Trends in PM2.5 and chemical component at the French EMEP sites

Anna Font, Aude Bourin, Corentin Gouillou, Cécile Debevec, Stéphane Sauvage

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23rd EMEP Task Force on Measurements and Modelling (TFMM)

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Background

- **Fine particles ($PM_{2.5}$)** 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 µg m^{-3} as annual limit; 15 µg m^{-3} as daily mean) (Bressi et al., 2021)
- **Chemical composition** of $PM_{2.5}$ essential to assess the **sources** contributing to mass concentrations
- In **France**, **five background sites** monitored $PM_{2.5}$ mass concentrations and chemical composition between **2014 – 2020**
- **Temporal trends in $PM_{2.5}$** 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

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Aims

- To undertake the **chemical mass balance of $PM_{2.5}$** mass concentrations based on the **main ions** along the years at the five remote sites monitoring $PM_{2.5}$ 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 $PM_{2.5}$** concentrations in association with **changes in emission patterns removing** any possible **influence from meteorological and long-range transport** characteristics

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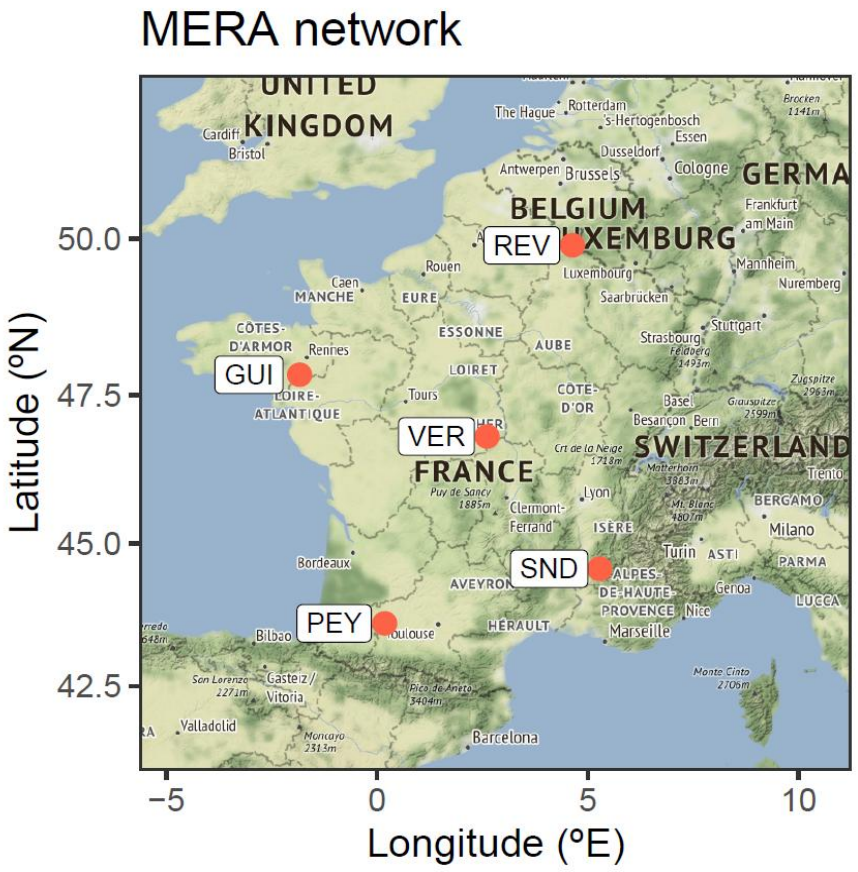
French EMEP network (MERA): $PM_{2.5}$ chemical composition



