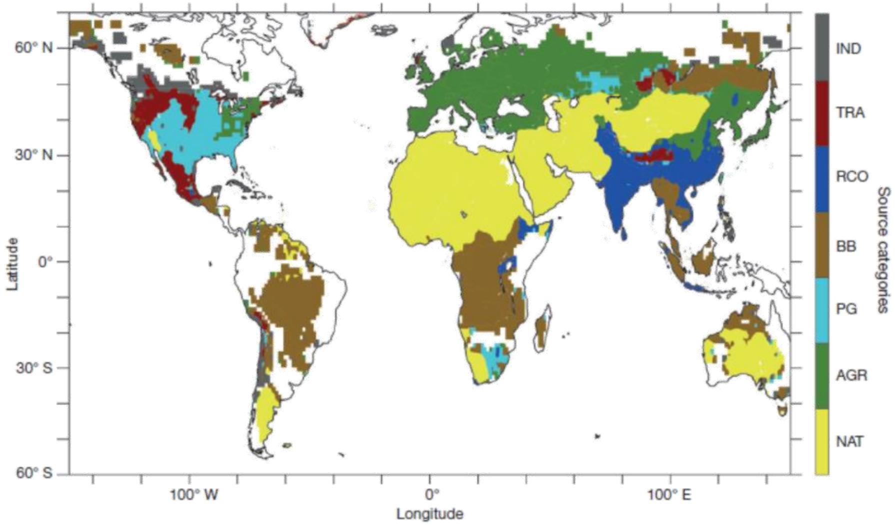
WHY IT MATTERS?

Formation of aerosols

Ammoniated aerosols degrade urban air quality, impact the global radiation budget, and *affect human health*.



EEA, 2015

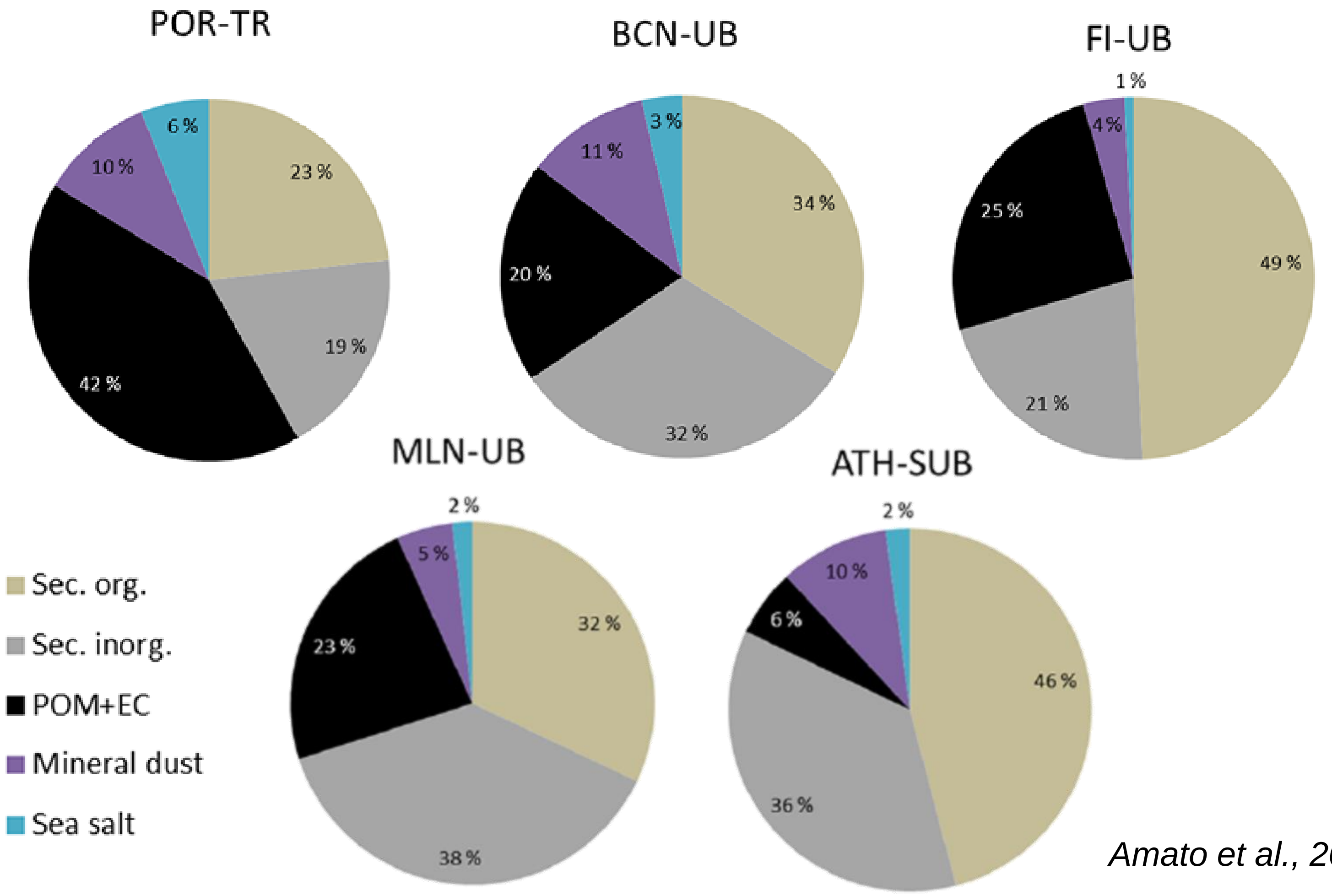


$PM_{2.5}$ Source categories responsible for the largest impact on mortality linked to outdoor air pollution in 2010

Lelieveld et al., 2015

Agriculture has a remarkably large impact on $PM_{2.5}$, and is the leading source category in Europe, Russia,Turkey,Korea, Japan and the Eastern USA. Since NH_3 abundance is often limiting in secondary $PM_{2.5}$ formation, reduction of its emissions can make an important contribution to air quality control.

Why it matters?



Amato et al., 2016

The secondary inorganic aerosol fraction contributes to the total observed particle mass at similar or higher levels than the primary fraction. Control secondary particles precursors is essential to develop effective action plans against $PM_{2.5}$

Why it matters?

NH_3 sources in urban environments (↑NO_X, ↑SO_2)

-Traffic emissions (TWC, SCR) → It is essential to jointly evaluate plans for reducing different air pollutants, in order to avoid unwanted effects

-Sewage system

-Domestic and commercial waste containers

-Outdoor markets

-Direct human emissions

-Domestic animals emissions

-Biomass burning

-Industry (fertilizers, gasifiers, petrochemicals, …)

And…infuenced by temperature changes (mainly seasonally), wind speed or direction, boundary layer deep and mixing, regional NH_3 emissions, dry deposition, and gas-to-particle partitioning

WHY IT MATTERS?

