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# Trends in PM<sub>2.5</sub> and chemical components at the French EMEP sites

**Anna FONT, Aude BOURIN, Corentin GOUILLOU,  
Cécile DEBEVEC, Stéphane SAUVAGE**

**5 May 2022**

**23<sup>rd</sup> EMEP Task Force on Measurements and  
Modelling (TFMM)**



## Background

- **Fine particles (PM<sub>2.5</sub>)** are well-known to have an **impact on climate, ecosystems** as well as **human-health**
- **Background sites in western and central Europe exceeding the WHO limits** (5  $\mu\text{g m}^{-3}$  as annual limit; 15  $\mu\text{g m}^{-3}$  as daily mean) (Bressi et al., 2021)
- **Chemical composition** of PM<sub>2.5</sub> essential to assess the **sources** contributing to mass concentrations
- In **France, five background sites** monitored PM<sub>2.5</sub> mass concentrations and chemical composition between **2014 – 2020**
- **Temporal trends in PM<sub>2.5</sub>** is a common tool to evaluate **changes over** time and **assess the impact** of any possible **policy** aiming to reduce primary emissions
- Trends in atmospheric components not only influence by **changes in emissions** but also changes in **meteorology** and **transport patterns** that might occur



## Aims

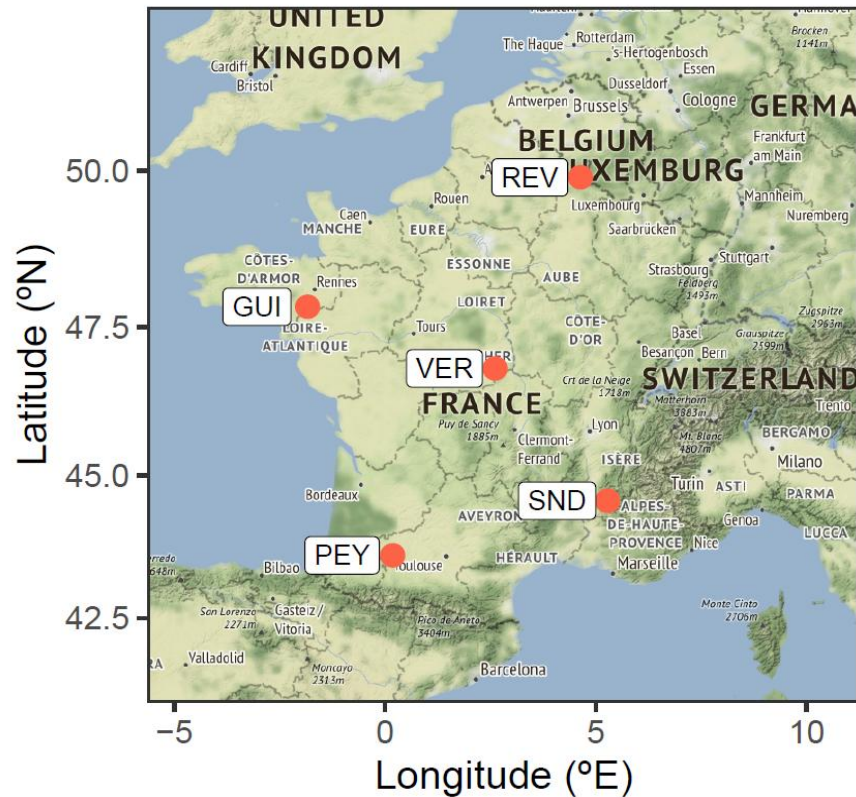
- To undertake the **chemical mass balance of PM<sub>2.5</sub>** mass concentrations based on the **main ions** along the years at the five remote sites monitoring PM<sub>2.5</sub> and chemical composition in **France in 2014 – 2020**.
  - To review **conversion factors** used to calculate source concentrations especially that used to account **organic matter (OM)** from **organic carbon (OC)**
- **To evaluate trends in PM<sub>2.5</sub>** concentrations in association with **changes in emission patterns removing** any possible **influence from meteorological and long-range transport** characteristics



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# French EMEP network (MERA): PM<sub>2.5</sub> chemical composition

MERA network



- MERA / EMEP sites where PM<sub>2.5</sub> chemical composition is available for 2014 - 2020
- PM<sub>2.5</sub> hourly mass concentrations (TEOM, TEOM-FDMS, BAM, FIDAS)
- Daily chemical composition every 6<sup>th</sup> day (14% year)
  - quartz filters (Pallflex Tissuquartz 2500 QAT-UP, 47 mm in diameter) + Partisol 2025i
  - OC & EC measurements: punch of 15 cm<sup>2</sup> is analysed by the Sunset instrument following EUSAAR2 protocol
  - Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>; and Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>: digestion in pure water of a punch of 15.85 cm<sup>2</sup> and analysis ion chromatography
  - Monthly field blanks; averaged by season and removed from filter measurements except for OC & EC
  - No LOD correction applied



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# Mass closure calculations and OC to OM conversion factor



$$PM_{2.5} = [OM] + [EC] + [SIA] + [sea\ salt] + [mineral\ dust] + [trace\ elements] + \epsilon \quad (1)$$