- **MERA / EMEP** sites where **$PM_{2.5}$ chemical composition** is available for **2014 - 2020**
- **$PM_{2.5}$ hourly mass concentrations** (TEOM, TEOM-FDMS, BAM, FIDAS)
- **Daily chemical composition** every 6th day (14% year)
  - quartz filters (Pallflex Tissuquartz 2500 QAT-UP, 47 mm in diameter) + Partisol 2025i
  - **OC & EC measurements:** punch of 15 cm^2 is analysed by the Sunset instrument following EUSAAR2 protocol
  - **Ca^{2+}, K^+, Mg^{2+}, Na^+, NH_4^+; and Cl^-, NO_3^-, SO_4^{2-}** : digestion in pure water of a punch of 15.85 cm^2 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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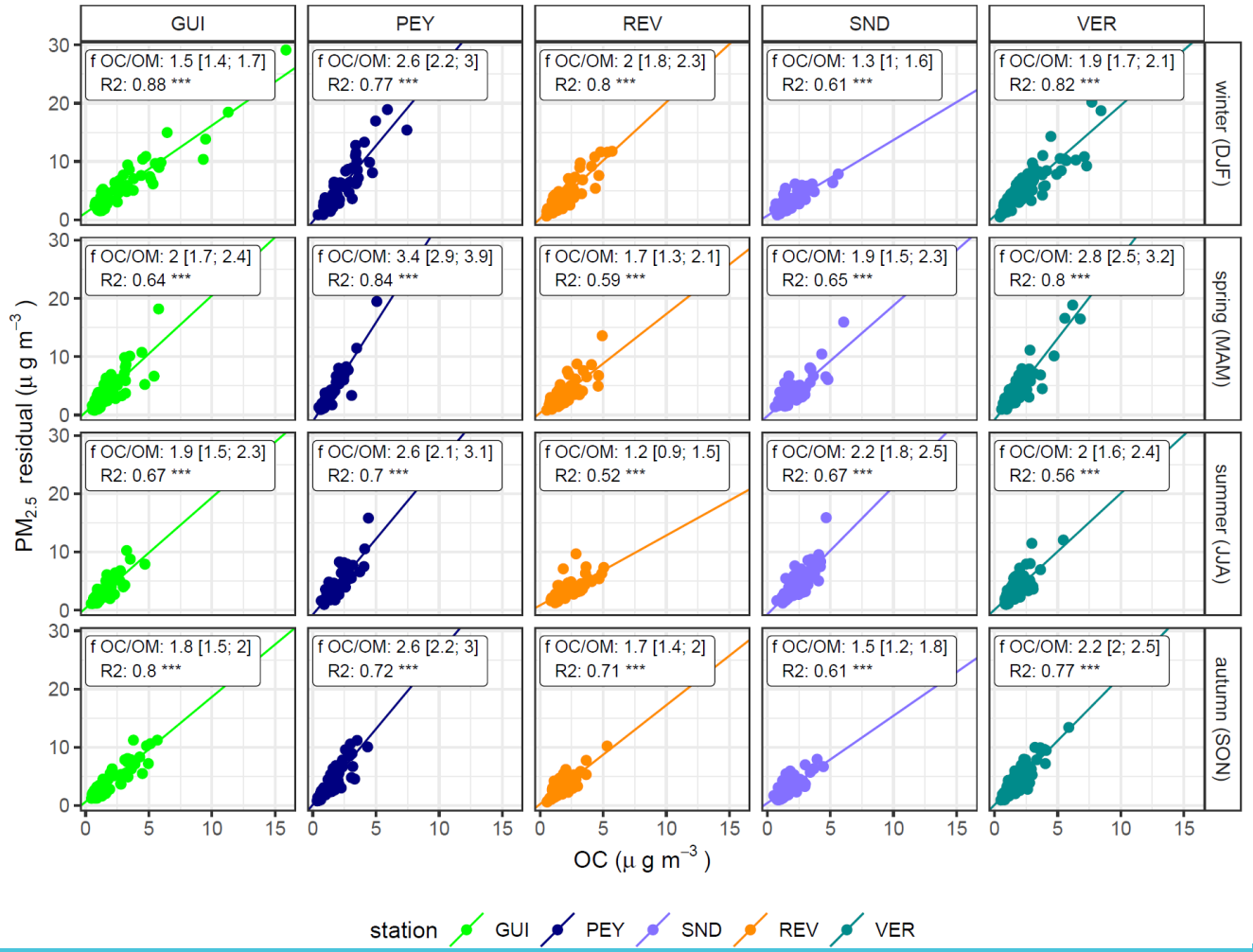
Mass closure calculations and OC to OM conversion factor



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

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

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

Fitted by OLS

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Mass closure calculations and OC to OM conversion factor

$PM_{2.5}$ mass closure: comparison with measurements

		GUI	PEY	REV	SND	VER
Fixed $f_{OC:OM}$ = 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^2	0.88^{***}	0.70^{***}	0.88^{***}	0.72^{***}	0.89^{***}
	Avg res (%)	0.6 (7%)	2.1 (28%)	-0.4 (-6%)	-0.6 (-11%)	1.2 (16%)
Single $f_{OC:OM}$ per site	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^2	0.88^{***}	0.69^{***}	0.89^{***}	0.72^{***}	0.88^{***}
	Avg res (%)	1.0 (12%)	0.5 (7%)	-0.2 (-3%)	-0.6 (-11%)	0.4 (5%)
$f_{OC:OM}$ season & site	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^2	0.88^{***}	0.71^{***}	0.88^{***}	0.73^{***}	0.88^{***}
	Avg res (%)	0.6 (7%)	0.4 (5%)	-0.1 (-1%)	-0.5 (-9%)	0.4 (5%)