NH_3 sources in urban environments (↑NO_2, ↑SO_2)

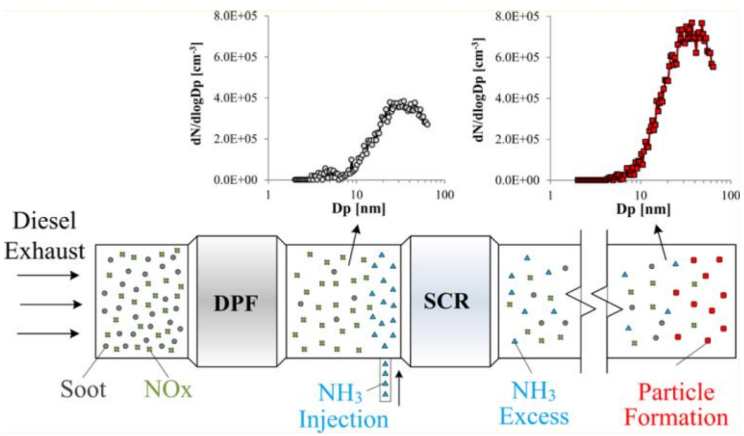
Traffic emissions-"Ammonia slip"

The introduction of gasoline-powered vehicles equipped with three-way catalytic converters and diesel-powered vehicles adopting selective catalytic reduction (SCR) system resulted in increased NH_3 emissions from traffic

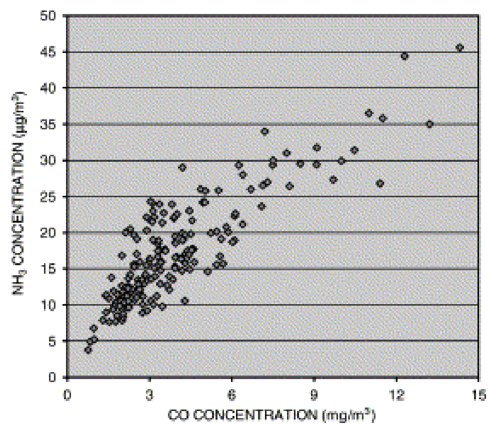
Higher on-road NH_3 emission factors were obtained for the gasoline vehicle than for the diesel

High NH_3 emissions were observed during cold start

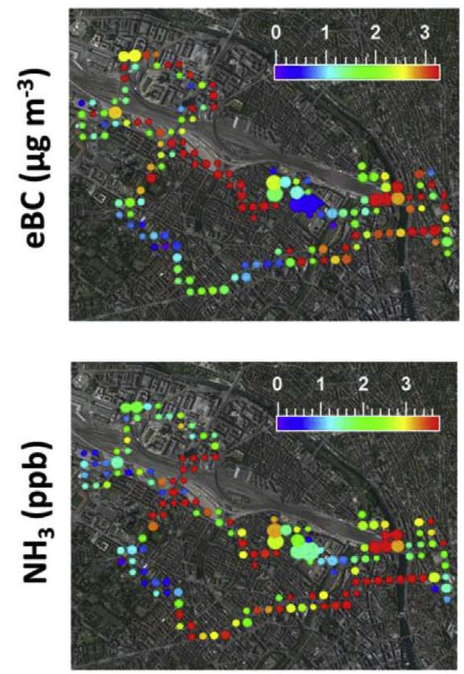
Suarez-Bertoa and Astorga, 2016



NH_3 injection resulted to an increase of the particle number concentration inside the tailpipe (*Amanatidis et al. 2014*)



Perrino et al,. 2002



Similar spatial distribution of BC and NH_3 in north-European cities (*Elser et al., 2018)*

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CHALLENGES

- According to the European commission NH_3 emissions have exhibited the smallest reductions since 2000 (9 % in the EU-28 and 5 % in the EEA-33) in the last years. Greater efforts are needed to reduce emissions by 2030
- Few countries have established systematic networks to measure NH_3 at urban and rural backgrounds
- No standard measurement method have been established (passive samplers, chemiluminescence, …)
- NH_3 emissions inventories uncertain: urban sources

  -Relationship between emissions and mode of vehicle operation
- Contribute to errors in assessing $PM_{2.5}$

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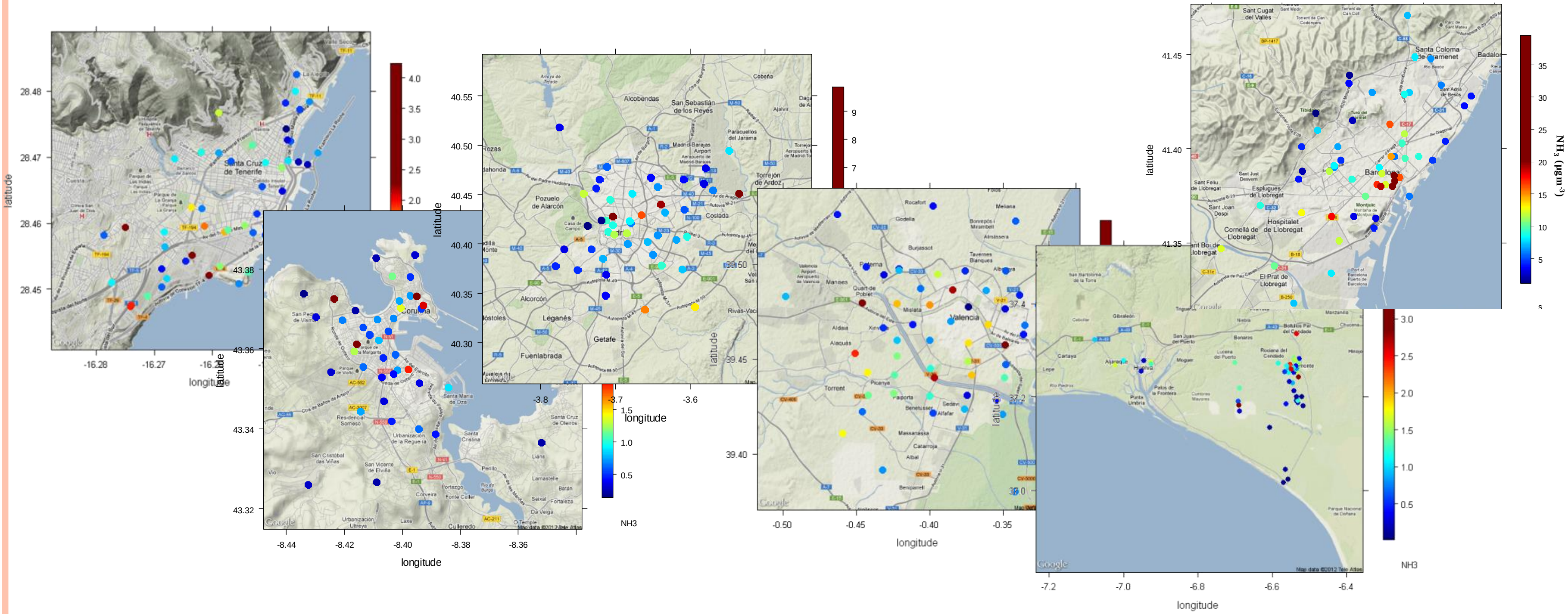
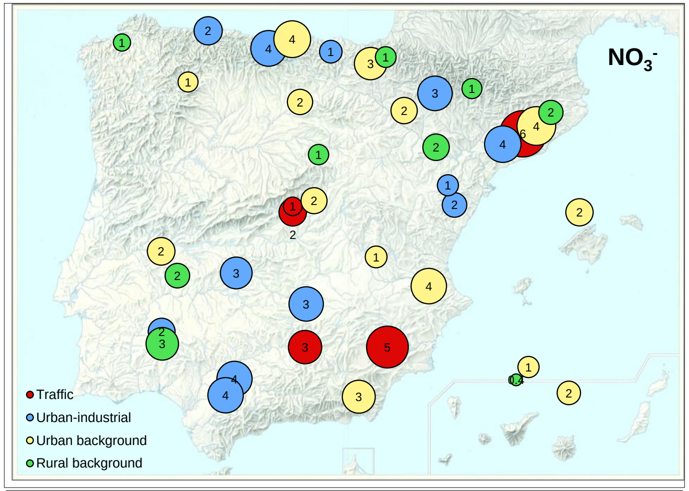
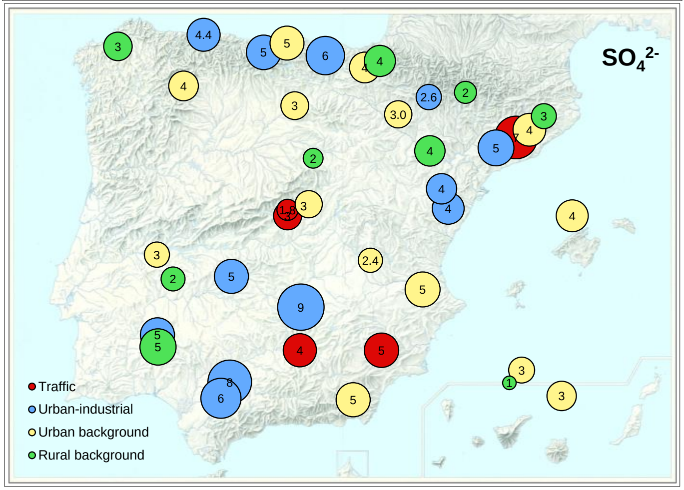
Urban ammonia measurements
Our experience

