SEMI-VOLATILE ORGANIC CONTAMINANTS (SVOCs) IN THE SE OF SPAIN: PASSIVE AIR SAMPLING AND A MODELLING APPROACH

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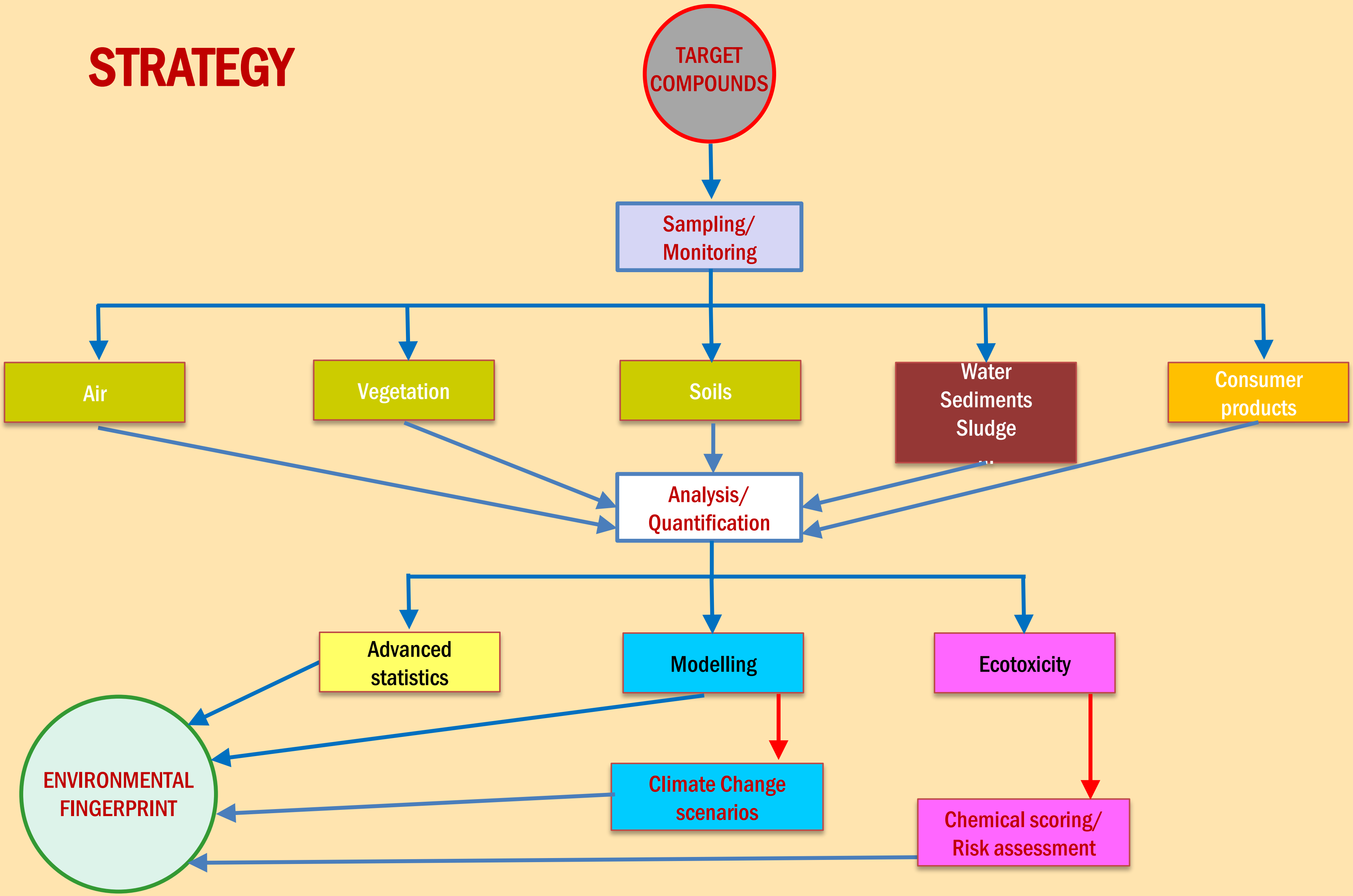
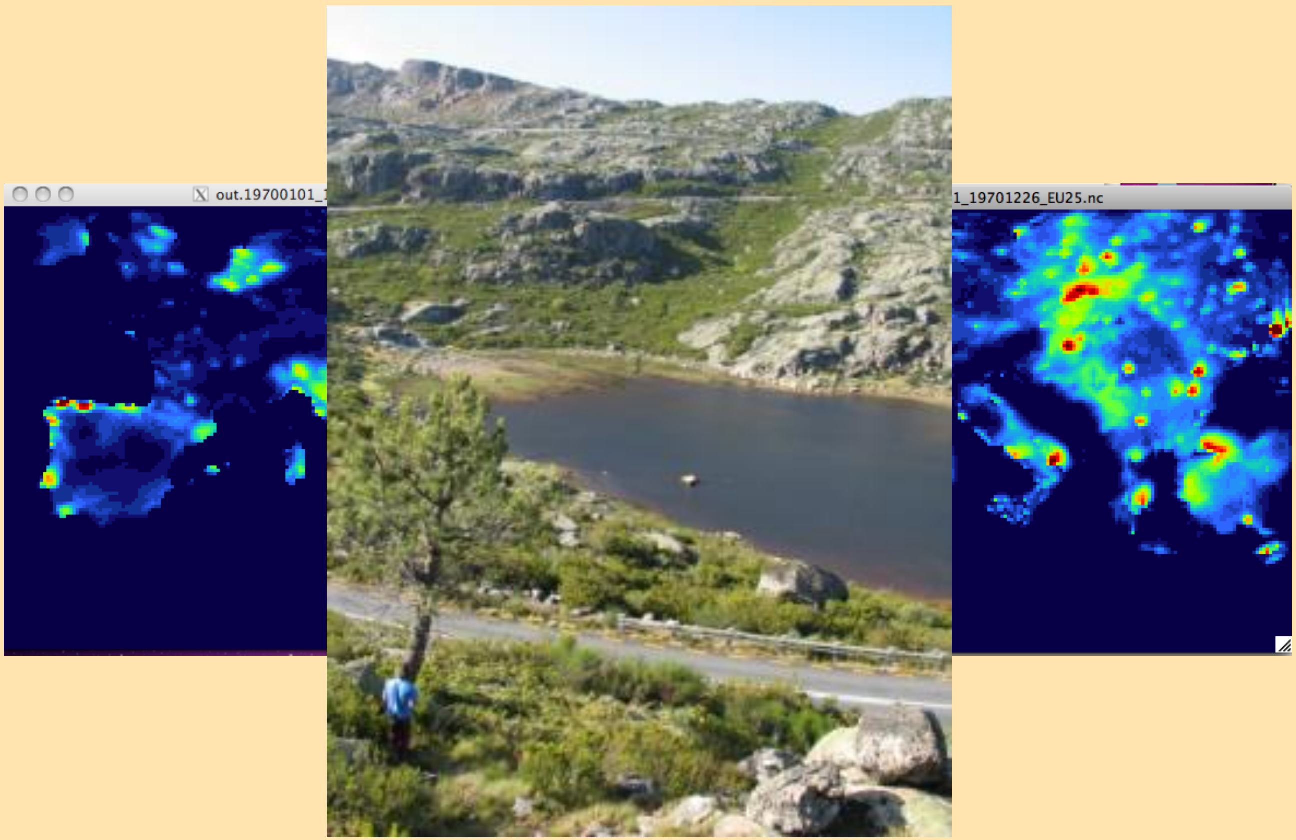
MOTIVATION AND OBJECTIVES

STRATEGY



TARGET COMPOUNDS
Sampling/ Monitoring
Air
Vegetation
Soils
Water
Sediments
Sludge
Consumer products
Analysis/ Quantification
Advanced statistics
Modelling
Ecotoxicity
ENVIRONMENTAL FINGERPRINT
Climate Change scenarios
Chemical scoring/ Risk assessment

FIELD DATA + MODELS = GOOD CHEMISTRY?