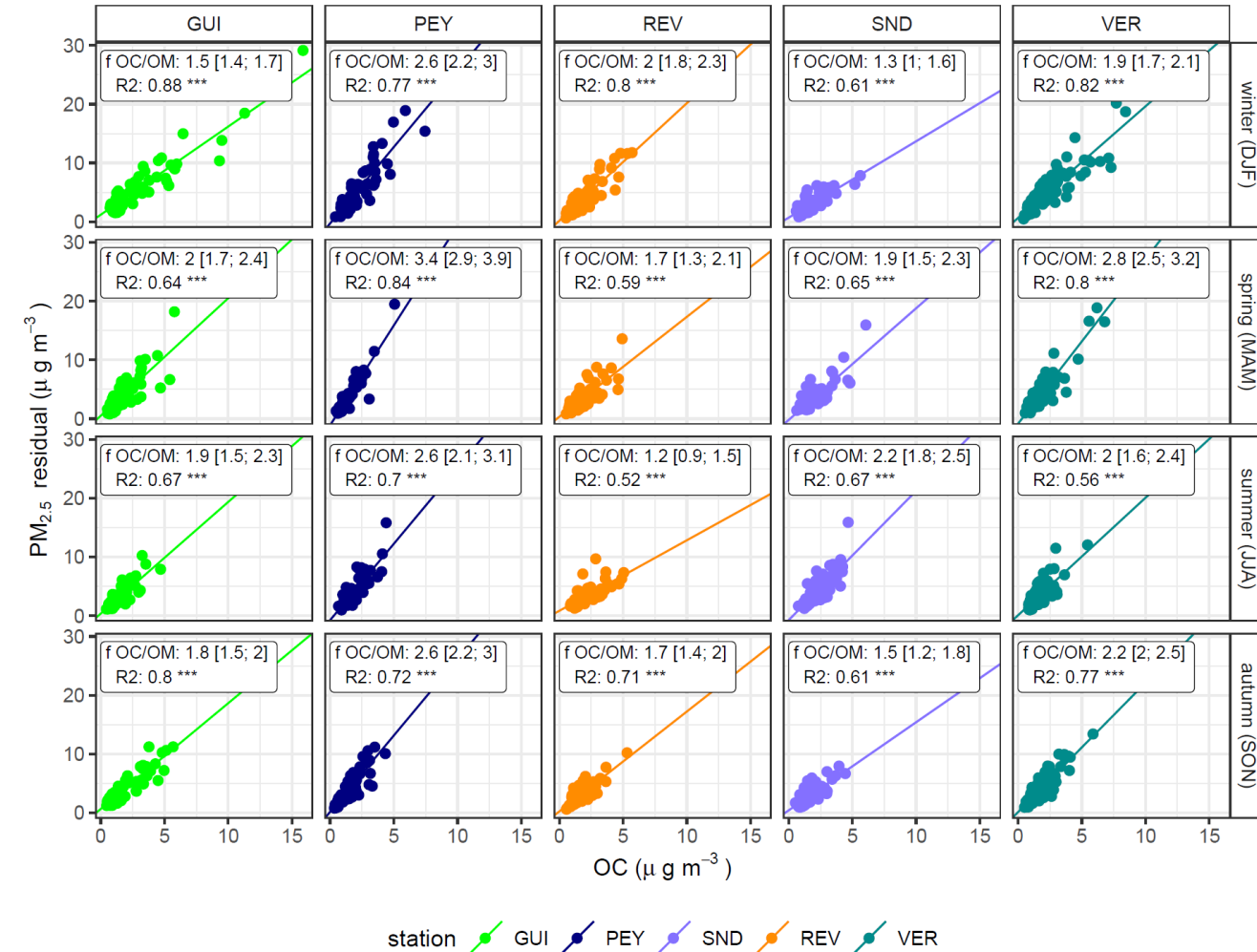
$$[SIA] = [NO_3^-] + [nss-SO_4^{2-}] + [NH_4^+] \quad (2)$$

$$[OM] = f_{OC:OM} * [OC] \quad (3)$$

Determination of  $f_{OC:OM}$  by **site**; and by **season** and **site**:

$$f_{OC:OM} = ([PM_{2.5}] - ([EC] + [SIA] + [sea\ salt] + [mineral\ dust] + [trace\ elements])/OC \quad (3)$$

Fitted by OLS





## Mass closure calculations and OC to OM conversion factor

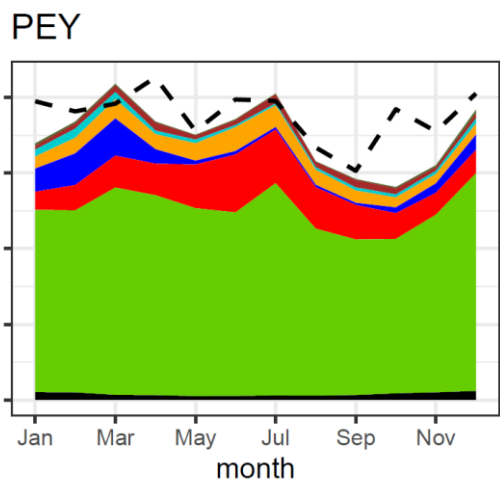
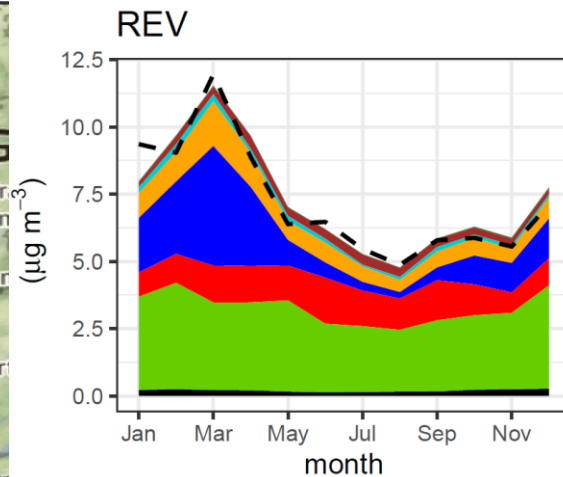
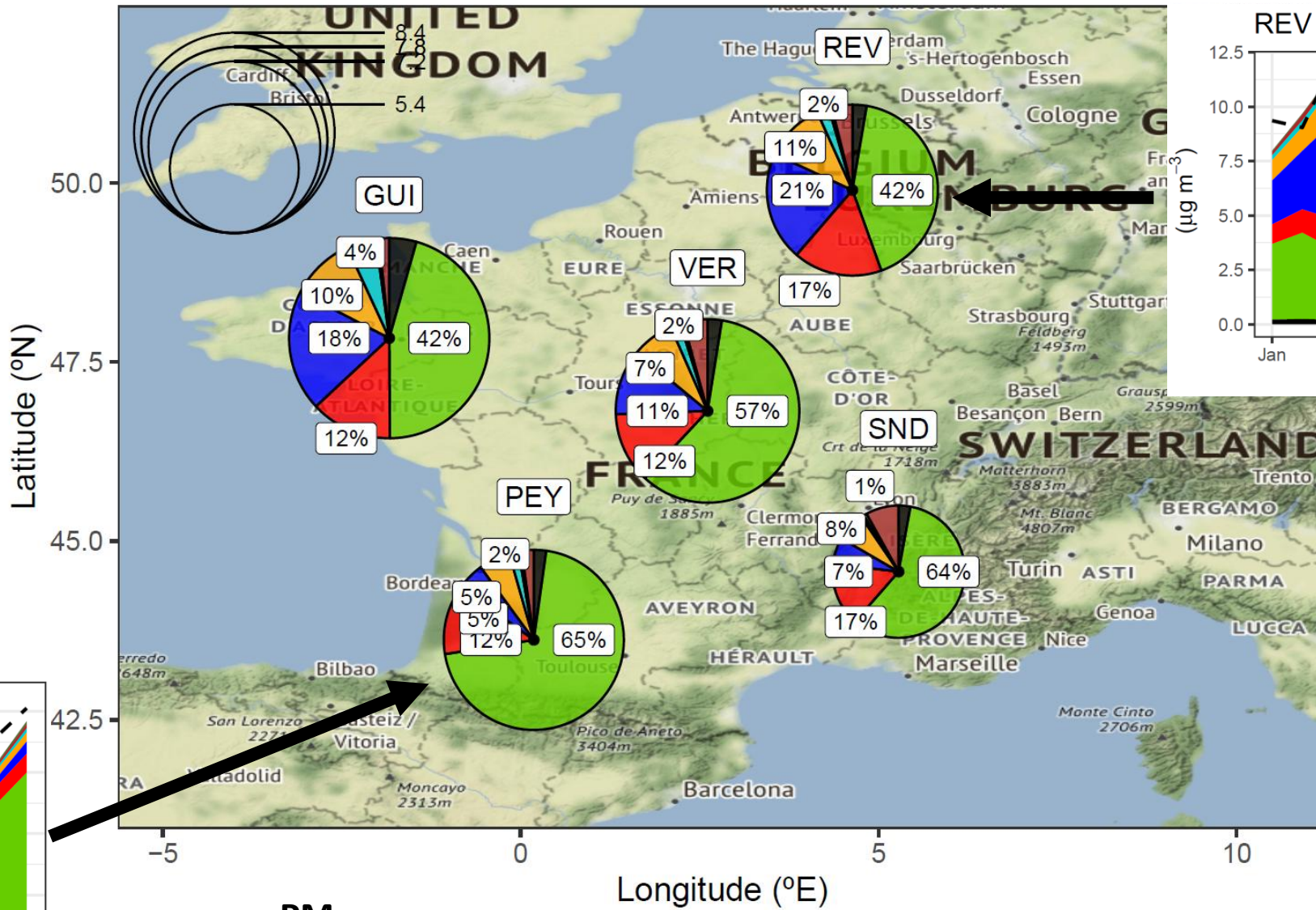
### *PM<sub>2.5</sub> mass closure: comparison with measurements*