	NH$_3$ (μgm^{-3}) in fall-winter				NH$_3$ (μgm^{-3}) in spring-summer			
CITY	Mean	Max	Min	St. Dev	Mean	Max	Min	St. Dev
Barcelona	4.5	12.5	0.8	2.1	9.2	39.6	1.1	6.6
Madrid	2.3	6.7	0.6	1.3	2.6	9.9	0.4	1.8
A Coruña	1.5	15.1	0.2	2.2	0.8	4.1	0.1	0.8
Valencia	1.5	4.7	0.2	0.9	0.5	2.3	0.1	0.4
Sta. Cruz de Tenerife	2.8	20	0.1	3.8	1.2	3.5	0.0	0.9
Huelva	1.6	5.9	0.2	1.0	1.6	34.9	0.1	4.7



URBAN AMMONIA MEASUREMENTS

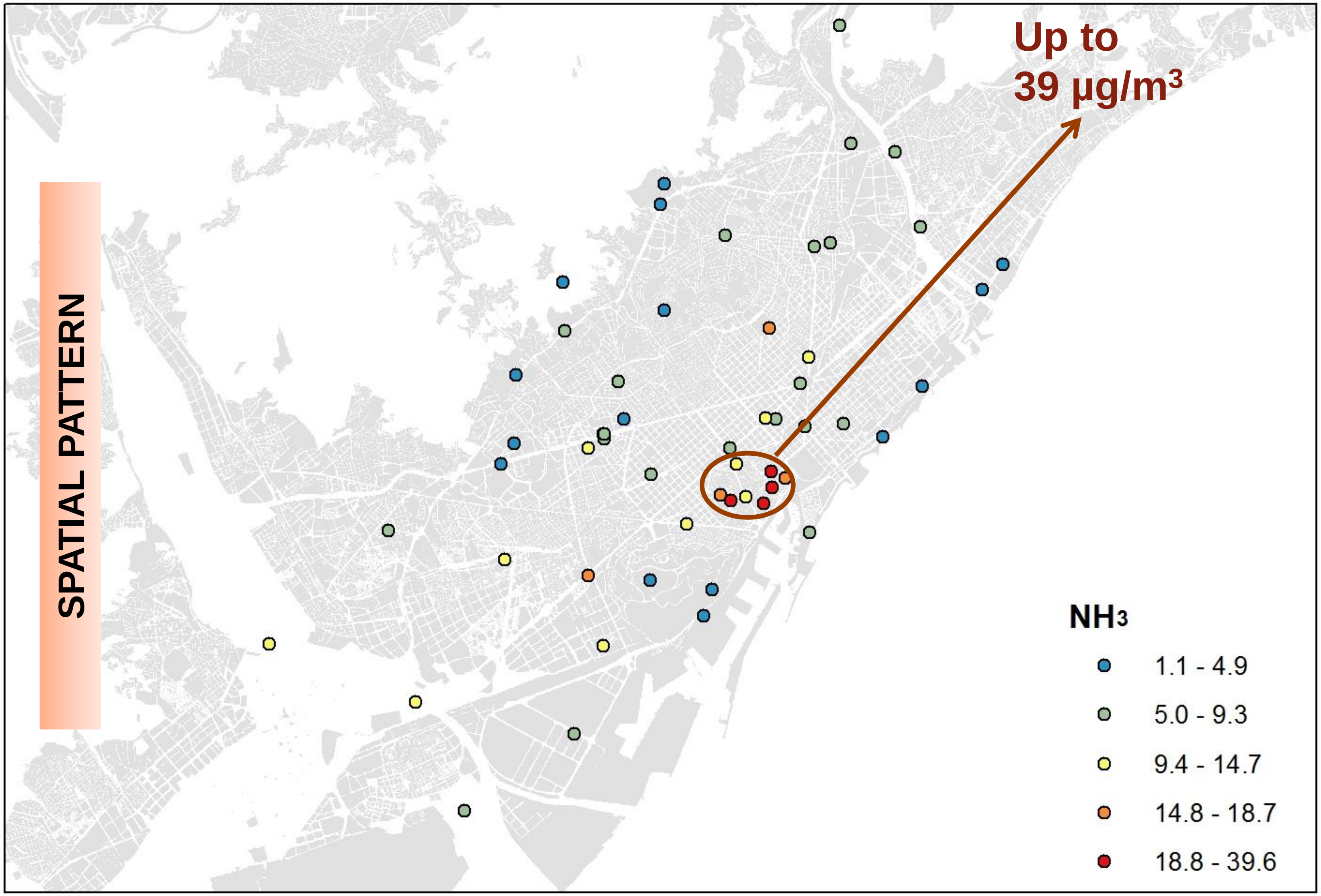




Could NH_3 concentrations explain differences in SIA?