OBJECTIVES

The main objective of this work was to assess the levels and the spatial and temporal patterns of some SVOCs (HCB, PCBs, BFRs, PAHs and musks) in the Levantine coast (south-east Iberian Peninsula). Field data and CTMs were combined to produce a comprehensive overview of a region with a severe lack of information on these chemicals of concern.

Underlying questions :

1. Can we establish a reliable monitoring network for the target pollutants over SE Iberian Peninsula based on passive air sampling?

2. How does a state-of-the-art chemistry transport model reproduce the presence of SVOCs (BaP) in our domain?

TARGET COMPOUNDS

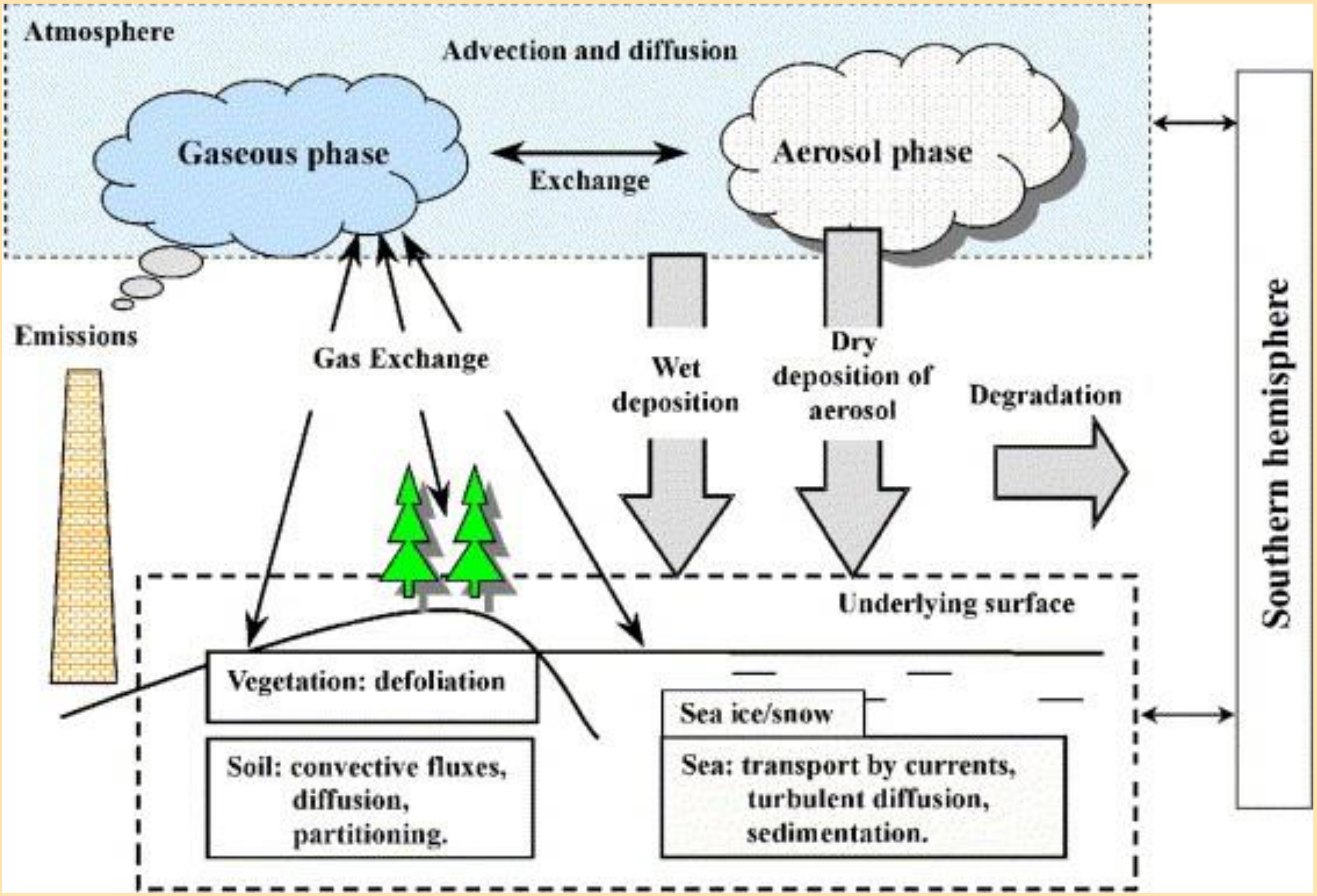
SEMIVOLATILE ORGANIC COMPOUNDS (SVOCs)

- Boiling point range: 240-260 to 380-400 ºC
- Natural and anthropogenic sources
- High environmental half-lives - persistence in numerous matrices
- Prone to long-range atmospheric transport (LRAT)
- High toxicity at low concentrations - carcinogenic and mutagenic properties
- Examples: OCPs, PCBs, PBDEs, PAHs… ("legacy" pollutants)

  Musks, siloxanes, OPFRs… ("emerging" pollutants)

SVOCs ENVIRONMENTAL DISTRIBUTION

Gas and particulate phases



ANALYSED IN THIS WORK

Organochlorine pesticides (OCPs)

- HCB

Polychlorinated biphenyls (PCBs)

- 28, 52, 77, 81, 101, 105, 114, 118, 123, 126, 138, 153, 156, 157, 167, 169, 189, 180, 209

Brominated flame retardants (BFRs)

- BDEs 28, 47, 85, 99, 100, 153, 154, 183; HBB, PBT, PBEB

Polycyclic aromatic hydrocarbons (PAHs)

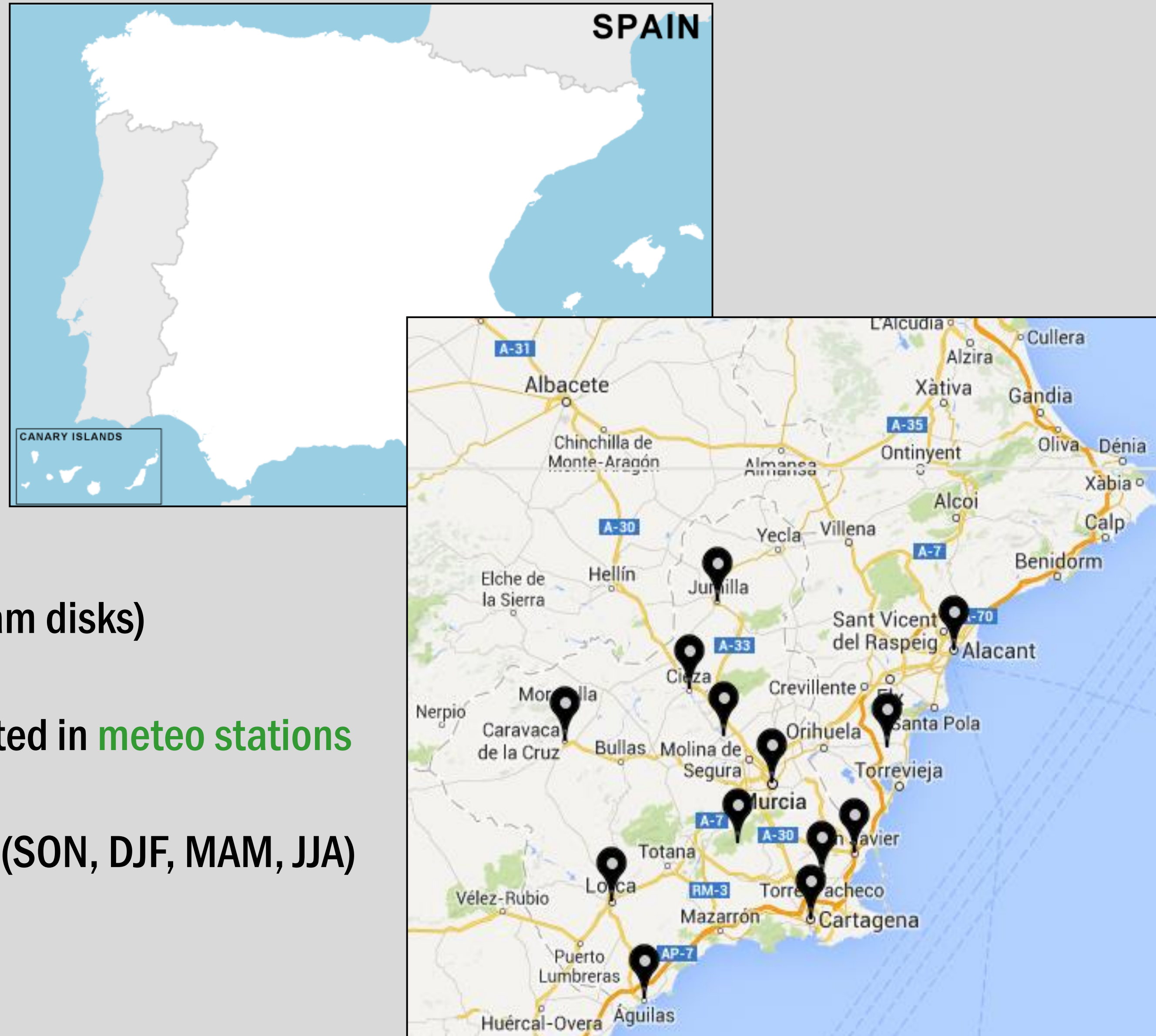
- 16 EPA PAHs (Naph, Acy, Ace, Fluo, Phen, Ant, Flt, Pyr, BaA, Chry, BbF, BkF, BaP, IcdP, DahA, BghiP)