		GUI	PEY	REV	SND	VER
<b>Fixed</b> $f_{oc:om} = 1.8$	Slope	0.94 [0.91 – 0.98]	0.71 [0.67 – 0.76]	0.94 [0.91 – 0.98]	0.95 [0.90 – 1.00]	0.84 [0.82 – 0.87]
	R <sup>2</sup>	0.88 <sup>***</sup>	0.70 <sup>***</sup>	0.88 <sup>***</sup>	0.72 <sup>***</sup>	0.89 <sup>***</sup>
	Avg res (%)	0.6 (7%)	2.1 (28%)	-0.4 (-6%)	-0.6 (-11%)	1.2 (16%)
<b>Single <math>f_{oc:om}</math> per site</b>	Slope	0.90 [0.87 – 0.94]	0.90 [0.84 – 0.95]	0.93 [0.90 – 0.96]	0.95 [0.90 – 1.00]	0.91 [0.88 -0.95]
	R <sup>2</sup>	0.88 <sup>***</sup>	0.69 <sup>***</sup>	0.89 <sup>***</sup>	0.72 <sup>***</sup>	0.88 <sup>***</sup>
	Avg res (%)	1.0 (12%)	0.5 (7%)	-0.2 (-3%)	-0.6 (-11%)	0.4 (5%)
<b><math>f_{oc:om}</math> season &amp; site</b>	Slope	0.91 [0.88 – 0.95]	0.91 [0.85 – 0.97]	0.95 [0.92 -0.98]	0.99 [0.94 – 1.04]	0.93 [0.90 – 0.97]
	R <sup>2</sup>	0.88 <sup>***</sup>	0.71 <sup>***</sup>	0.88 <sup>***</sup>	0.73 <sup>***</sup>	0.88 <sup>***</sup>
	Avg res (%)	0.6 (7%)	0.4 (5%)	-0.1 (-1%)	-0.5 (-9%)	0.4 (5%)

Better PM<sub>2.5</sub> mass closure achieved → reduction unaccounted mass



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--- PM<sub>2.5</sub>

- EC
- OM
- sea salt
- nssSO4
- NO3
- NH4
- nssK
- dust





## Methods: linear trends

- **Mann-Kendall test** to evaluate if **monotonic trends**
- **Theil-Sen method** to calculate the temporal trend (**rate of change**): median of all possible trends for all x-y date points combinations.
  - Monthly means from hourly PM<sub>2.5</sub> data
  - Monthly means from daily PM<sub>2.5</sub> and chemical composition data

**Mean trends (95% confidence interval)**

site	Hourly PM <sub>2.5</sub> data		Daily MERA filters	
	Trend (µg m <sup>-3</sup> year <sup>-1</sup> )	Trend (% year <sup>-1</sup> )	Trend (µg m <sup>-3</sup> year <sup>-1</sup> )	Trend (% year <sup>-1</sup> )
GUI <sup>A</sup>	-0.4 [-0.8, -0.1]*	-4.3 [-7.5, -0.8]*	-0.5 [-0.9, -0.2]**	-5.7 [-8.8, -2.3]**
PEY	-0.5 [-0.7, -0.3]***	-5.5 [-7.2, -3.8]***	-0.5 [-0.7, -0.3]***	-5.7 [-6.9, -3.3]***
REV	-0.5 [-0.7, -0.4]***	-6.1 [-7.5, -4.6]***	-0.7 [-0.9, -0.4]***	-7.2 [-8.9, -5.1]***
SND	-0.3 [-0.5, -0.1]**	-4.7 [-6.9, -2.4]**	-0.3 [-0.5, -0.1]**	-5.3 [-7.8, -2.7]**
VER	-0.6 [-0.9, -0.3]***	-6.5 [-9.0, -4.1]***	-0.7 [-1.0, -0.4]***	-8.0 [-9.9, -5.3]***

<sup>A</sup> trends calculated for 2014-2019

\*\*\*  $p < 0.001$  \*\*  $p < 0.01$  \*  $p < 0.05$  +  $p < 0.1$





## Methods: random-forest modelling for de-weathered time series

- **Primary emission rates, meteorological conditions** and **long-range transport patterns** influence **PM<sub>2.5</sub> concentrations** as well as its **chemical components**
- **Random-forest modelling** is a **machine-learning** method based on **decision-trees** (Grange et al., 2017)
- **Multiple trees** were built to reproduce concentrations using **temporal, meteorological and transport explanatory variables** using 70% of the data time series; the **remaining 30%** of the data is used **to evaluate the performance** of the model
- **De-weathered algorithm** calculates the time series for a given atmospheric component based on an iterative
- **Limitation:** chemical composition is based on **daily** filter **measurements** sampled every 6<sup>th</sup> day while meteorological and long-range transport data is available at a higher time resolution
  - **Proposed solution:** use 3-hourly met data and long-range transport data to predict 3 –h chemical data; daily averages to compared modelled vs daily measured data