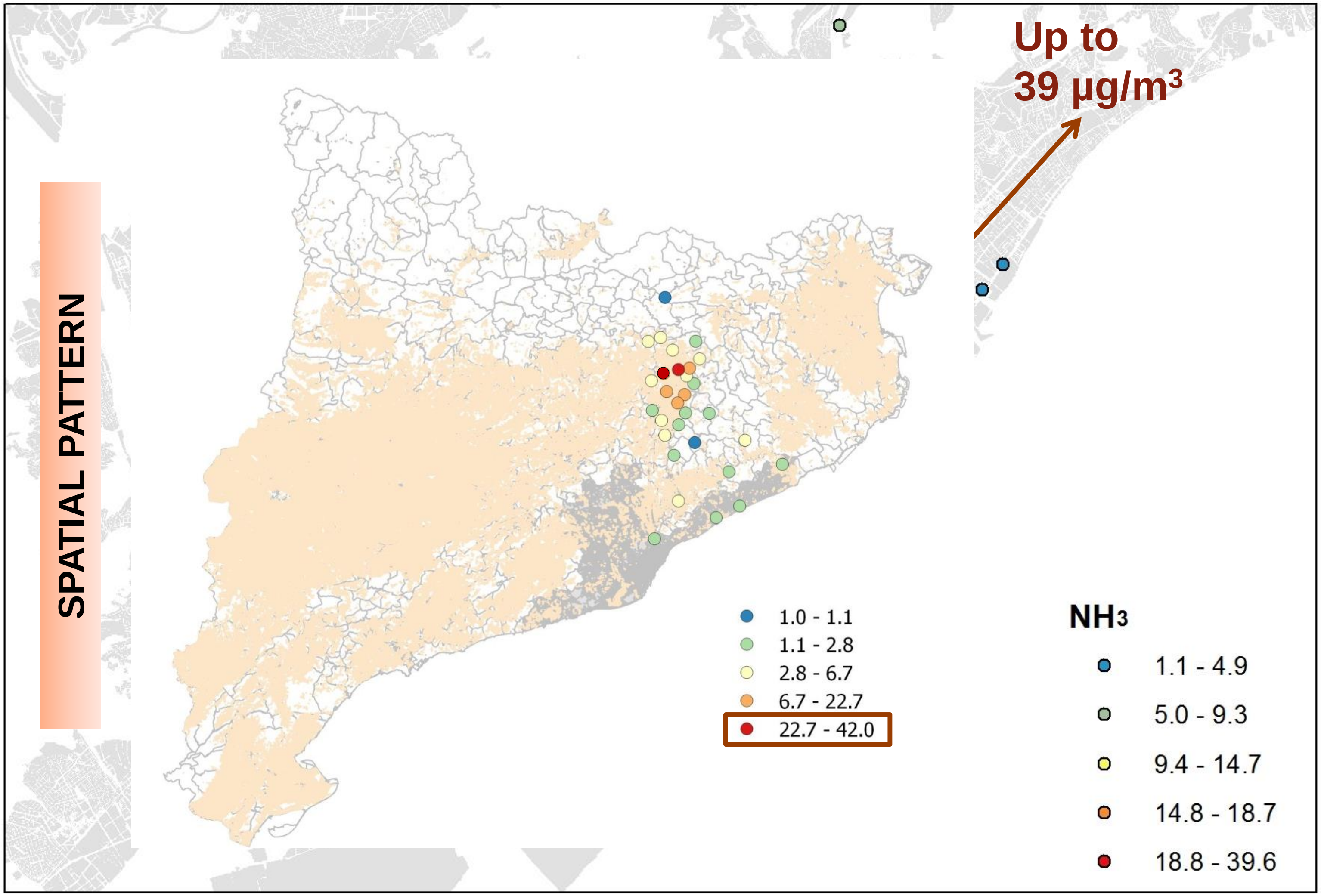
Large cities such as Madrid, with a fleet of vehicles much higher than the rest of Spanish cities, have nitrate levels close to 2.5 $\mu g/m^3$, much lower than those in Barcelona (higher than 4 $\mu g/m^3$)