Musks

- Cashmeran (DPMI), celestolide (ADBI), traseolide (ATII), phantolide (AHMI), tonalide (AHTN), galaxolide (HHCB), musk moskene (MM), musk xylene (MX), musk ketone (MK), musk ambrette (MA)

SAMPLING AND ANALYSIS

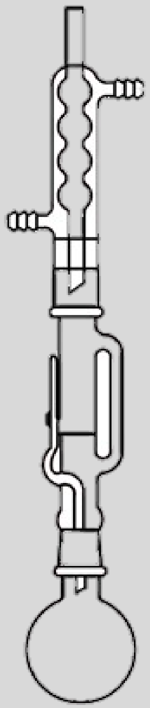
SAMPLING



- PUFs (polyurethane foam disks)
- 13 sampling sites located in meteo stations
- 4 seasonal campaigns (SON, DJF, MAM, JJA)
- 4 x 3 months exposure

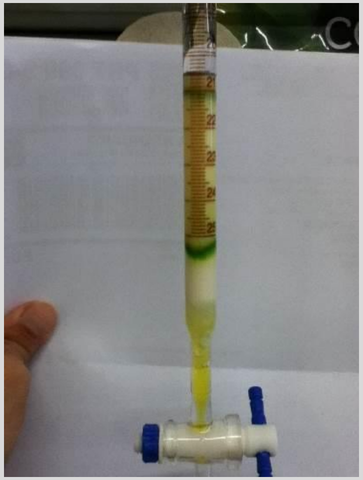
EXTRACTION AND CLEAN-UP

PAHs, PCBs, PBDEs, HCB and musks in passive air samples (PUFs)



SOXHLET extraction

- HEX/DCM (1:1)



CLEAN-UP 1 – Glass columns

- Alumina (5 g)
  Activated at 400 ºC
- Condit: 50 mL HEX/DCM (1:1)
- Elution: 50 mL HEX/DCM (1:1)

CLEAN-UP 2 - GPC

- Bio-Beads® S-X3 (6 g)
  Pre-expanded overnight in Hex/DCM (1:1)
- Conditioning: HEX/DCM (1:1)
- Elution: 40 mL HEX/DCM (1:1) – first 15 mL discarded

GC-MS

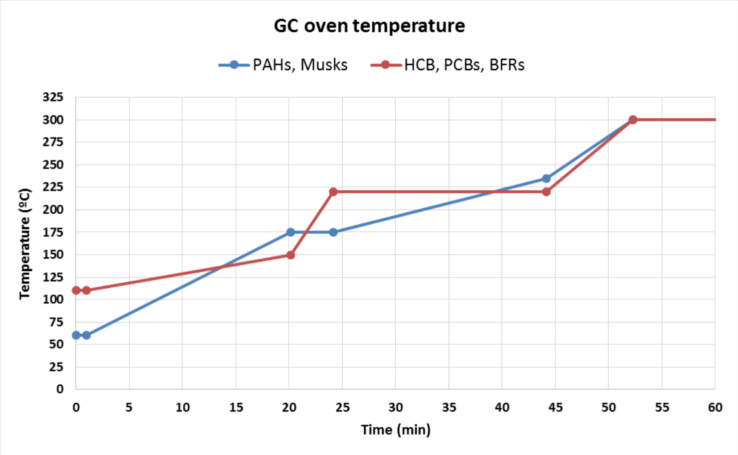
PAHs, PCBs, PBDEs, HCB and musks in in passive air samples (PUFs)

Capillary columns

HCB, PCBs and BFRs CP-Sil 8 CB (50 m × 0.25 mm, 0.12 μm)

PAHs and Musks DB-5 ms (30 m × 0.25 mm, 0.25 μm)

GC oven temperature programs



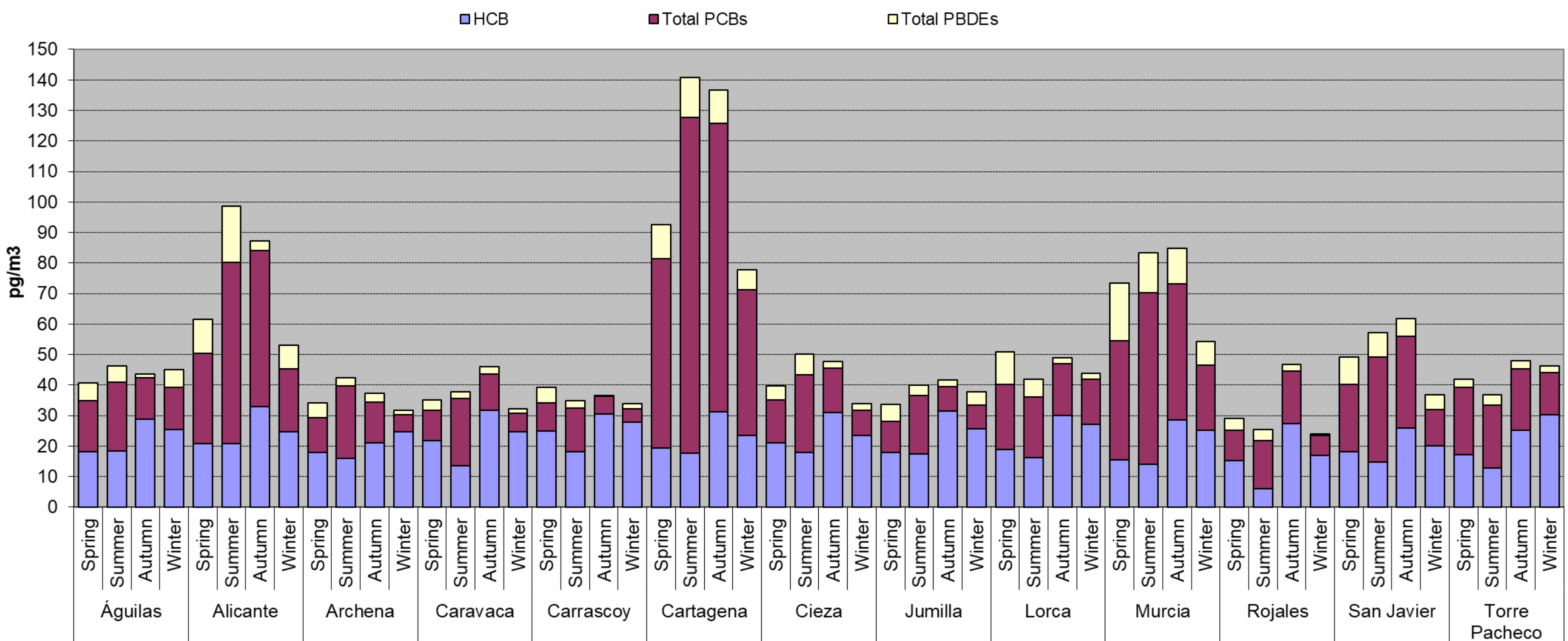
Method validation:

- **LODs:** 0.9 pg g^{-1} (PCB 52) – 488 pg g^{-1} (IcdP)
- **Precision (%RSD):** 1.2% (PCB 126) – 17.8% (BghiP)
- **Accuracy (%Rec):** Average recoveries of 88±8% (PAHs), 94±4% (PCBs), 88±2% (BFRs), 85±5% (HCB), 90±3% (Musks)

MORE INFO: J.A. Silva, N. Ratola, S. Ramos, V. Homem, L. Santos, A. Alves, "An analytical multi-residue approach for the determination of semi-volatile organic pollutants in pine needles", *Analytica Chimica Acta*, 858: 24-31, 2015.