Better $PM_{2.5}$ mass closure achieved → **reduction unaccounted mass**

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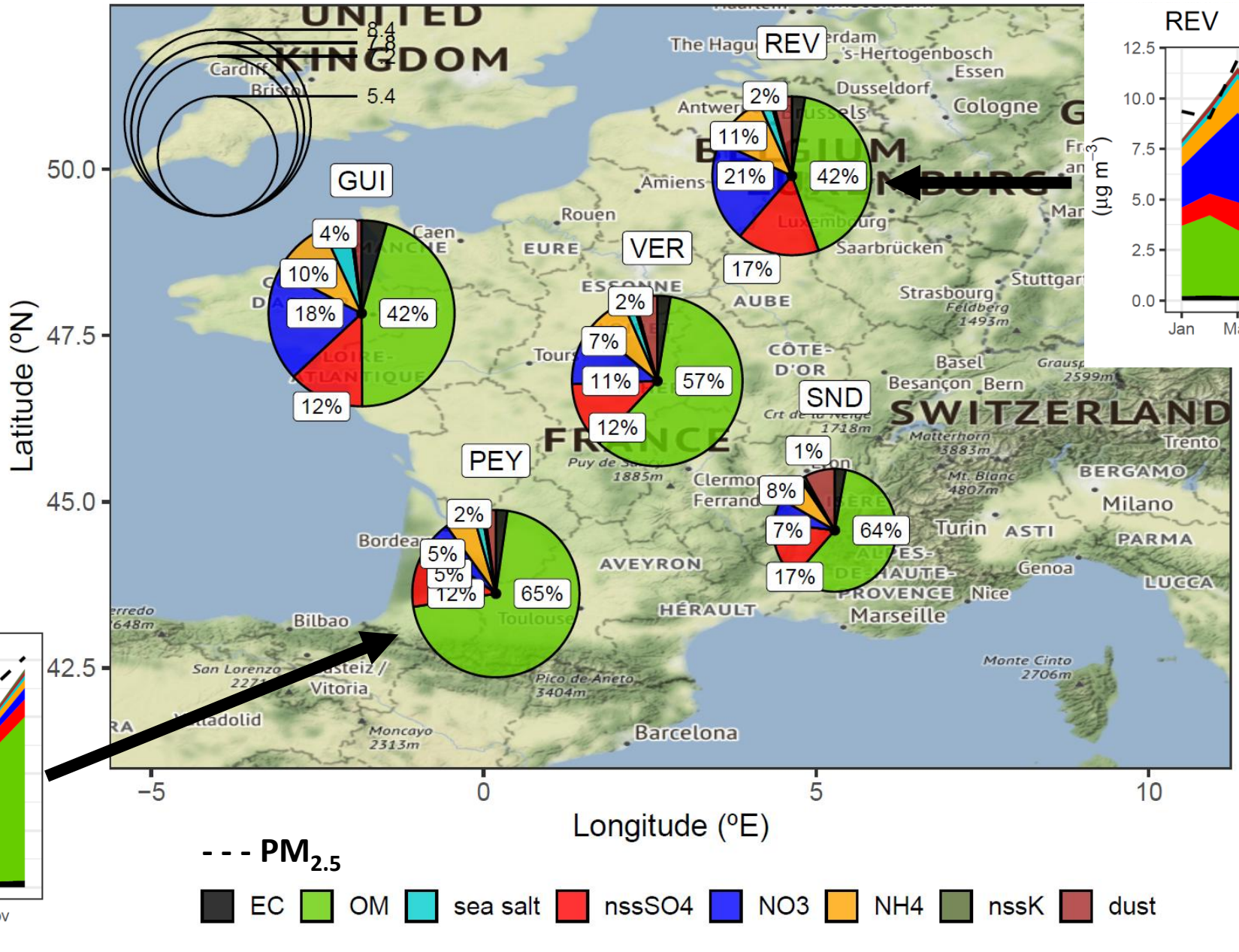