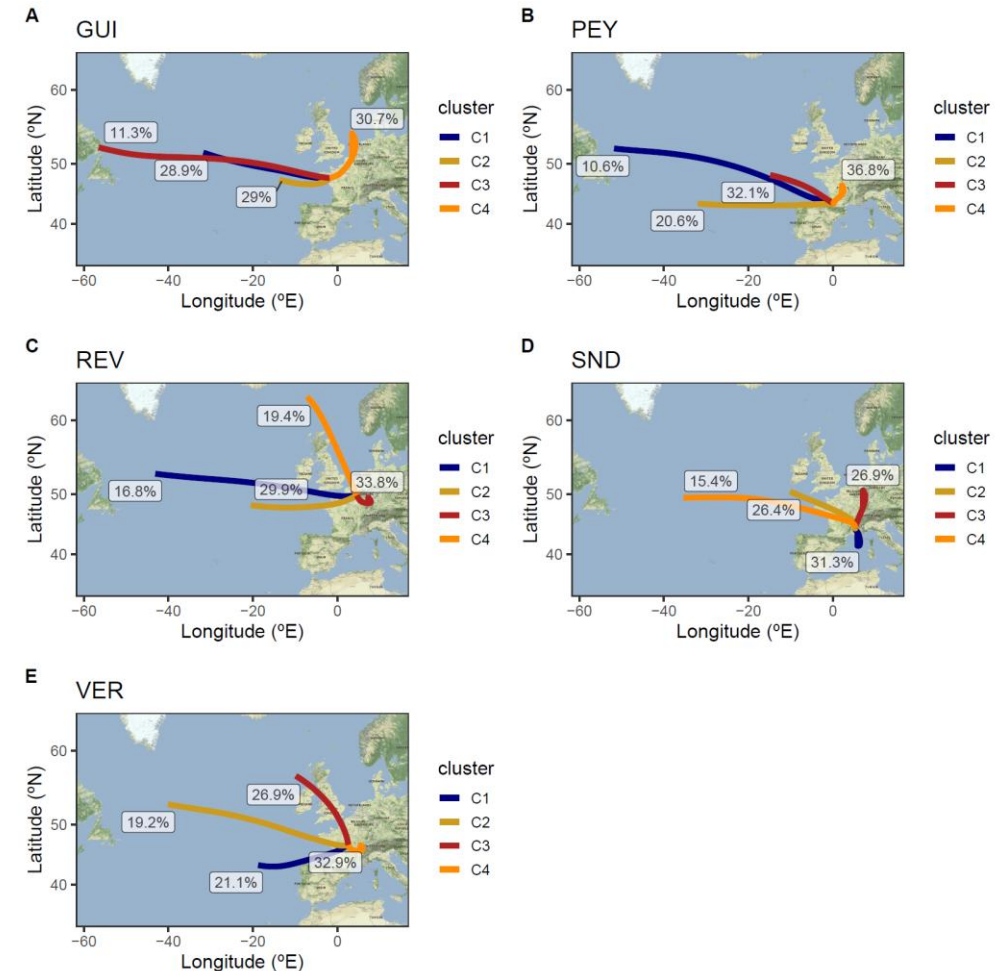




# Methods: random-forest modelling for de-weathered time series

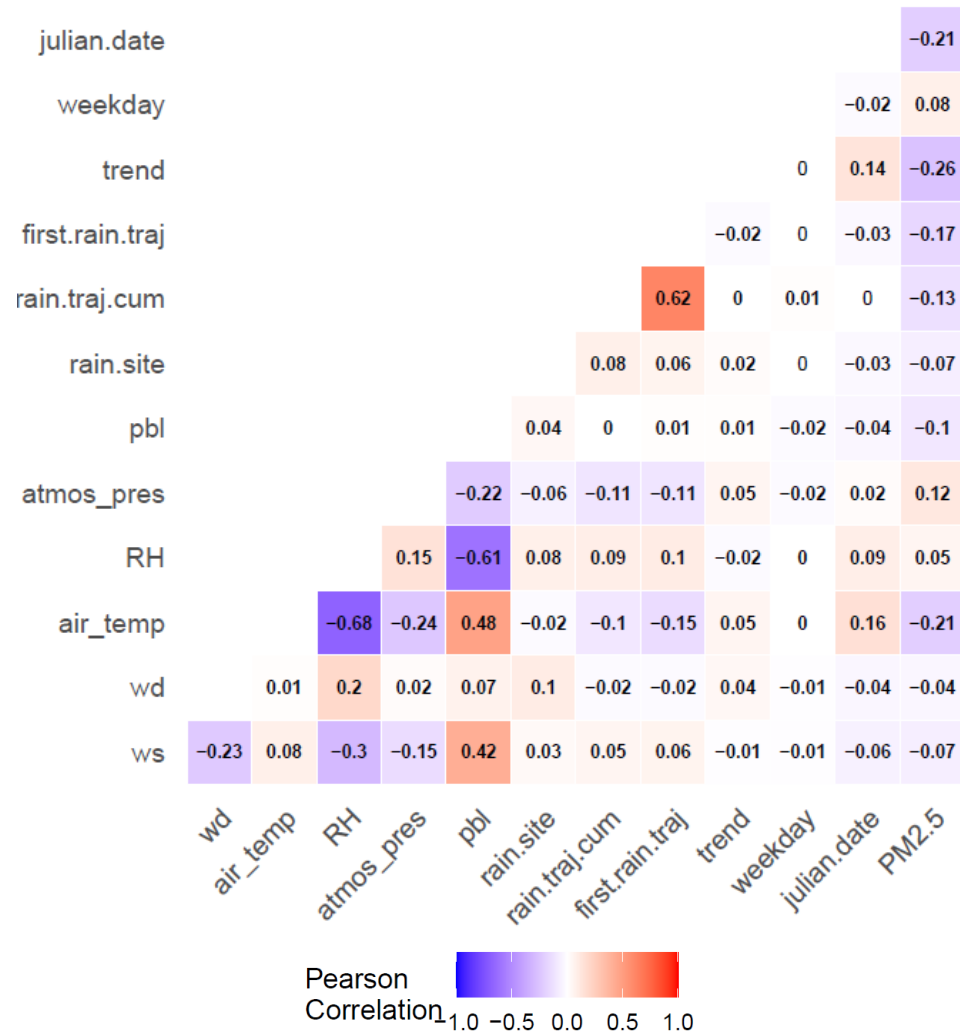
- **Temporal variables**
  - Day of the week
  - Julian date (to capture seasonal variability)
  - Decimal date (to capture long-term trends)
- **Meteorological variables**
  - Wind speed
  - Wind direction
  - Temperature
  - Atmospheric pressure
  - Relative humidity
  - Mixing layer height (from GFS model)
  - Precipitation at the site (from GFS model)
- **Long-range transport**
  - Backtrajectory cluster (Hysplit - GFS; release at 500 m)
  - Cumulative rain along the trajectory
  - Hour back main rain episode ( $> 0.2$  mm)