FIELD-BASED RESULTS

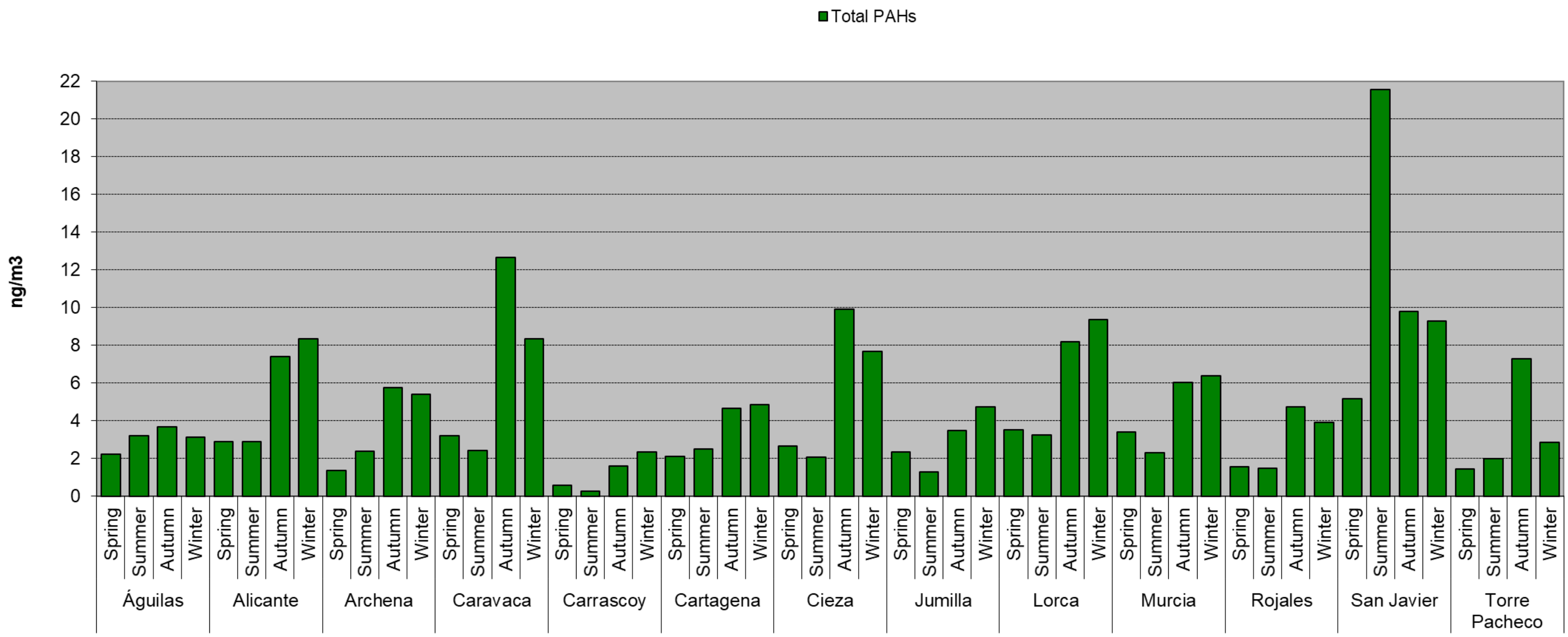
POPs



Total PCBs: 4.3-110.2 pg/m^3; **Total BFRs:** 0.04-18.4 pg/m^3; **HCB:** 5.9-33.1 pg/m^3

- Levels in background locations for PCBs and BFRs are similar
- Higher levels reflect a predominant urban/industrial fingerprint
- HCB is extremely prone to long-range atmospheric transport (LRAT), hence the more distributed presence within the domain of study

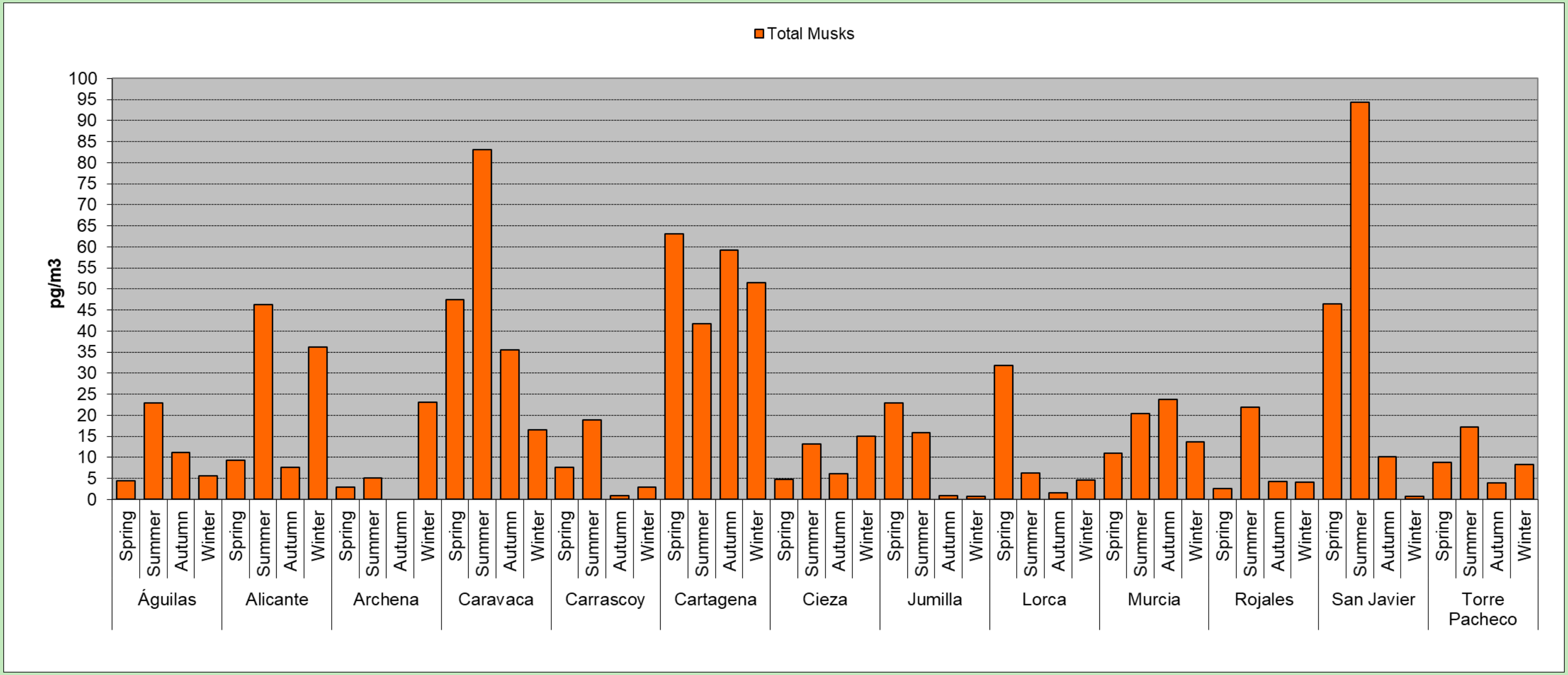
PAHs



Total PAHs: 0.3 – 21.6 ng/m^3

- Tend to reflect local natural or anthropogenic sources
- San Javier is the site with higher concentrations, airport located nearby
- Typical warmer-to-colder months increasing trend