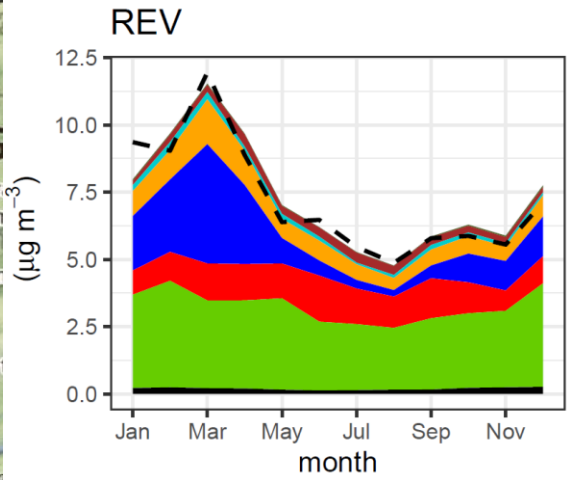

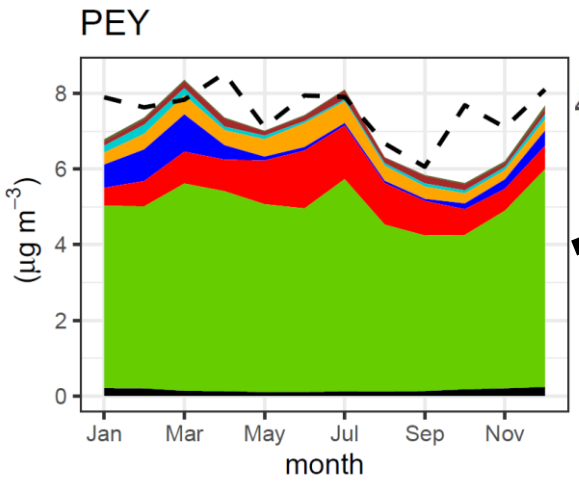

- - - $PM_{2.5}$

EC OM sea salt nssSO4 NO3 NH4 nssK dust

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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 $PM_{2.5}$ data
  - Monthly means from daily $PM_{2.5}$ and chemical composition data

Mean trends (95% confidence interval)

	Hourly $PM_{2.5}$ data		Daily MERA filters	
site	Trend (µg m^{-3} $year^{-1}$)	Trend (% $year^{-1}$)	Trend (µg m^{-3} $year^{-1}$)	Trend (% $year^{-1}$)
GUI[A]	-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]***

[A] trends calculated for 2014-2019
*** $p < 0.001$ ** $p < 0.01$ * $p < 0.05$ + $p < 0.1$

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

- **Primary emission rates, meteorological conditions** and **long-range transport patterns influence $PM_{2.5}$ 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 6th 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

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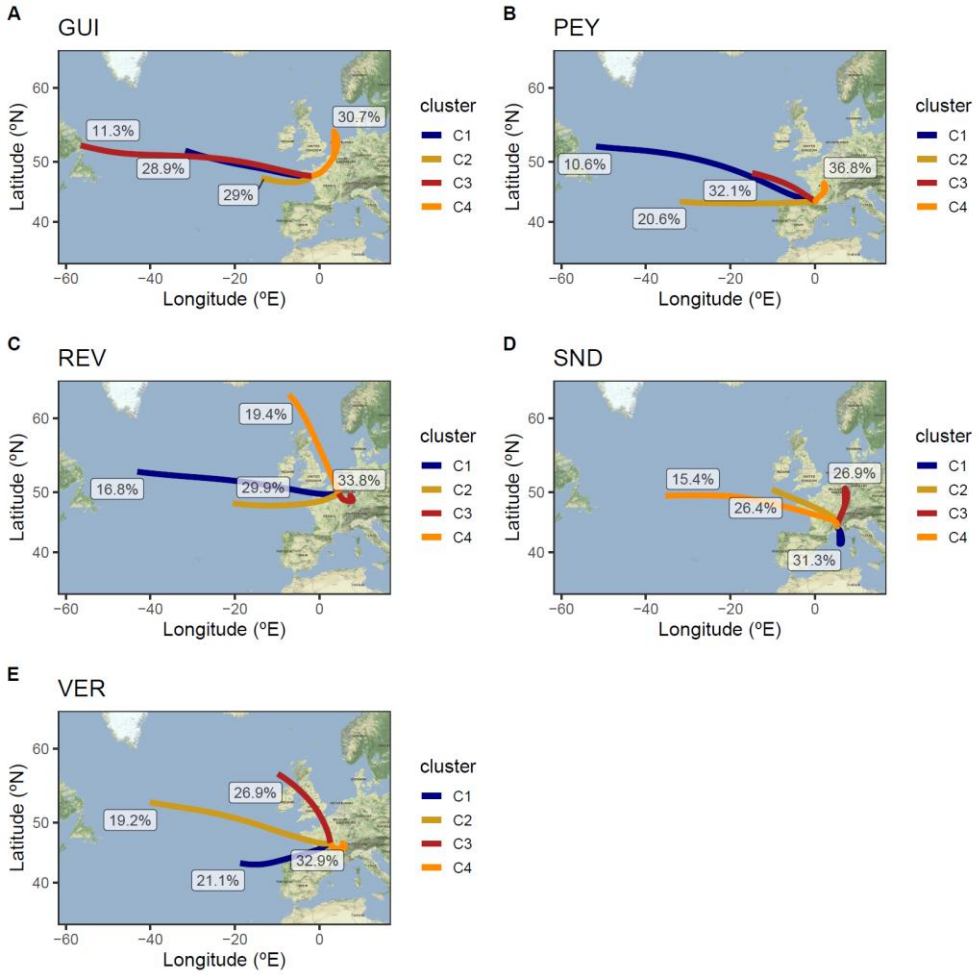
Methods: random-forest modelling for de-weathered time series