## Main backtrajectory cluster





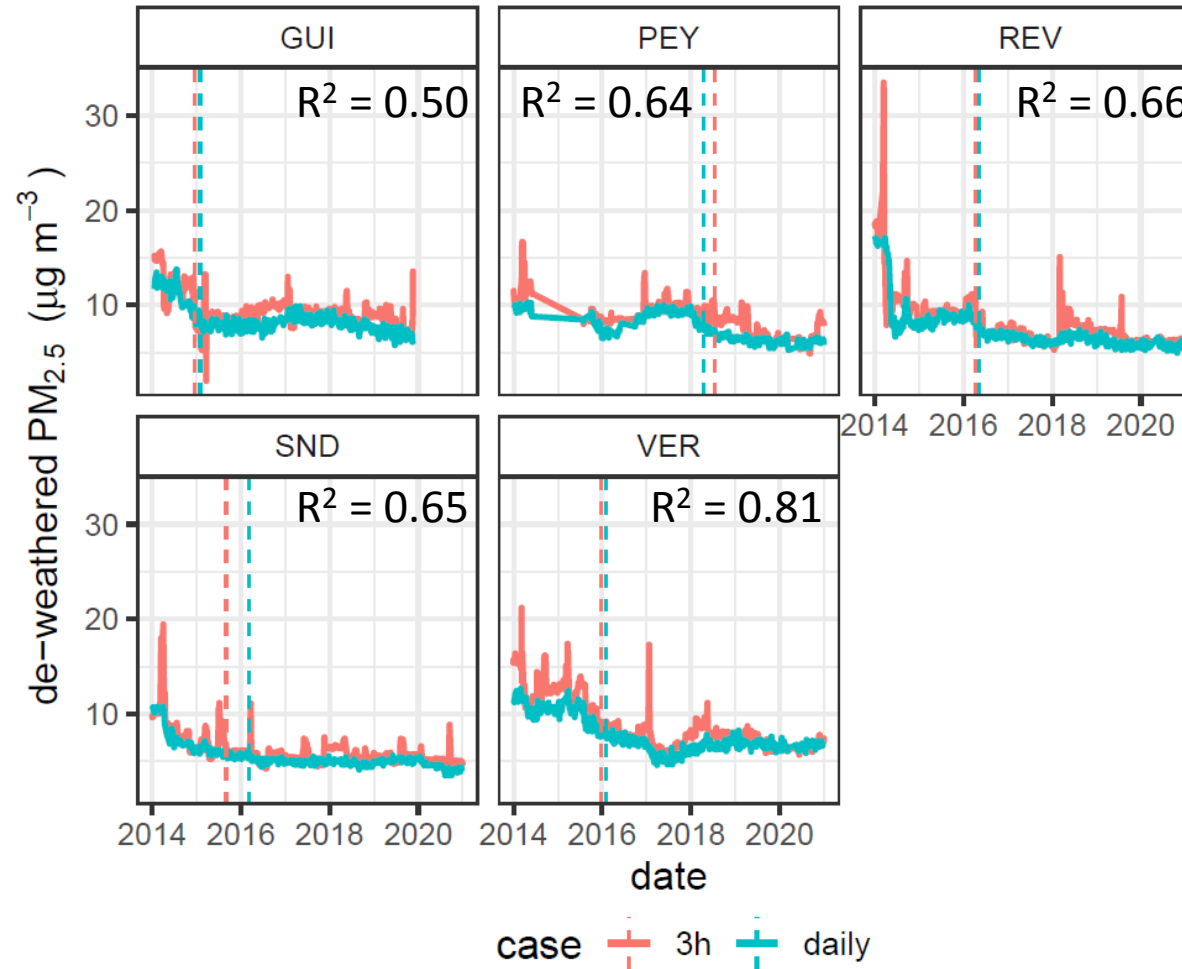
## Methods: Pearson correlation between explanatory variables



### Variables chosen:

- Wind speed
- Wind direction
- Air temperature
- Atmospheric pressure
- Cluster
- Cumulative rain along back-trajectory
- Trend
- Weekday
- Julian date

# Comparison de-weathered time series: daily vs 3 h explanatory data



Vertical line: **change point** (based on the Buishand Range Test)



# Comparison de-weathered time series: daily vs 3 h explanatory data

## Evaluation of the random-forest model

site	Daily explanatory data			3 h explanatory data		
	Slope [95% CI]	RMSE ( $\mu\text{g m}^{-3}$ )	R <sup>2</sup>	Slope [95% CI]	RMSE ( $\mu\text{g m}^{-3}$ )	R <sup>2</sup>
GUI <sup>A</sup>	0.752 [0.647, 0.873]***	5.09	0.41	0.940 [0.938, 0.942]***	1.67	0.96
PEY	0.754 [0.642, 0.884]***	3.83	0.40	0.910 [0.908, 0.912]***	1.16	0.95
REV	1.026 [0.881, 1.194]***	5.44	0.28	0.923 [0.921, 0.926]***	1.49	0.95
SND	0.679 [0.593, 0.776]***	3.37	0.44	0.905 [0.903, 0.907]***	1.10	0.94
VER	0.773 [0.687, 0.870]***	5.29	0.57	0.947 [0.946, 0.949]***	1.45	0.97

## Linear trends (Theil Sen slope)

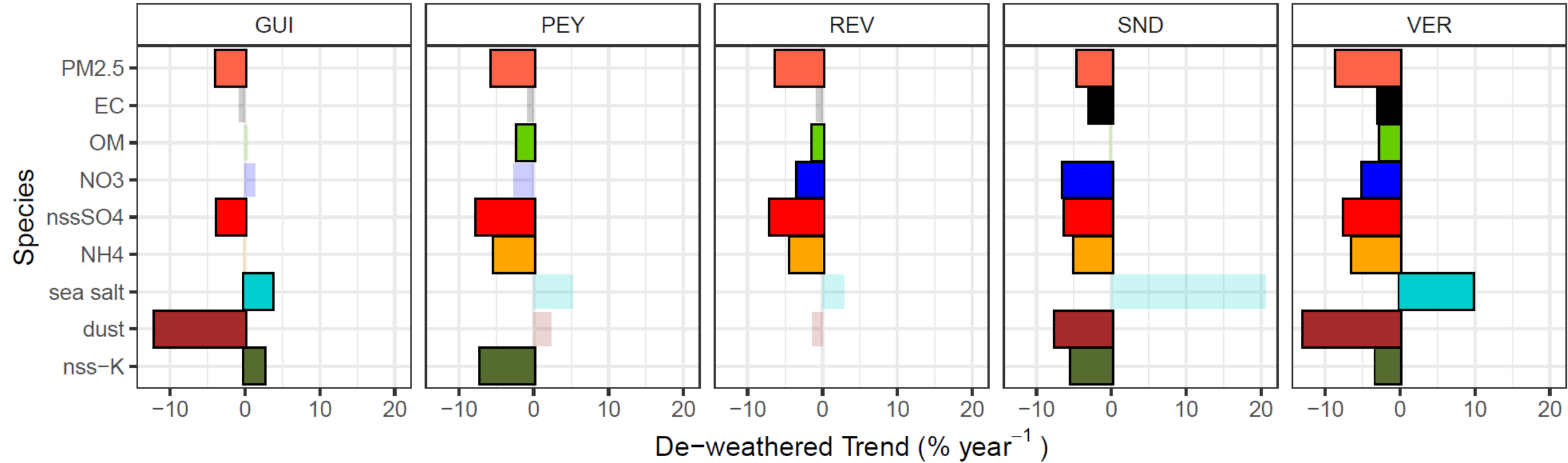
site	Daily explanatory data		3-hourly explanatory data	
	Trend ( $\mu\text{g m}^{-3} \text{ year}^{-1}$ )	Trend (% year <sup>-1</sup> )	Trend ( $\mu\text{g m}^{-3} \text{ year}^{-1}$ )	Trend (% year <sup>-1</sup> )
GUI <sup>A</sup>	-0.50 [-0.25, -0.79]***	-5 [-3, -8]***	-0.41 [-0.15, -0.69]***	-4 [-2, -6]***
PEY	-0.57 [-0.45, -0.68]***	-6 [-5, -7]***	-0.64 [-0.48, -0.88]***	-6 [-5, -7]***
REV	-0.51 [-0.41, -0.64]***	-6 [-5, -7]***	-0.63 [-0.56, -0.73]***	-7 [-6, -8]**
SND	-0.36 [-0.26, -0.44]***	-6 [-4, -7]***	-0.30 [-0.19, -0.44]***	-4 [-3, -6]***
VER	-0.62 [-0.35, -0.84]***	-7 [-4, -9]***	-0.96 [-0.67, -1.2]***	-9 [-7, -11]***