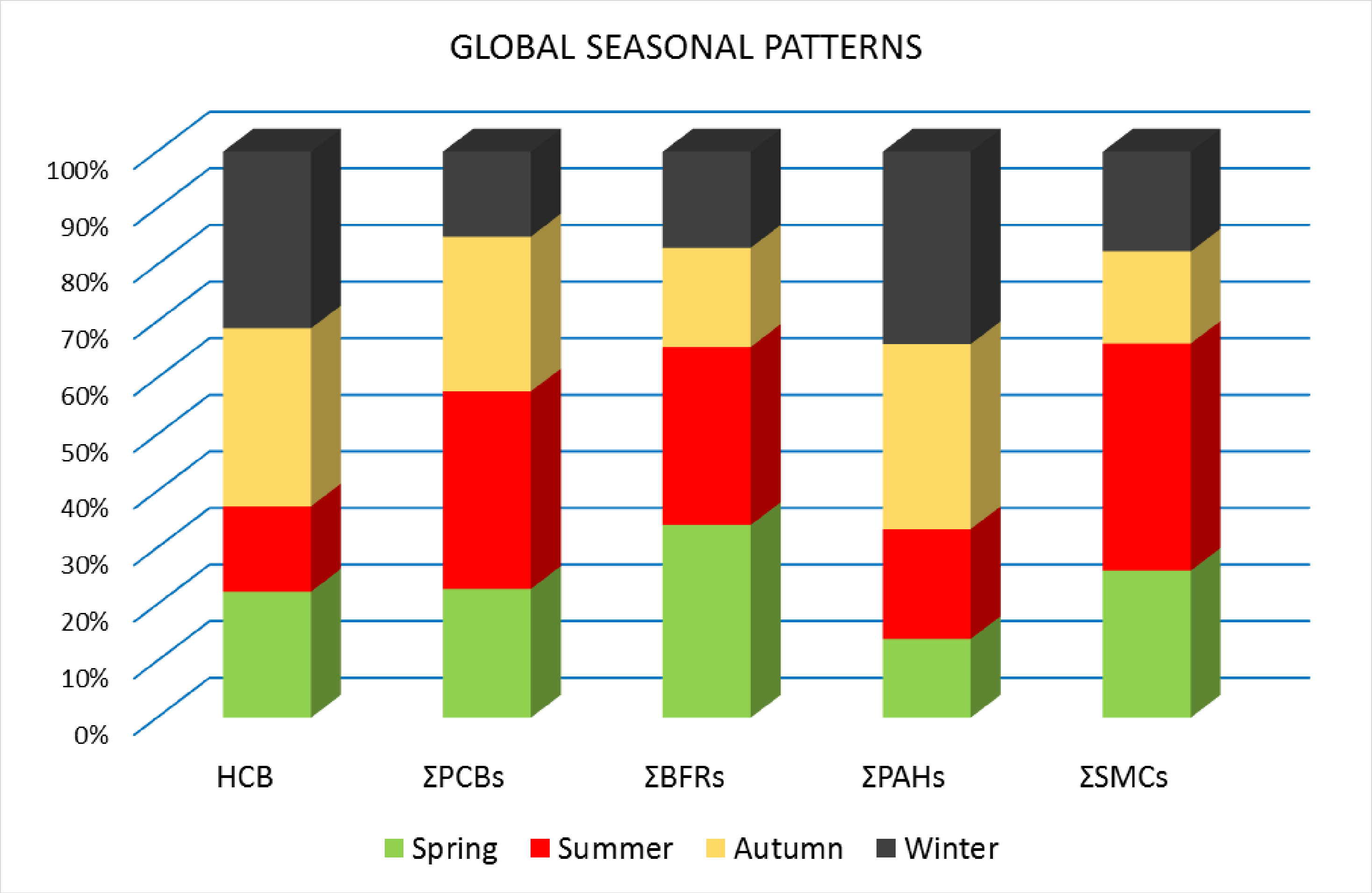
MUSKS



Total musks: n.d. – 0.094 ng/m^3

- Difficult to establish trends
- Challenging sample handling and analysis

SEASONAL PATTERNS



- Each family of compounds reveal a particular fingerprint
- A certain similitude can be found for HCB/PAHs and SMCs/BFRs

MODELLING
(BaP)

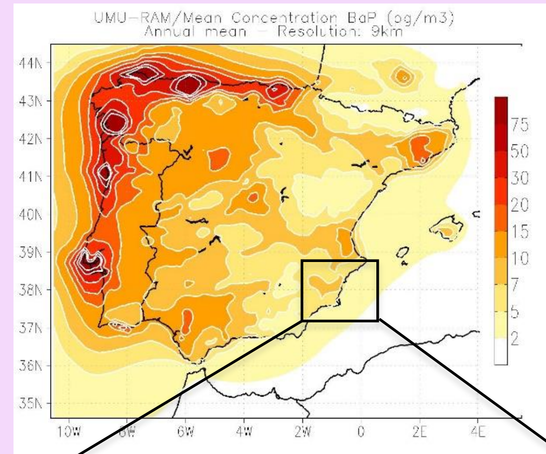
WRF-EMEP-CHIMERE

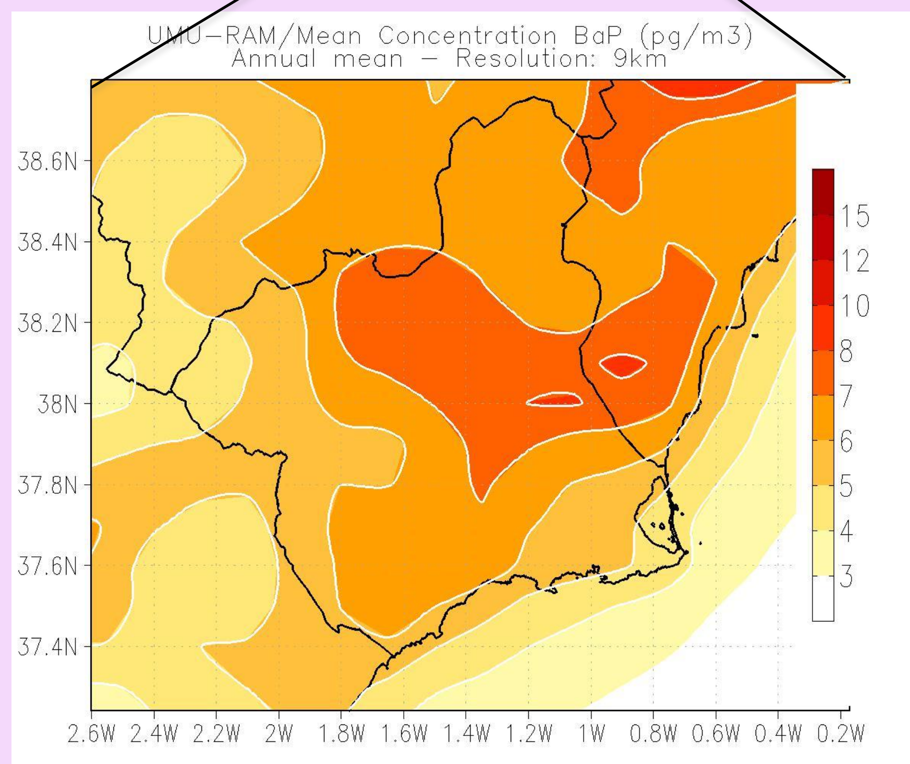
WRF parameterisations:

Microphysics → **WSM3**
Planetary BL → **Yonsei University**
Radiation → **CAM**
Soil → **Noah LSM**
Cumulus → **Kain-Fritsch**

CHIMERE parameterisations:

Chemical Mechanisms → **MELCHIOR2**
Aerosol chemistry → Inorganic (thermodynamic equilibrium with **ISORROPIA**) and organic (**MEGAN SOA** scheme) aerosol chemistry
Natural aerosols → **dust, re-suspension and inert sea-salt**
Boundary Cond → **LMDz-INCA+GOCART**