URBAN AMMONIA MEASUREMENTS



Reche et al., 2012; 2015

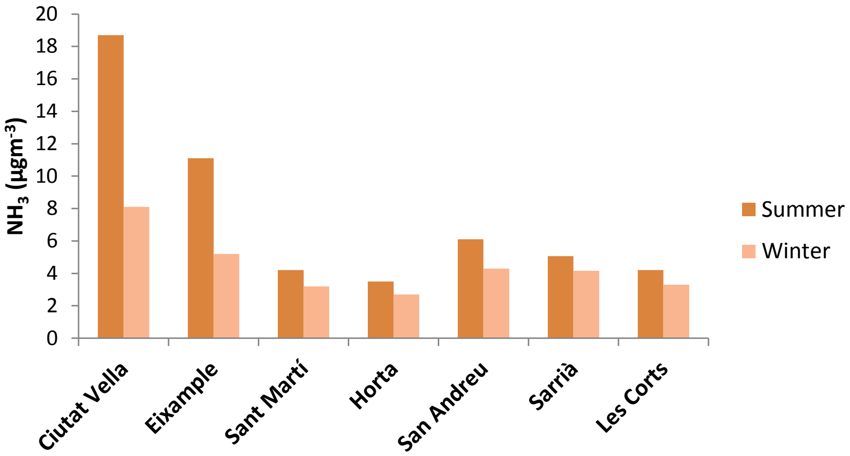
URBAN AMMONIA MEASUREMENTS

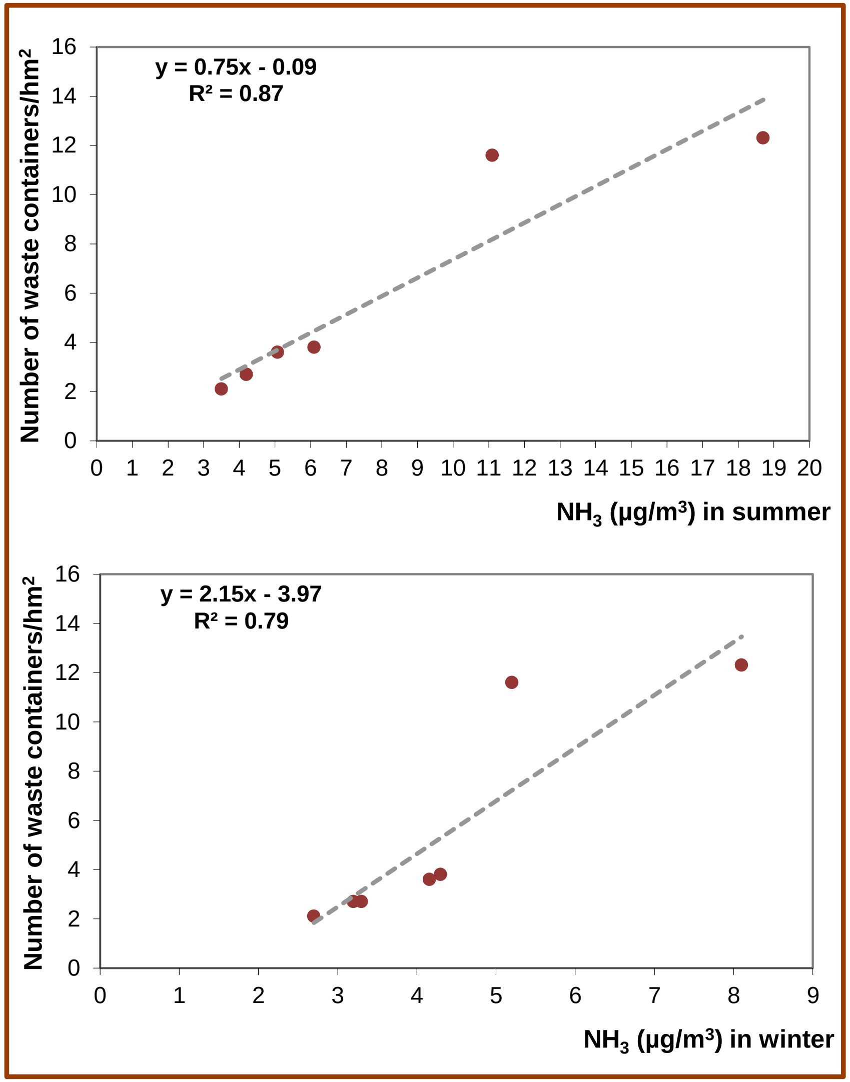


Reche et al., 2012; 2015

URBAN AMMONIA MEASUREMENTS

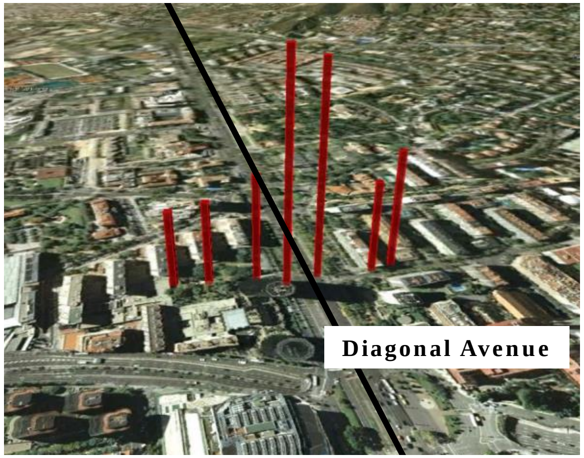