<sup>A</sup> trends calculated for 2014-2019

\*\*\*  $p < 0.001$  \*\*  $p < 0.01$  \*  $p < 0.05$  +  $p < 0.1$



# Results: Theil-Sen trends for de-weathered time series (3-h model)

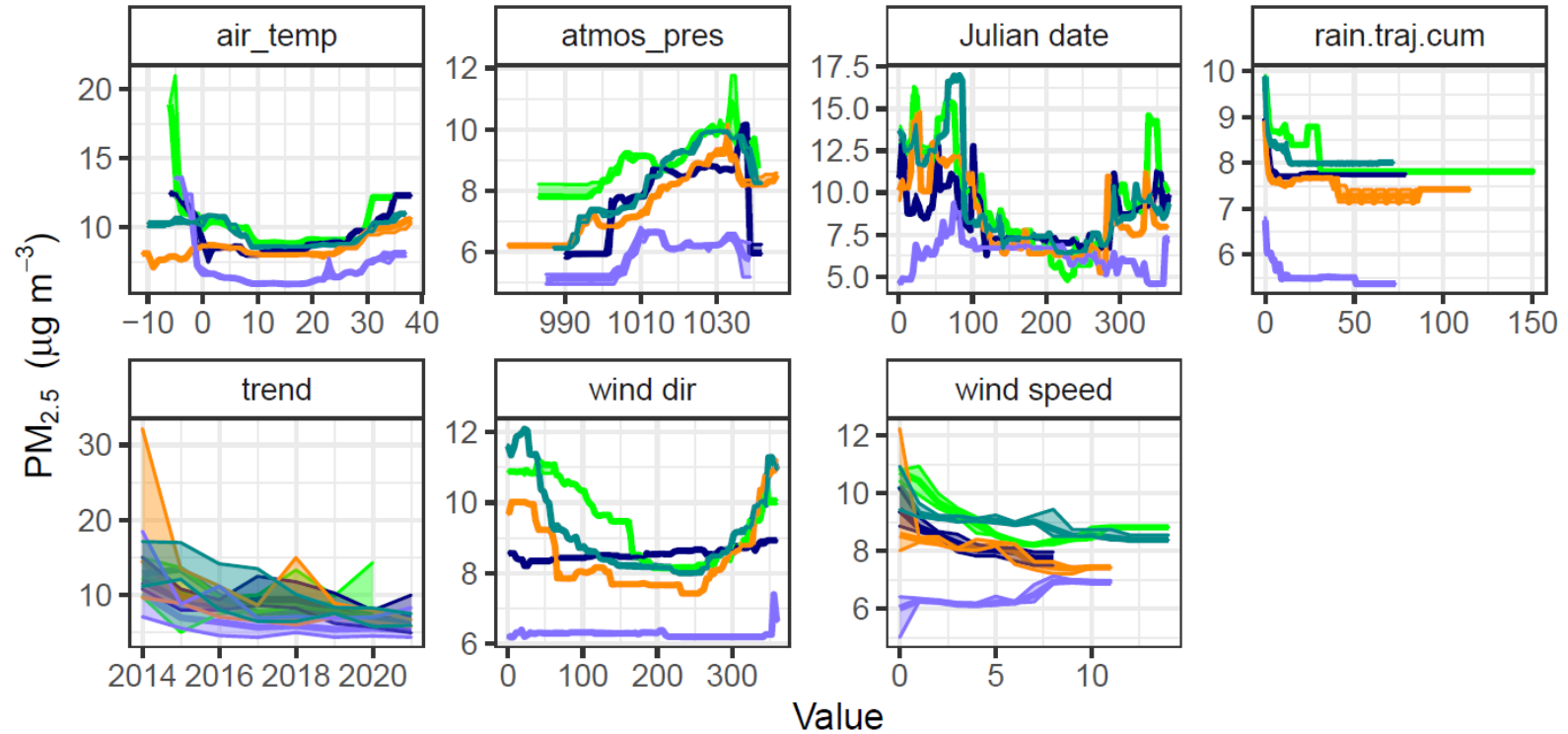
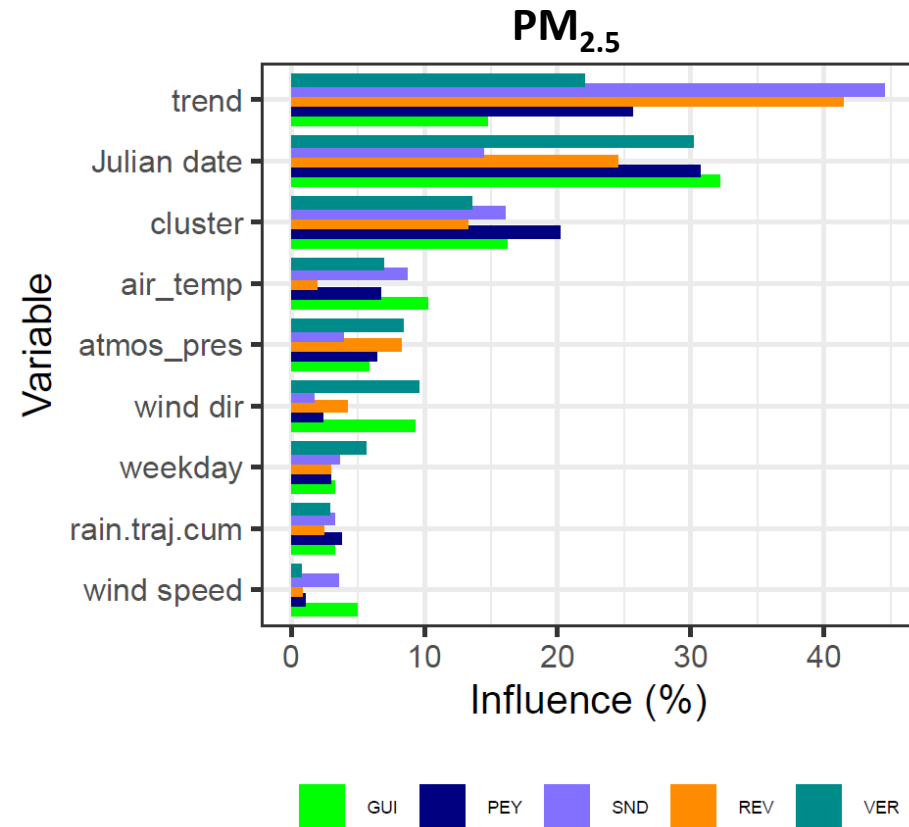