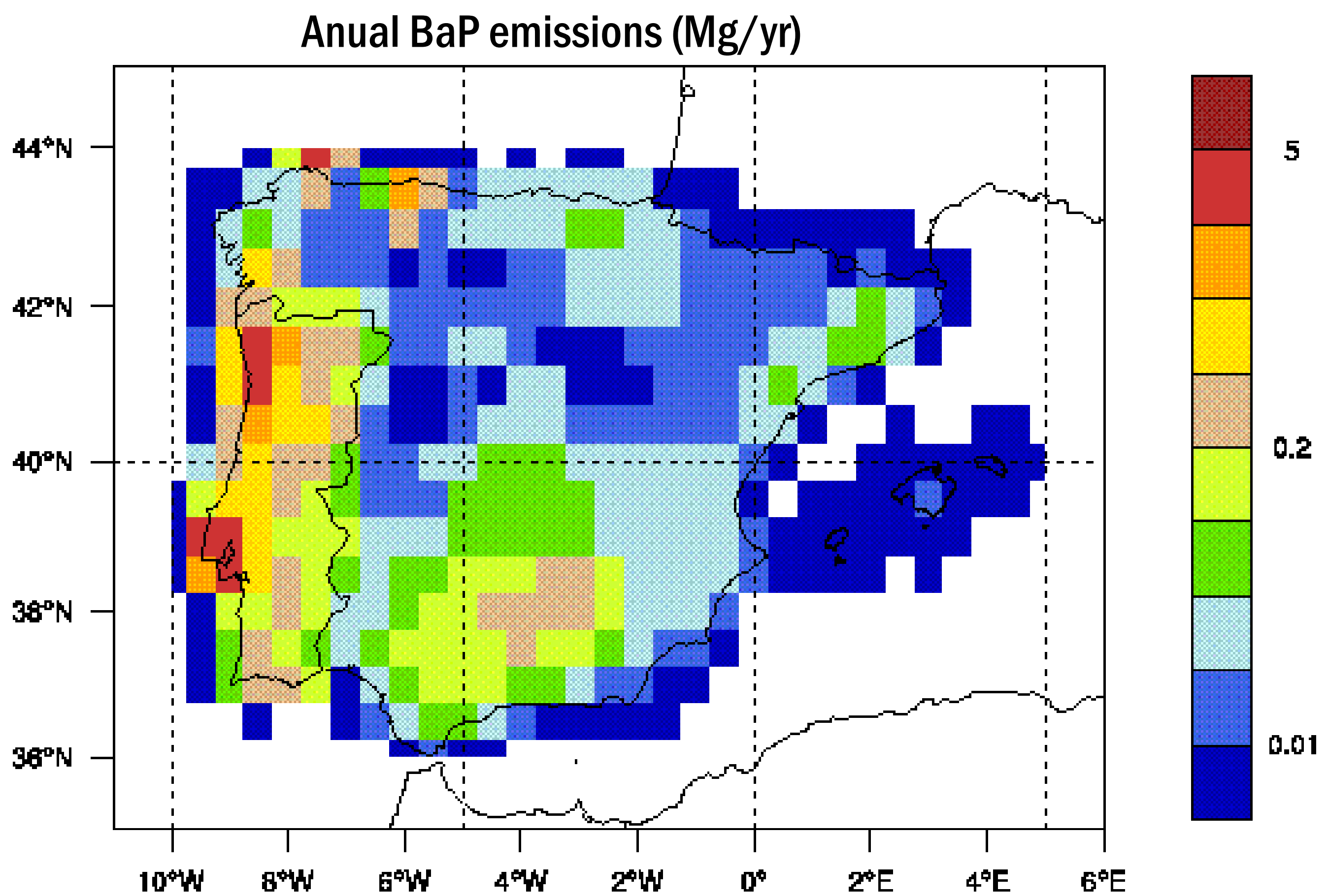




Simulated period:
2006-2010 driven by ERA-Interim

Preliminary results at 9 km horizontal resolution
Vertical Resolution: 30 layers (100 hPa)

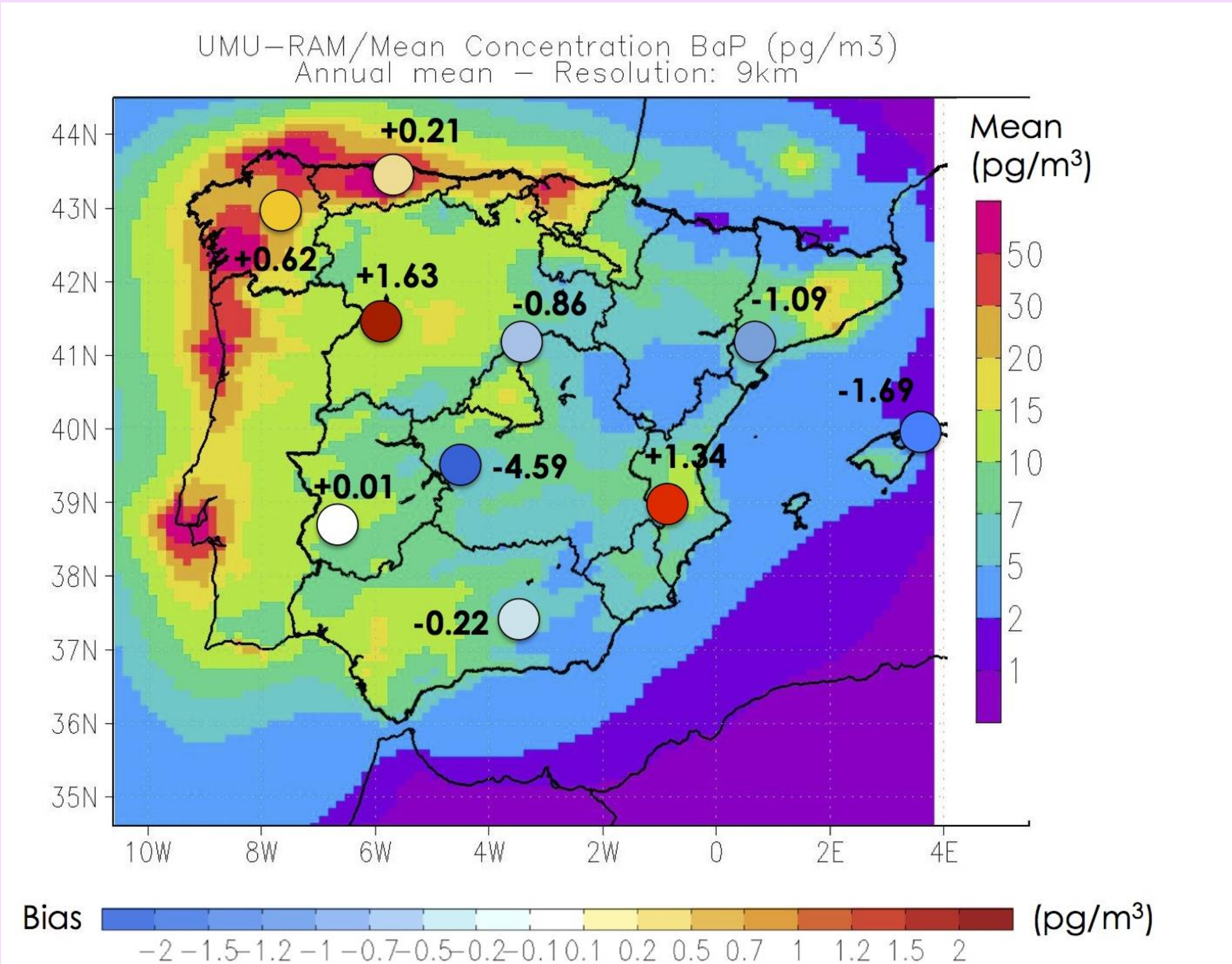
EMISSIONS (EMEP MSC-E)



Emissions on POPs are accesible as gap-filled emissions available for modelling purposes.

WebDab is the **emission database of EMEP** (Co-operative programme for monitoring and evaluation of long range transmission of air pollutants in Europe) open to public for interactive use via Internet.