HIGH POPULATION DENSITY-DENSE URBAN TOPOGRAPHY

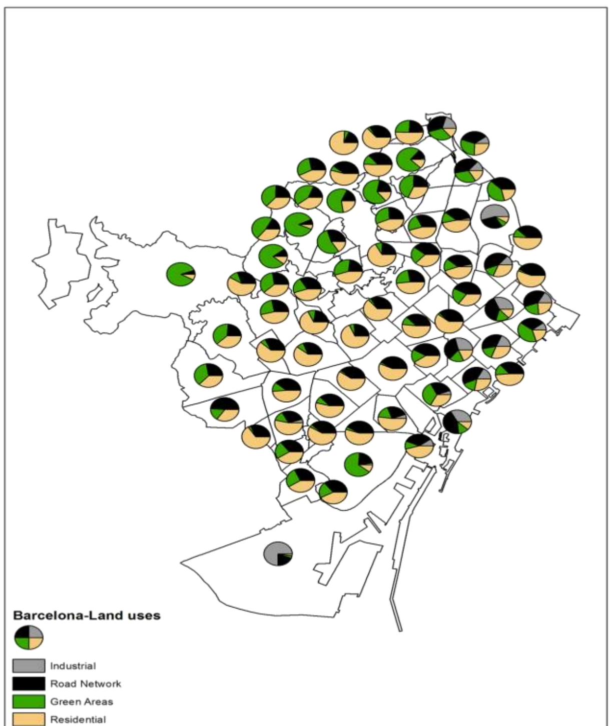




URBAN AMMONIA MEASUREMENTS

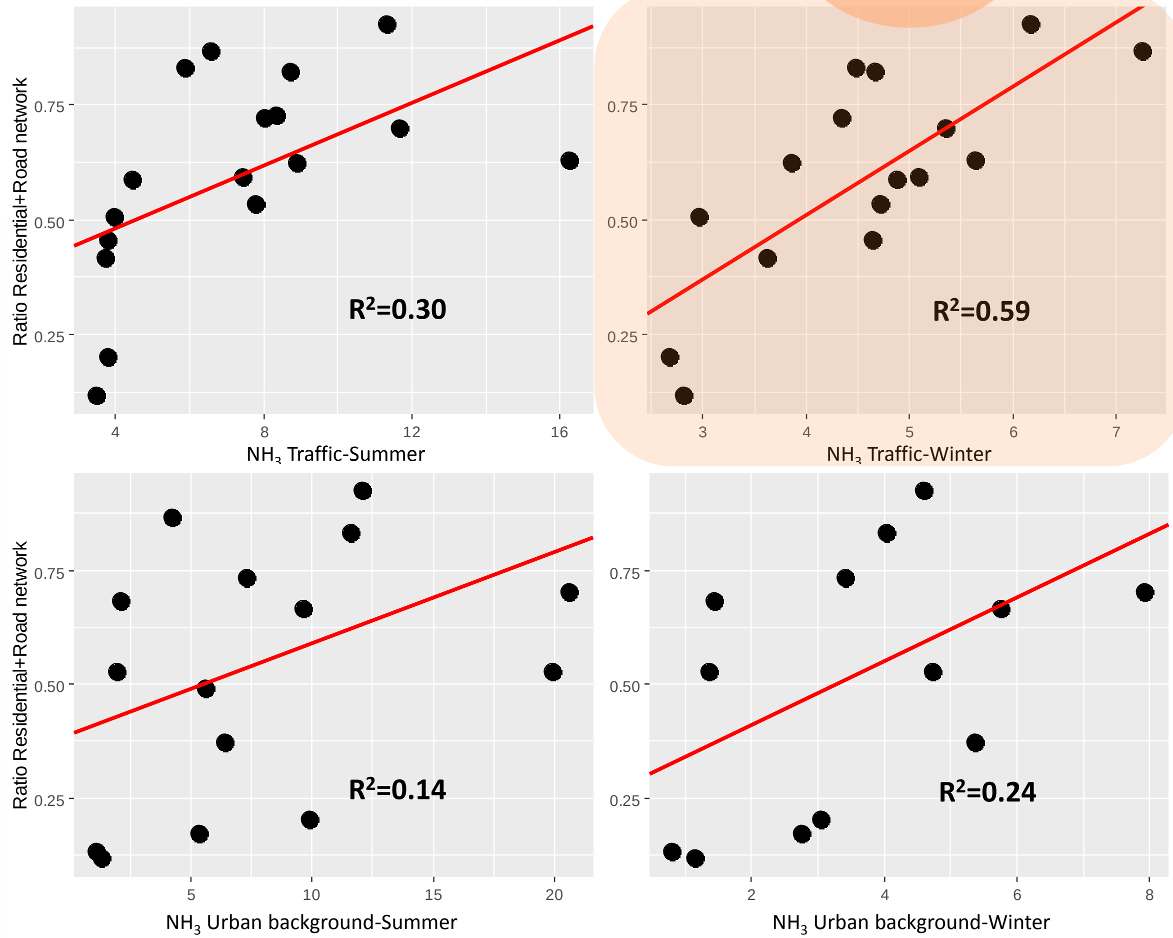
TRAFFIC EMISSIONS





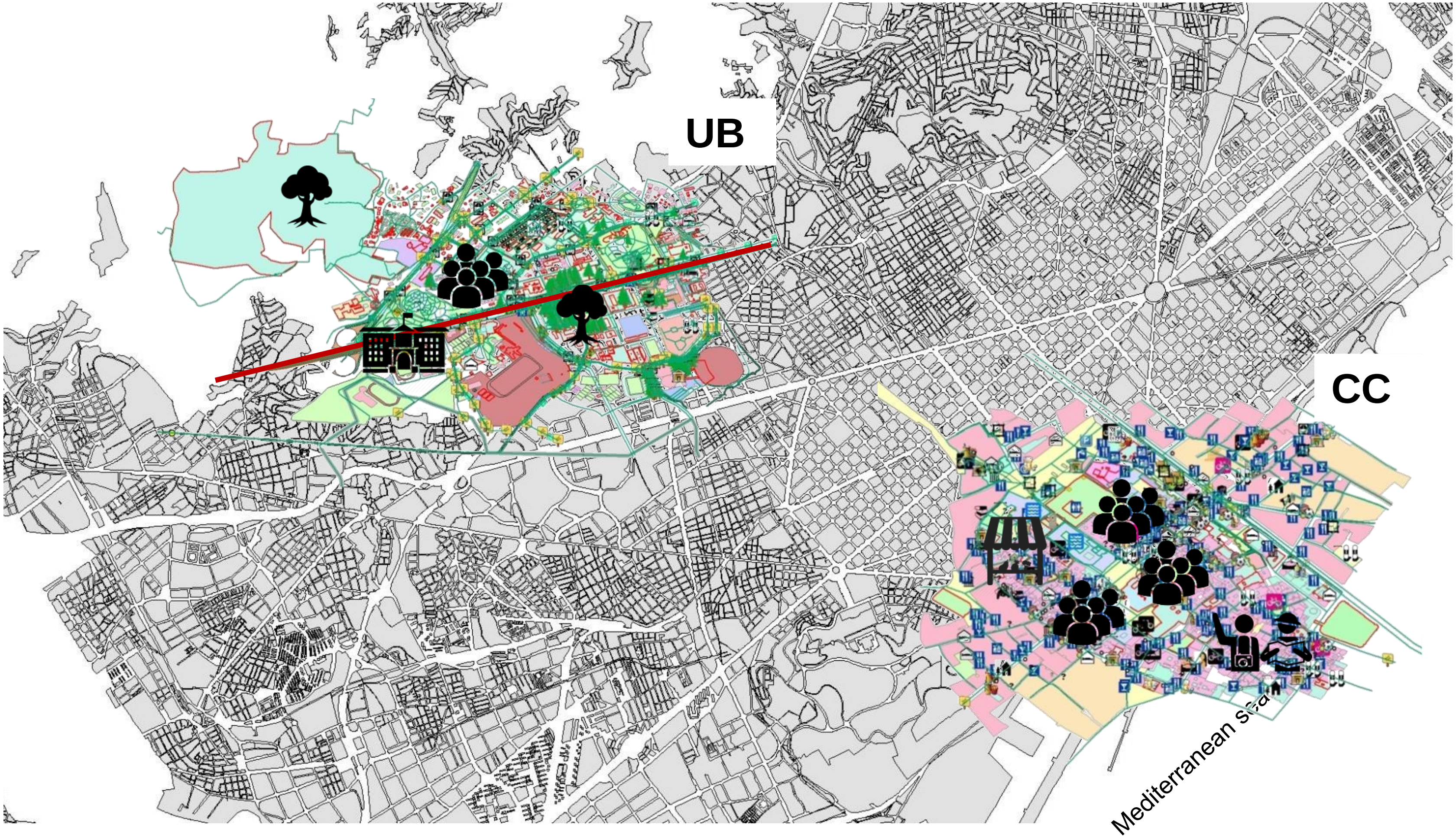
Correlation NH_3 vs Area for road network