Solid bar: trend significant at  $p < 0.05$



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# Results: influence of variables & partial dependency plots







## Conclusions

- **Annual PM<sub>2.5</sub>** concentrations at background sites in France ranged from **4.8 µg m<sup>-3</sup> to 11.6 µg m<sup>-3</sup>** for the period **2014 – 2020**, with the **majority of sites / years** exceeding the annual **WHO limit value** (5 µg m<sup>-3</sup>)
- **Better PM<sub>2.5</sub> mass closure** was achieved when using **site and seasonal specific  $f_{OC:OM}$  ratios**, with the unaccounted mass from -11% to 28% (fixed  $f_{OC:OM} = 1.8$ ); to -9% to 7%.
- The **chemical composition of fine aerosols** was at the French EMEP sites for 2014 - 2020: OM (42–65%), non-sea-salt sulphate (17–21%), nitrate (5–21%), ammonium (12–5%), mineral dust (2–9%), EC (2–4%), sea salt (1–4%) and non-sea-salt potassium (~1%).
- **OM was the main component of PM<sub>2.5</sub>** all year long
- **SIA** contributed mostly in **spring**
- The **contribution of OM** to PM<sub>2.5</sub> was **larger at the southern sites** whereas the contribution of **SIA** was **larger at the northern sites**.





## Conclusions

- **Better reproduction of PM<sub>2.5</sub> concentrations by random-forest modelling** when using **3-hourly** met and long-range transport information ( $R^2 > 0.90$  and  $RMSE < 1.5 \mu\text{g m}^{-3}$ )
- **Temporal variables had greater** role in explaining the **variability in PM<sub>2.5</sub> concentrations** (15 – 45%); followed by the **cluster variable** (~15%) representing the long-range transport
- De-weathered time series for PM<sub>2.5</sub> and the main components were built using the RF modelling
- All sites observed **downward trends in PM<sub>2.5</sub>**, at a rate of **-4 to -9% year<sup>-1</sup>** for the period **2014 - 2020**
- Downward trends in PM<sub>2.5</sub> were coincidental with the **downward trends in nss-SO<sub>4</sub><sup>2-</sup>** (**-4 to -8 % year<sup>-1</sup>**) associated with the decrease in SO<sub>2</sub> emissions (mean decrease of -8% year<sup>-1</sup> between 2014 – 2019 in France)
- **Reduction in NO<sub>3</sub><sup>-</sup>** concentrations from reduced NO<sub>x</sub> emissions **less evident** at the French EMEP sites: **3 out of 5 sites observed significant downward trends** (REV, SND and VER: -3% year<sup>-1</sup> to -6% year<sup>-1</sup>). For 2014-2020, NO<sub>x</sub> emissions in France decreased at a rate of -5% year<sup>-1</sup>.
- **Reduction in biomass burning** was observed with downward trends in **nss-K<sup>+</sup> at three sites** (VER, SND and PEY: -3 to -7 % year<sup>-1</sup>). One site observed a **significant upward trend (GUI)** (2% year<sup>-1</sup>)





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# Trends in PM<sub>2.5</sub> and chemical components at the French EMEP sites

**Many thanks for your attention**

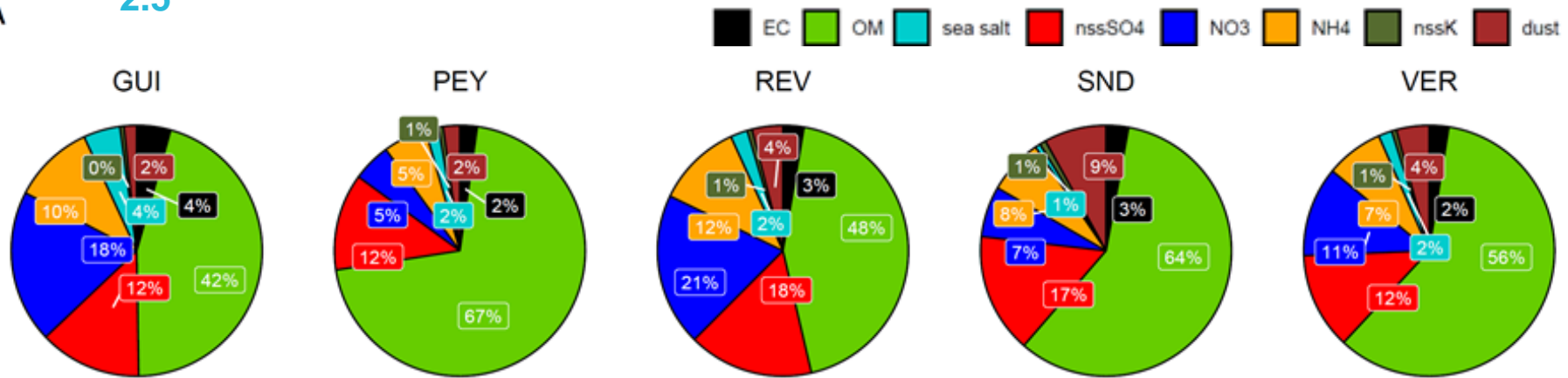
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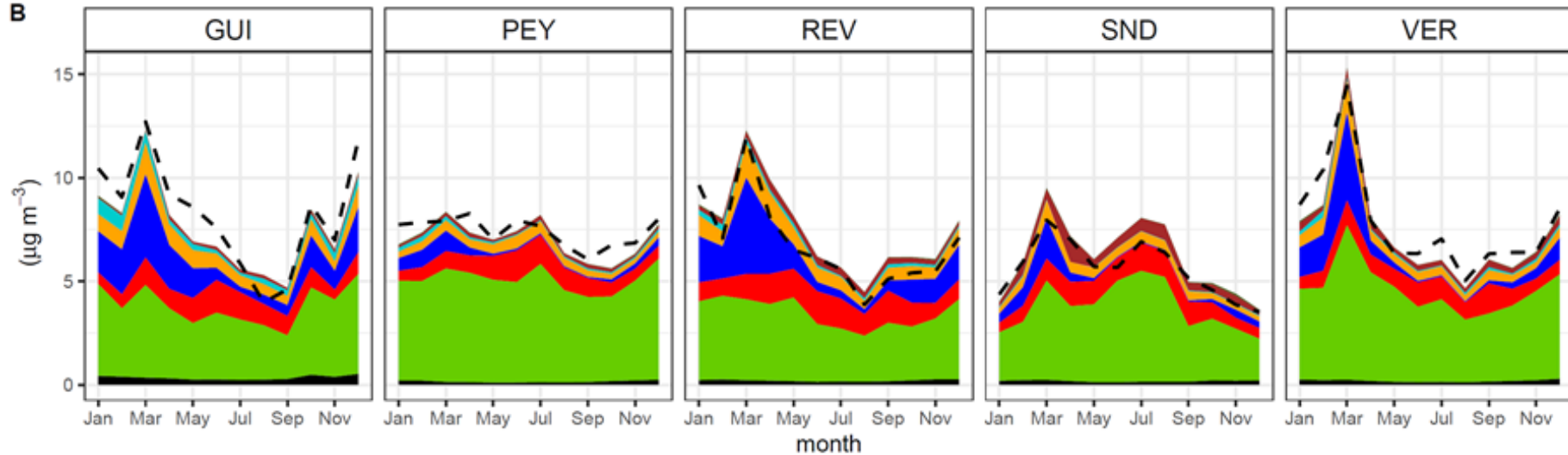