VALIDATION WITH FIELD DATA

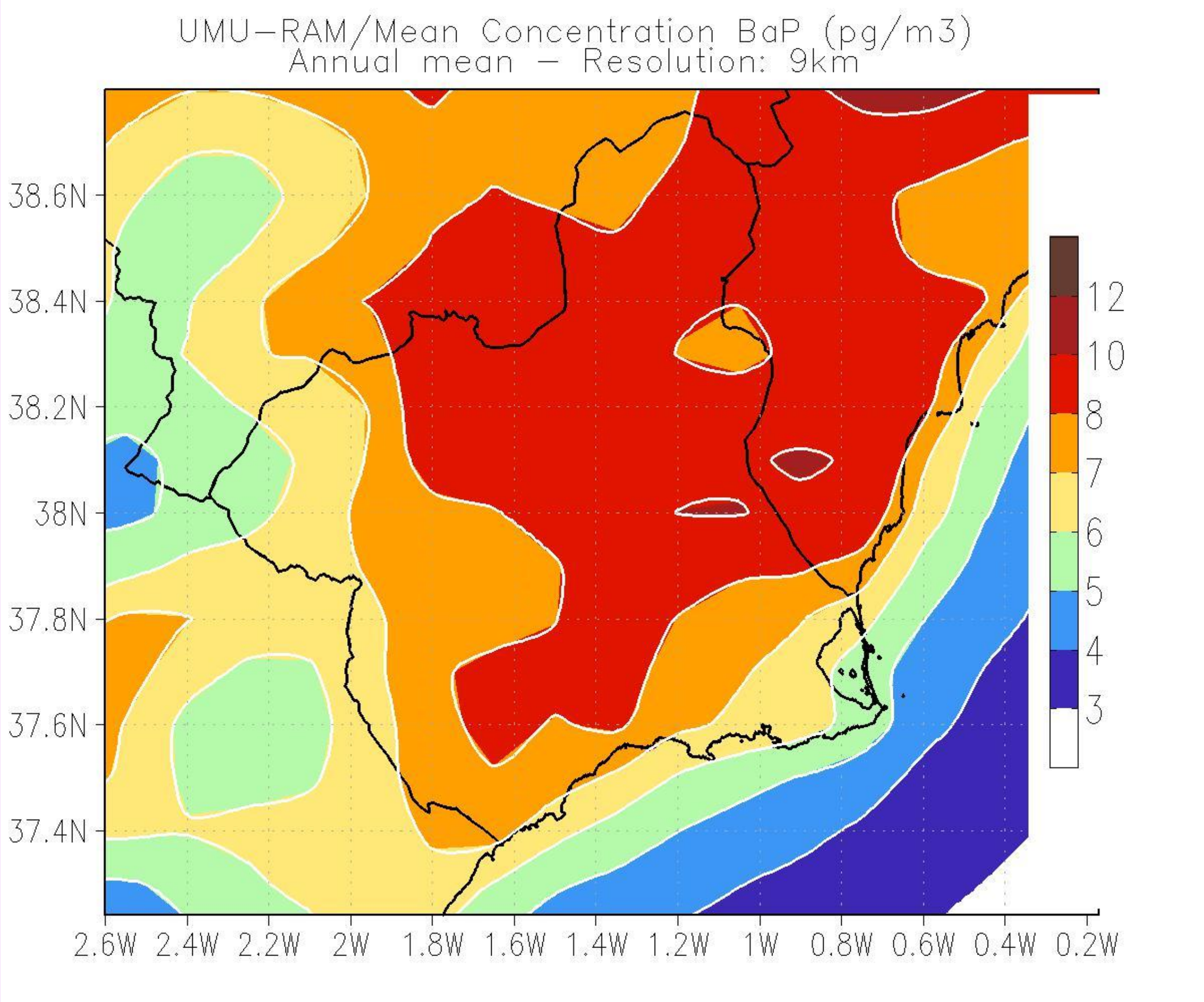


The modelled atmospheric concentrations of BaP present normalised biases under 30%. The fact that both +/- biases are found indicates that the model is not generally inclined towards overprediction or underpredicion.

The deviations only range between +1.63 pg m^{-3} over the northern Iberian Plateau (Peñausende station, close to the Spanish-Portuguese border) and -4.59 pg m^{-3} (San Pablo de los Montes station, in the southern-central Iberian Plateau).

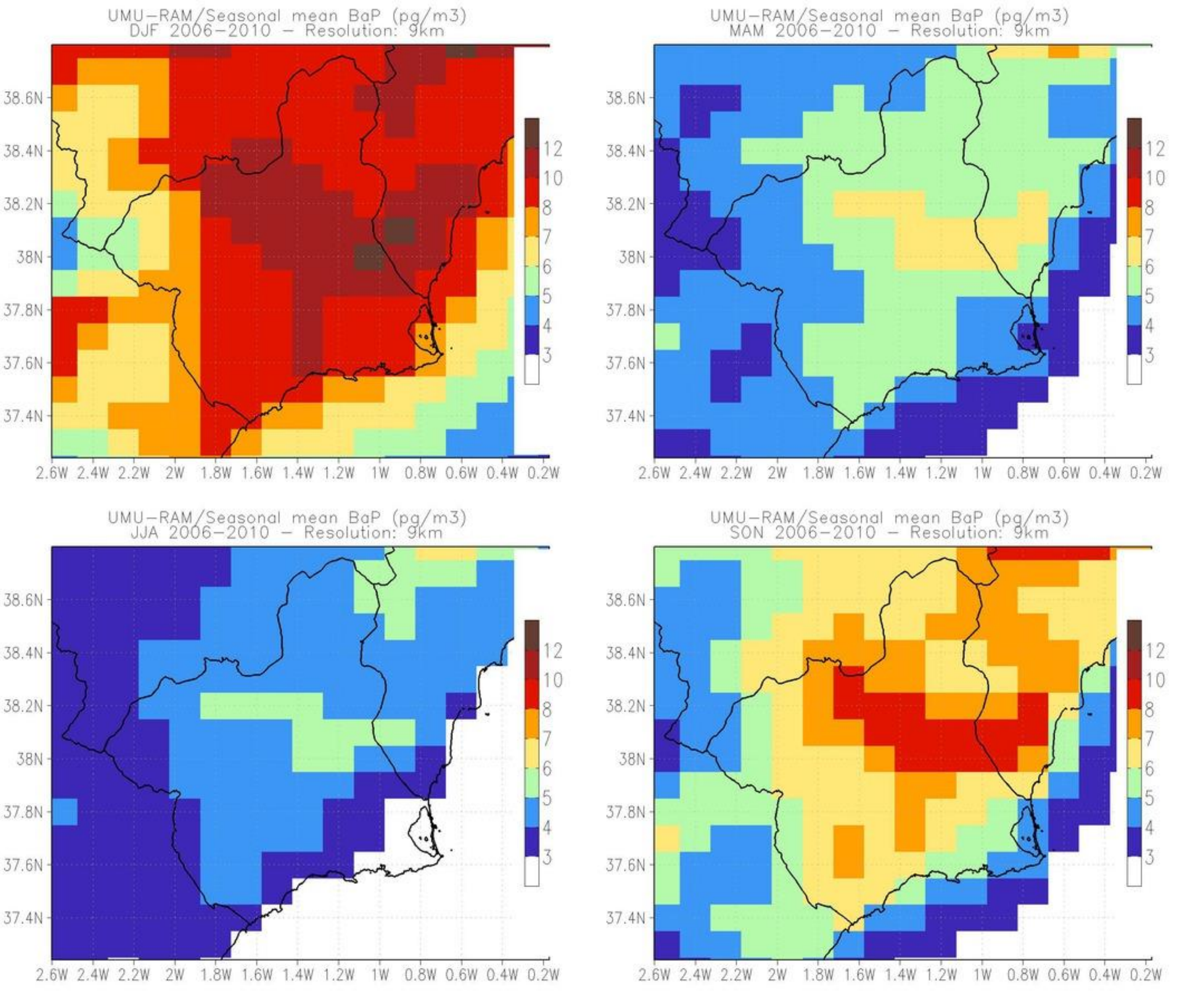
No EMEP measurements available over the target domain **(closest station, Zarra-Valencia)**