- **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



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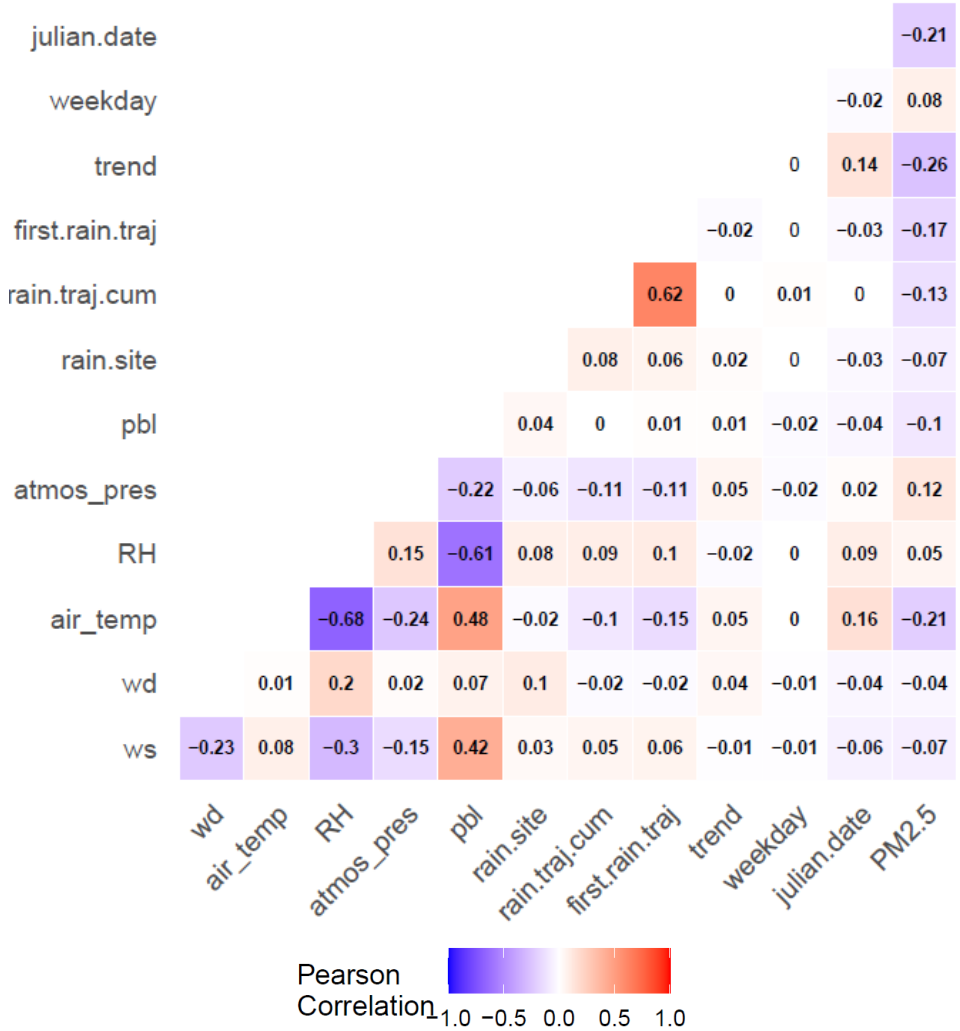
Methods: Pearson correlation between explanatory variables



Variables chosen:

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

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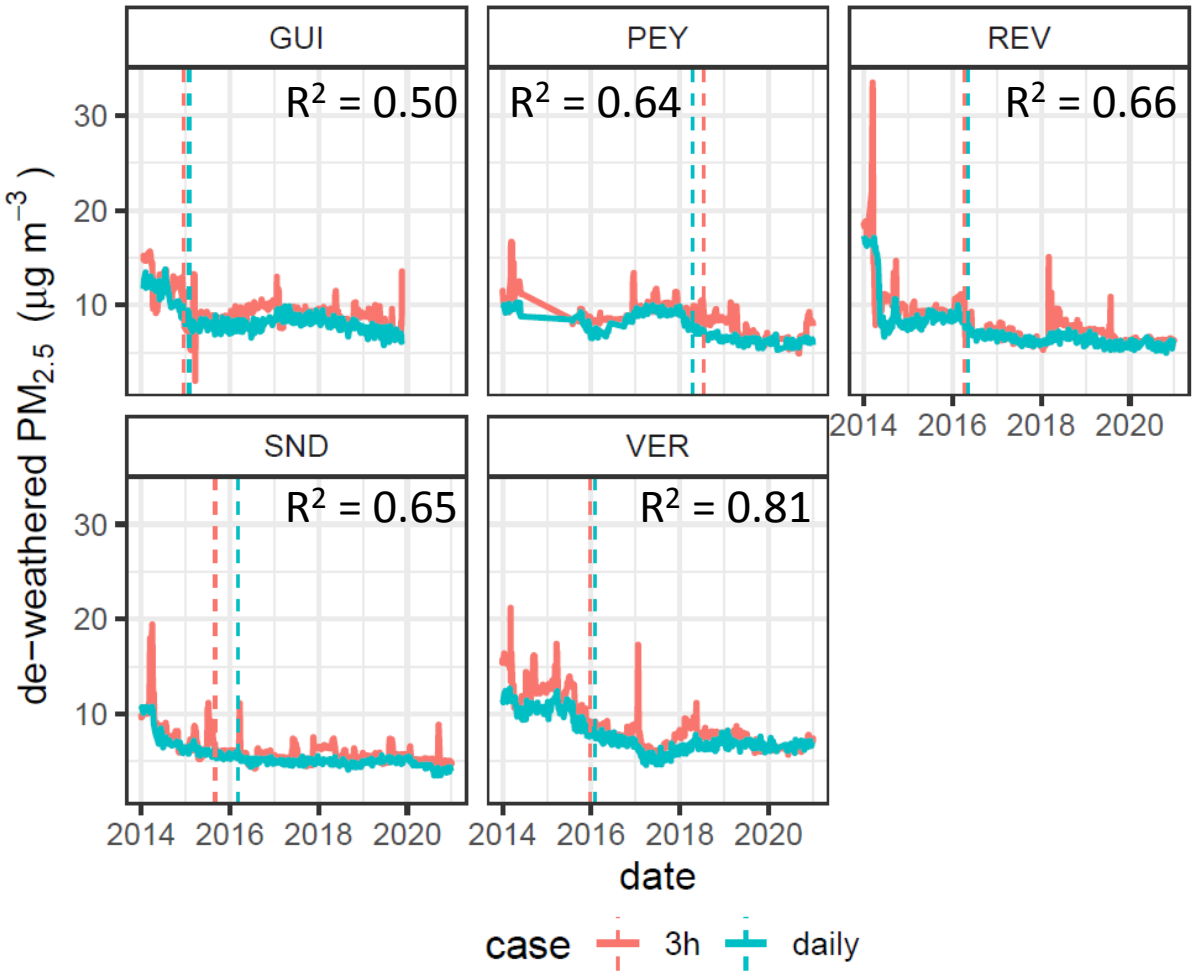
Comparison de-weathered time series: daily *vs* 3 h explanatory data



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

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

Evaluation of the random-forest model

	Daily explanatory data			3 h explanatory data		
site	Slope [95% CI]	RMSE (µg m^{-3})	R^2	Slope [95% CI]	RMSE (µg m^{-3})	R^2
GUI[A]	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)

	Daily explanatory data		3-hourly explanatory data	
site	Trend (µg m^{-3} year^{-1})	Trend (% year^{-1})	Trend (µg m^{-3} year^{-1})	Trend (% year^{-1})
GUI[A]	-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]***