# PM<sub>2.5</sub> mass closure

A



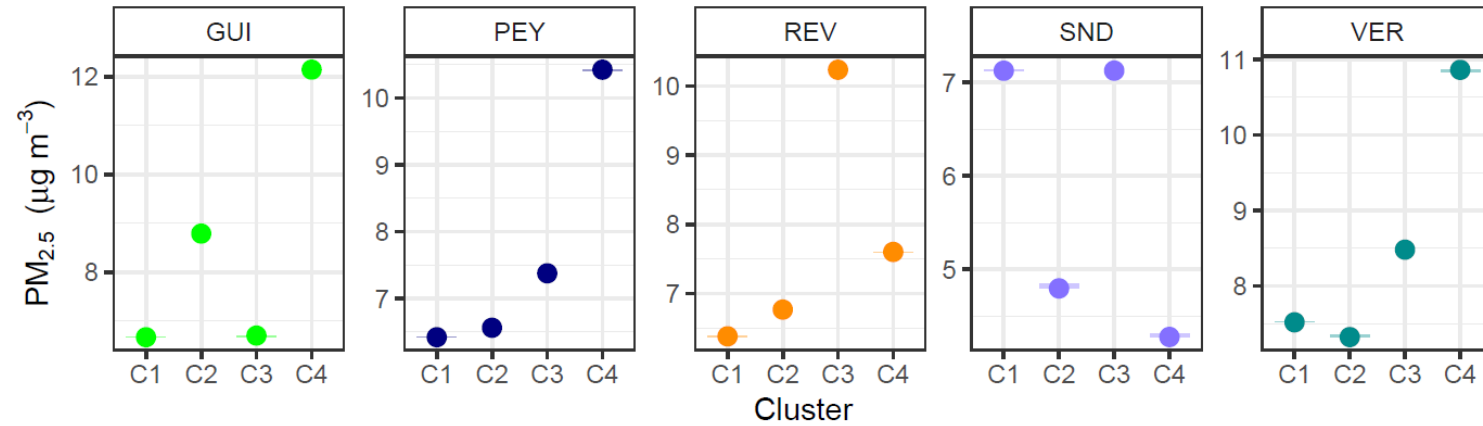
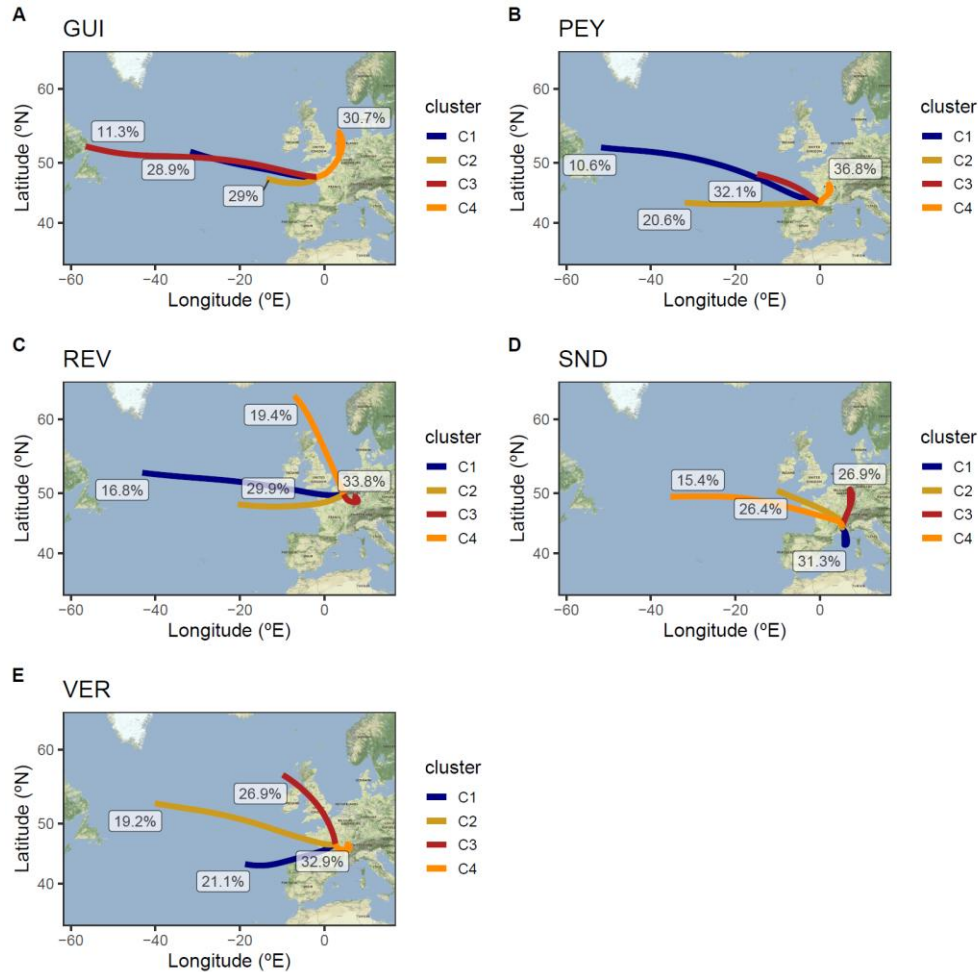
B





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# Results: partial dependency plots for the cluster variable



● GUI ● PEY ● SND ● REV ● VER