MODELLED BaP IN SE IBERIAN PENINSULA



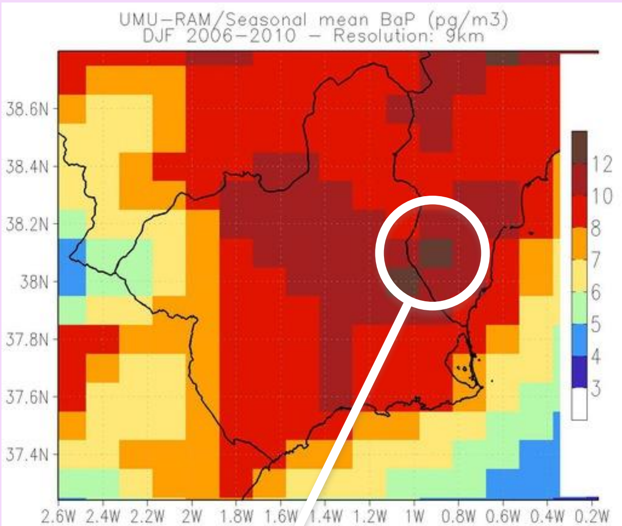
The maximum climatic BaP value is under 0.1 ng m^{-3}, with some areas exceeding the target value of 0.01 ng m^{-3}

SEASONALITY

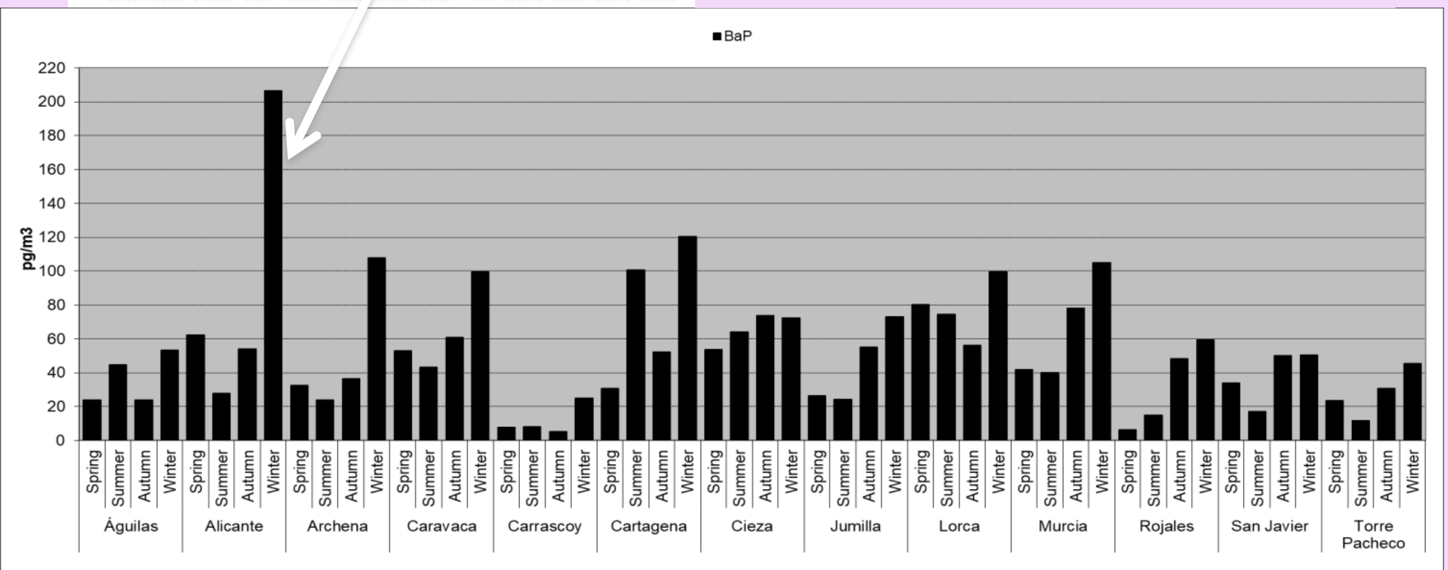


A general strong seasonality is observed in all the domain, with the highest values (over 12 pg m^{-3}) appearing at wintertime over large populated areas (Murcia) and industrial zones. The lowest concentrations are found during summertime over the Mediterranean sea.

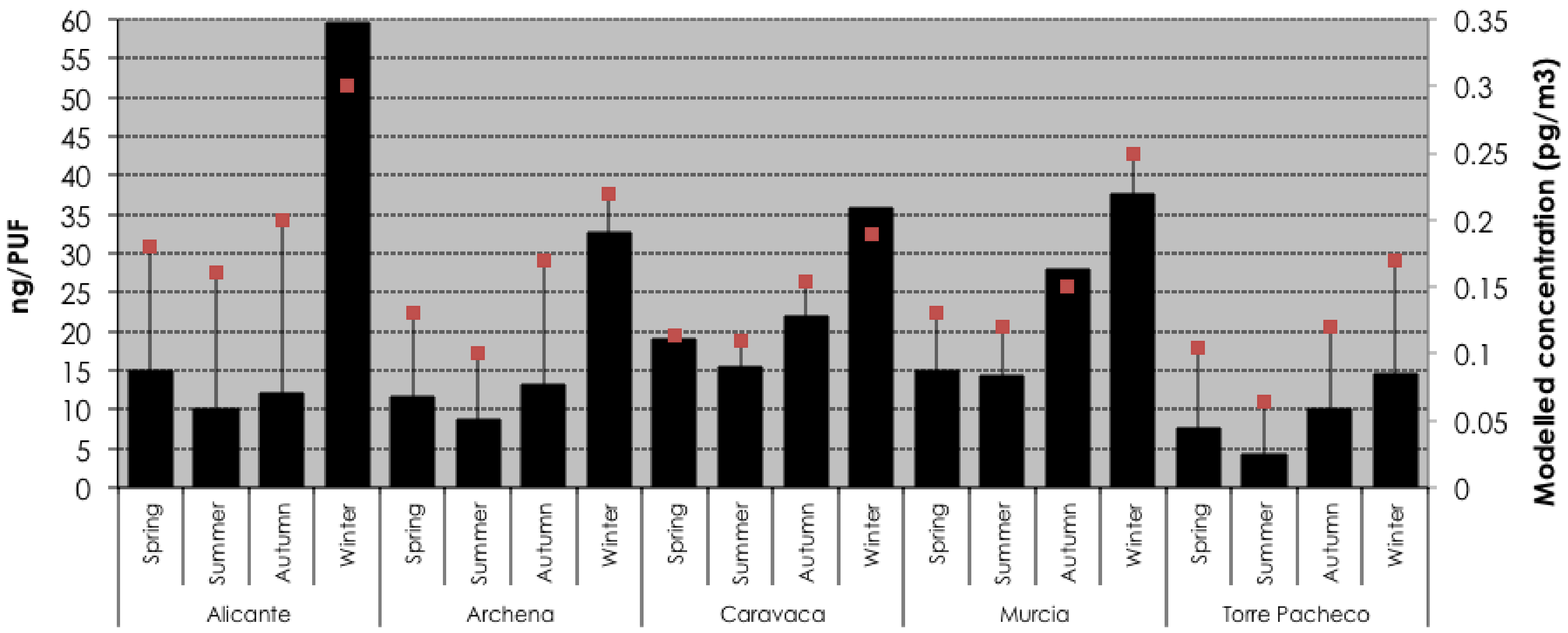
SEASONALITY



Largest change in BaP winter contribution in Alicante!



PUFs *versus* MODELS



Pearson correlation coefficient: r = 0.834

CONCLUSIONS

CONCLUSIONS

- Can we establish a reliable monitoring network for the target pollutants over SE Iberian Peninsula based on passive air sampling? **YES**

- How does a state-of-the-art chemistry transport model reproduce the presence of SVOCs (BaP) in our domain? **IN A GOOD WAY**

LIMITATIONS:

- BaP is almost entirely found in the atmosphere associated to particulate material, so passive sampling using PUFs may not be the best strategy, as it favours the entrapment of gas-phase chemicals
- Initial model validation represents a climatologically significant period (2006-2010) and not our BaP sampling period (2012-2013)

ACKNOWLEDGEMENTS

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- All the national and international partners of the aforementioned projects

- ICCE 2017 Conference Organisation.

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KEYNOTES: Cristina Branquinho, Elia Psillakis, Kurunthachalam Kannan, Maria Llompart, Pedro Jiménez-Guerrero

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