[A] trends calculated for 2014-2019

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

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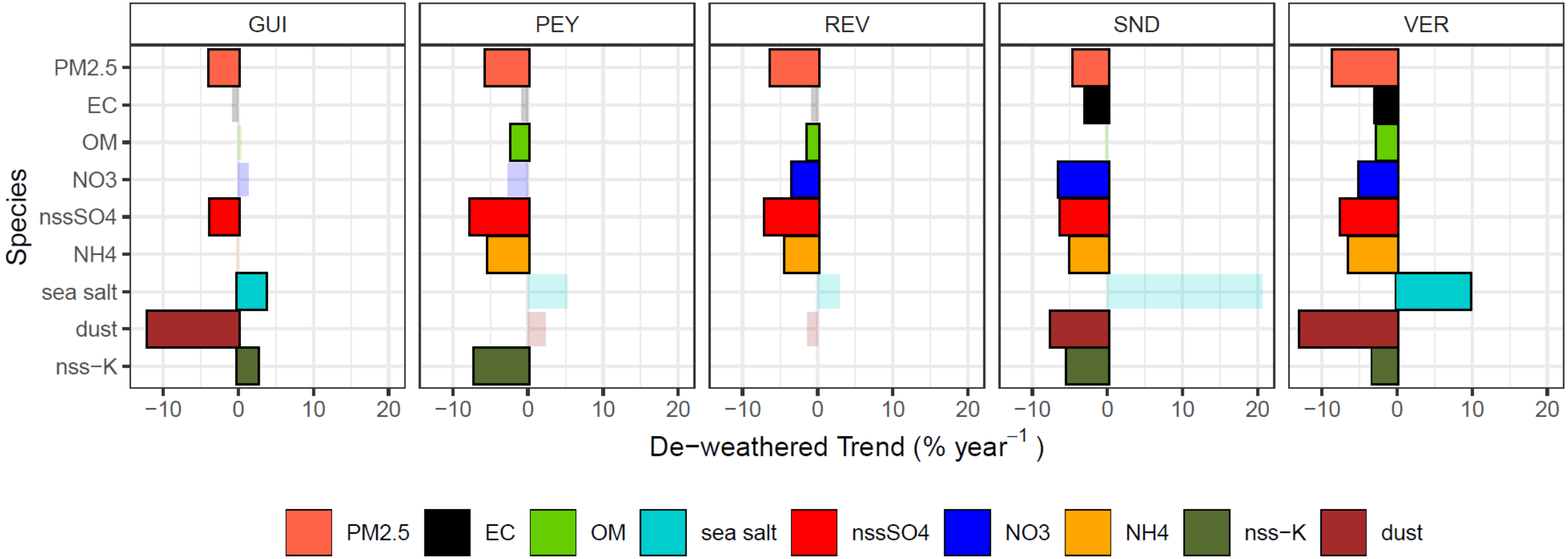
Results: Theil-Sen trends for de-weathered time series (3-h model)