Traffic sites in winter



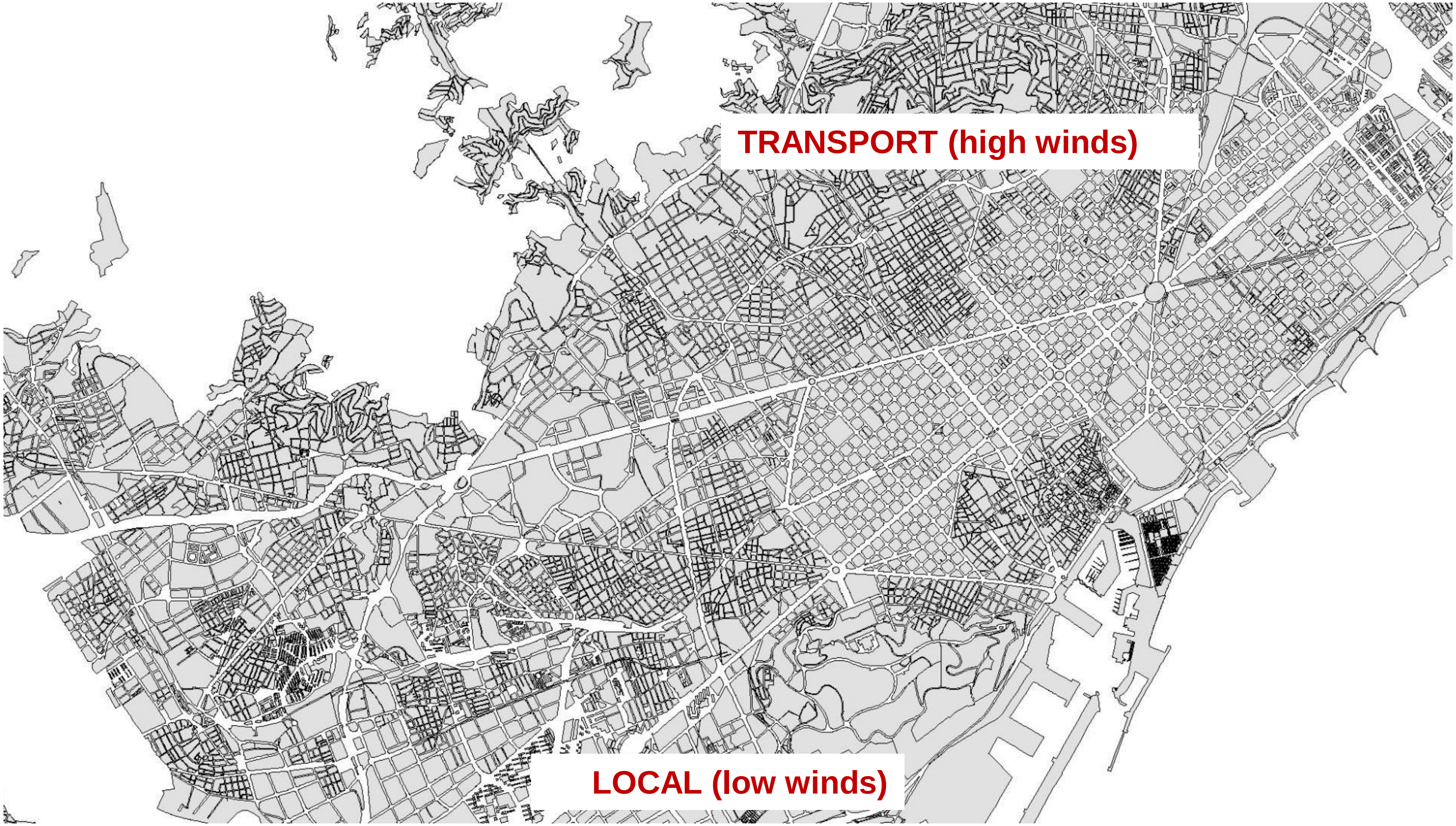
URBAN AMMONIA MEASUREMENTS

ON-LINE MEASUREMENTS



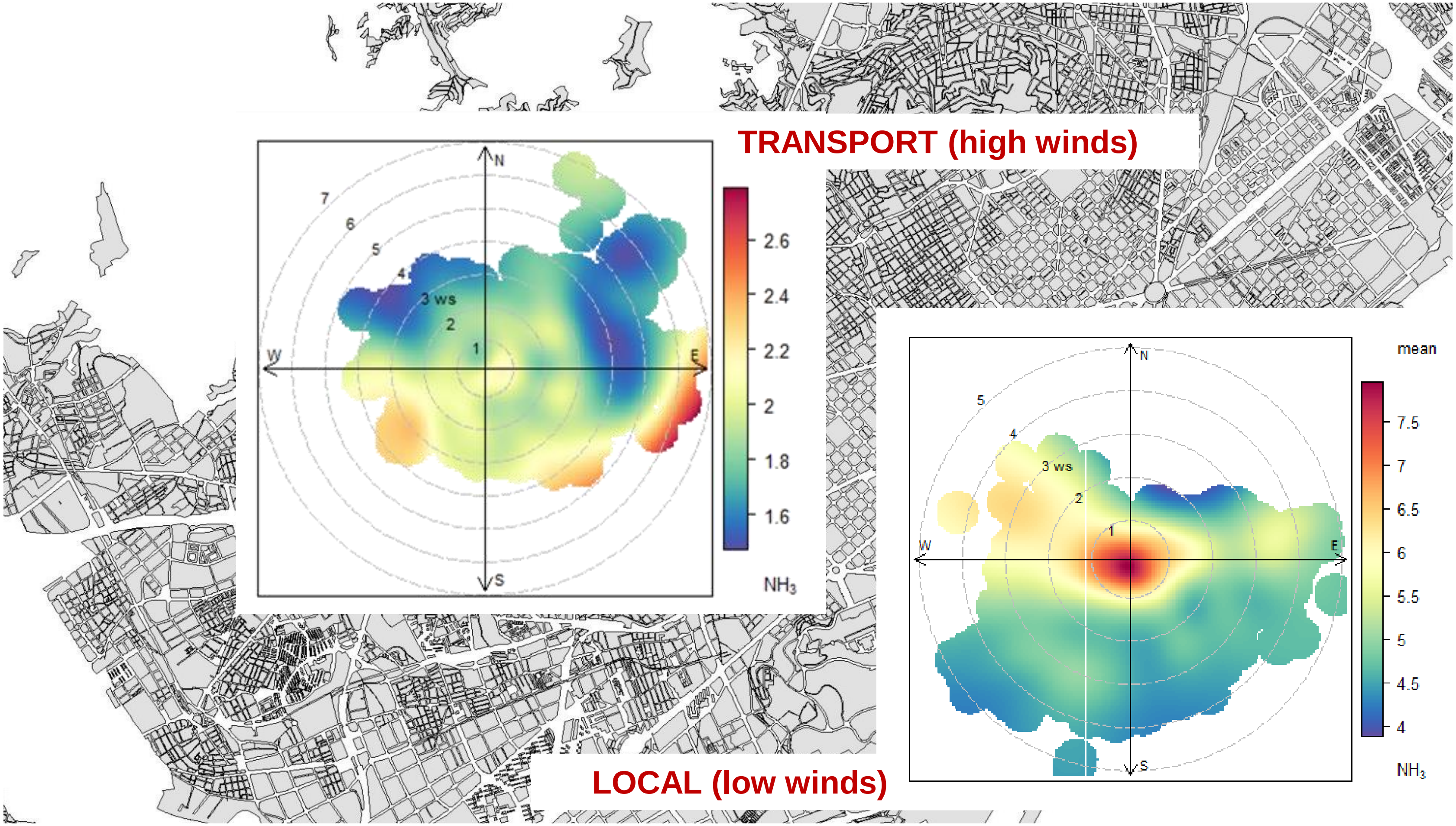
Pandolfi et al., 2012

URBAN AMMONIA MEASUREMENTS



Local origin for the measured concentrations of NH_3 at both sites

URBAN AMMONIA MEASUREMENTS



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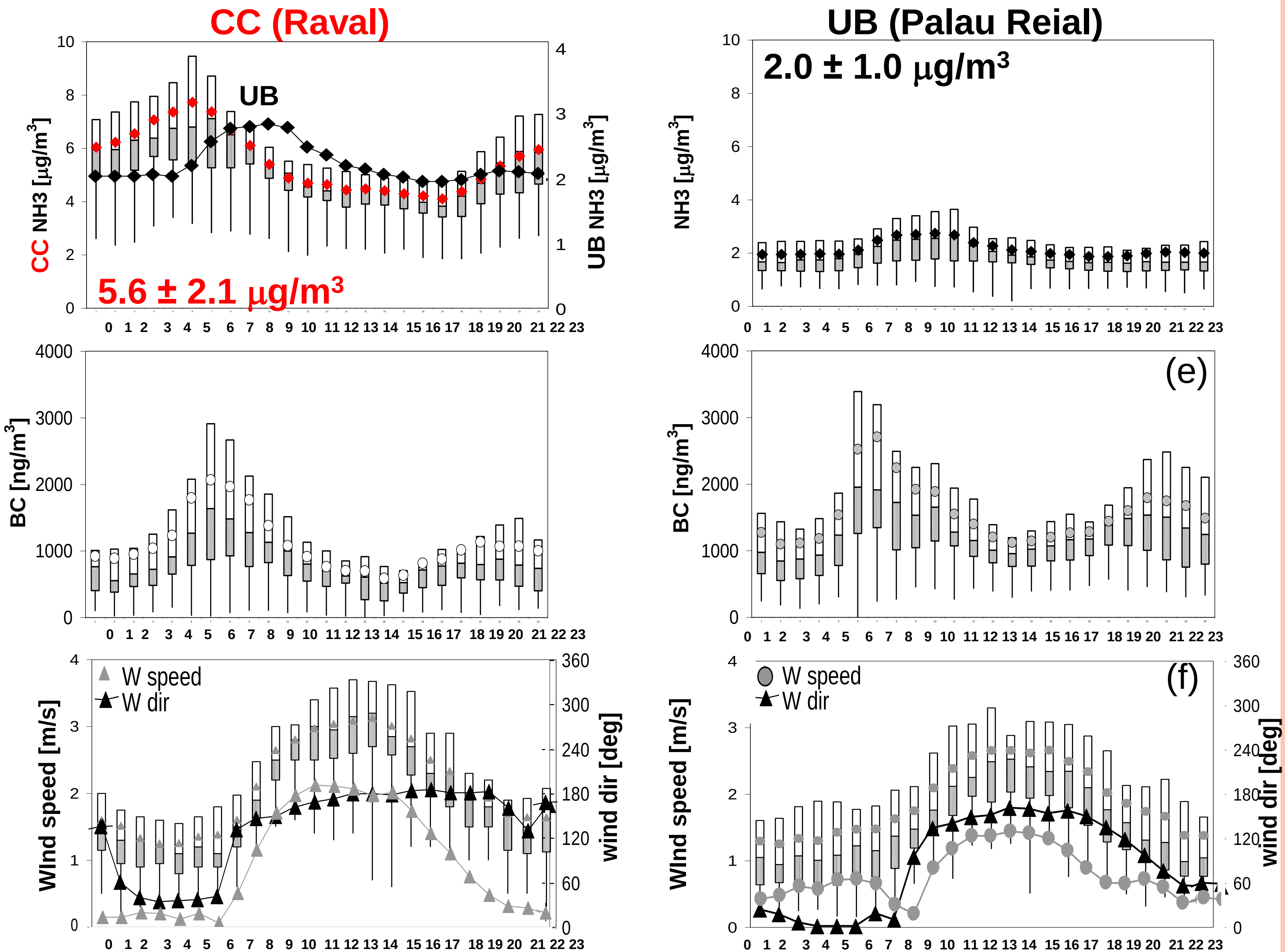

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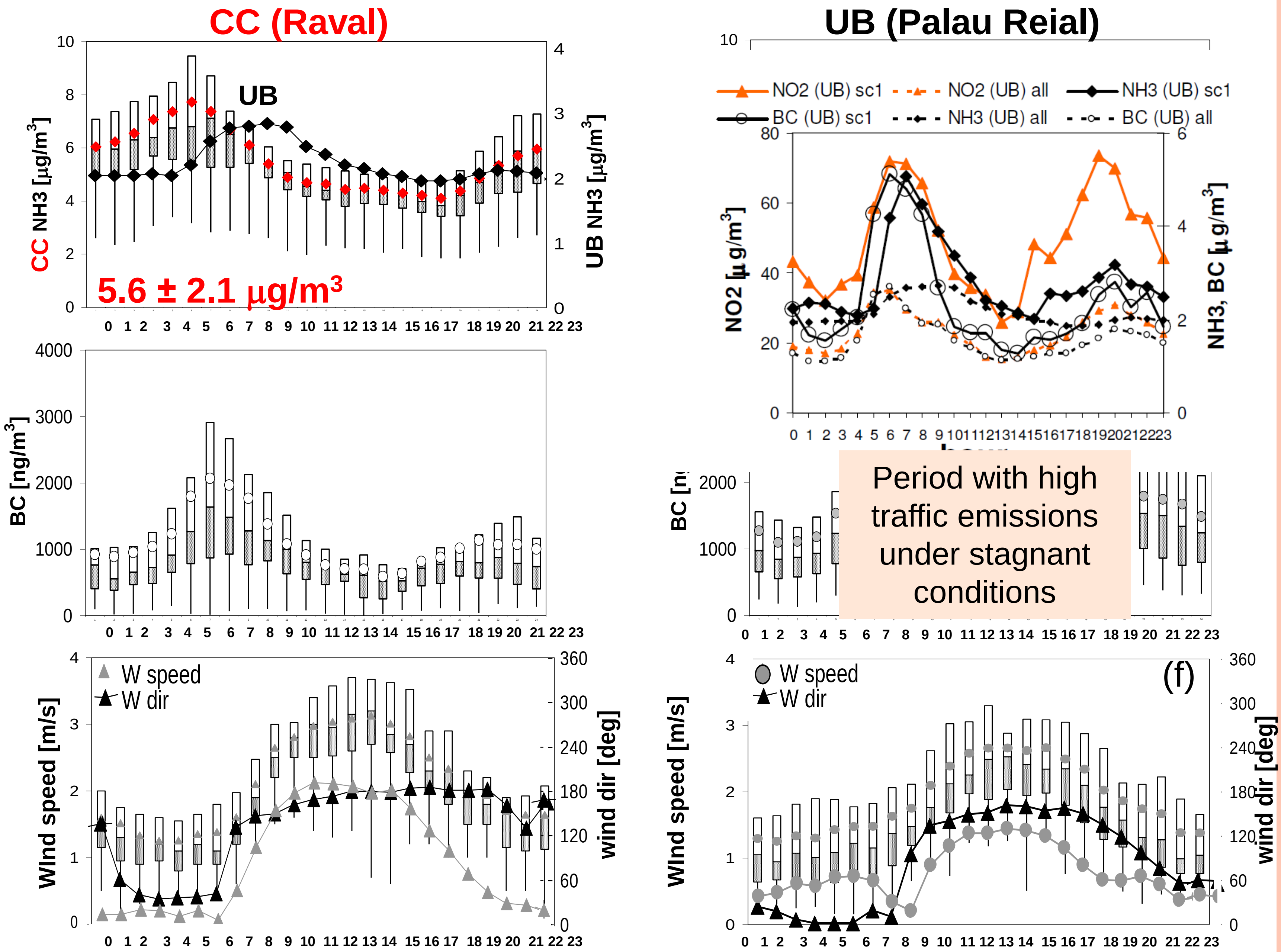
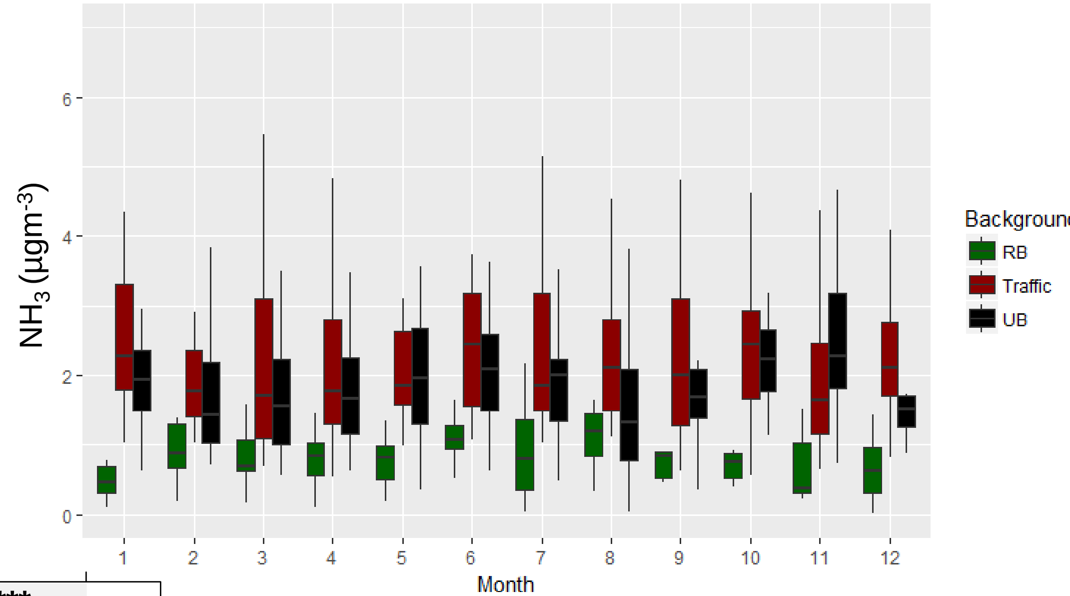
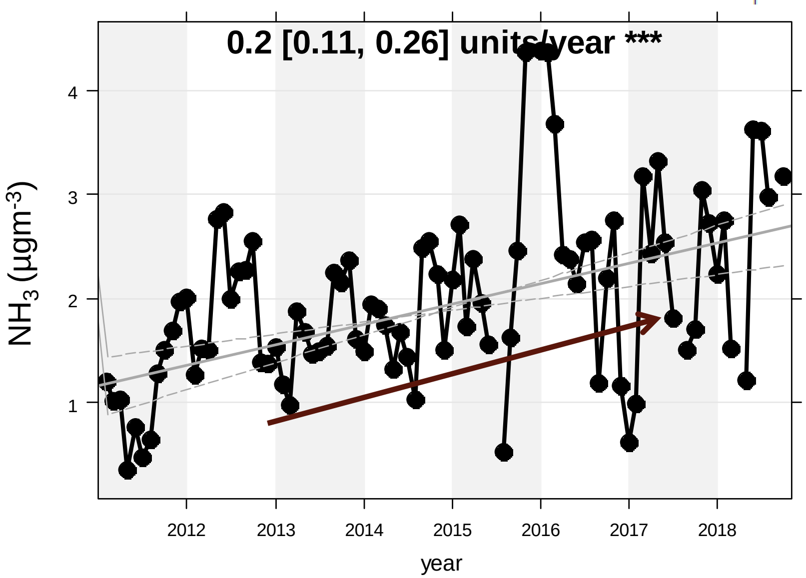


URBAN AMMONIA MEASUREMENTS

2011-2018 Measurements in Barcelona using diffusion tubes





Certain increase of NH_3 concentrations at the urban background.
NH_3 concentrations increase because NH_3 emissions increase and/or because less of the emitted NH_3 is transformed into the particle phase NH_4^+

Increase N desposition?

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FINAL REMARKS AND RECOMMENDATIONS

- Although agriculture is the main emission source of NH_3, urban emissions could be very relevant at a local scale, especially in environments with high NO_X and SO_2 concentrations

- That's why it is important monitoring spatial and time variation

- Ammonia-induced particle formation corresponds to an environmental problem which is not adequately addressed by current regulations

- Control secondary particles precursors is essential to develop effective action plans against $PM_{2.5}$ (made by 65-70% of secondary PM)

- Jointly evaluate plans for reducing different air pollutants, in order to avoid unwanted effects

CONTROL AMMONIA-SLIP IN DIESEL-SCR BUSES

AIR QUALITY NETWORK IN SPAIN RD102/20

Thank you