Solid bar: trend significant at $p<0.05$

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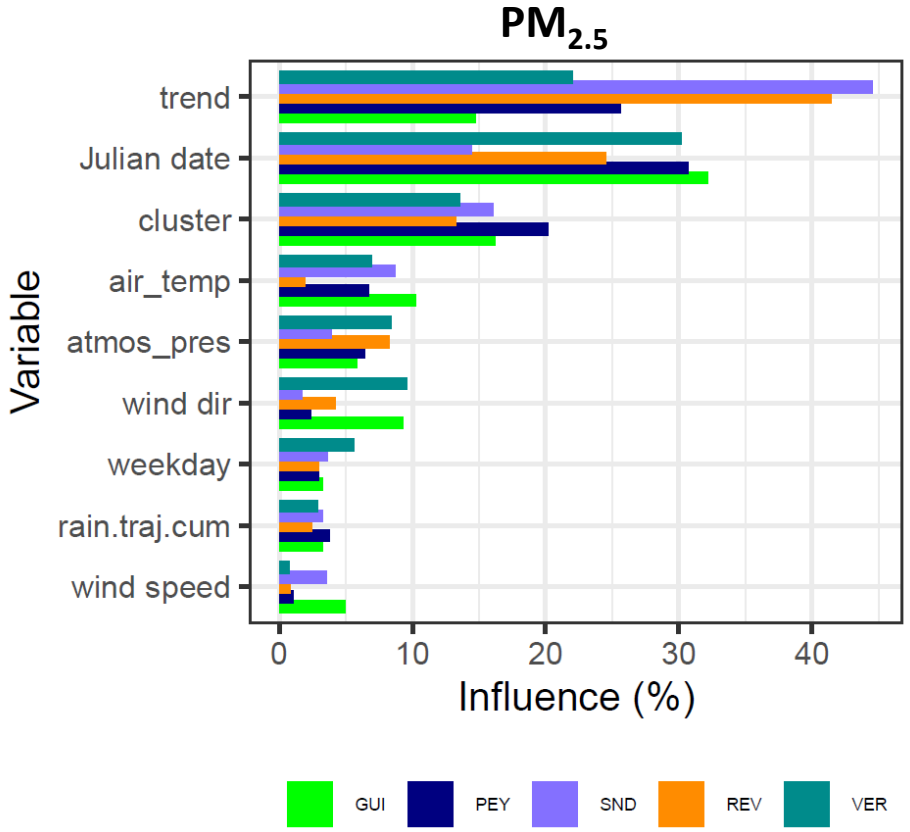
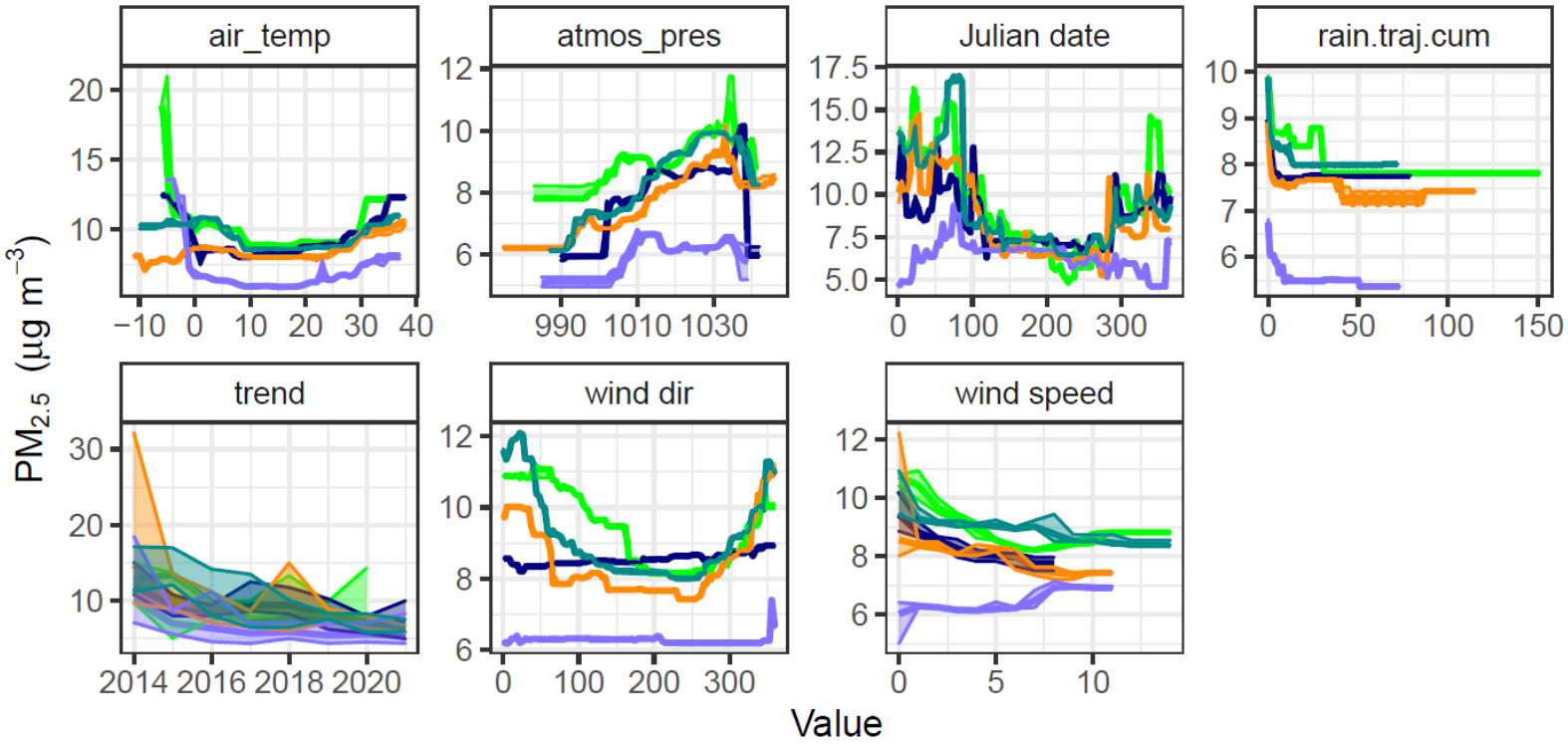
Results: influence of variables & partial dependency plots





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Conclusions

- **Annual $PM_{2.5}$** concentrations at background sites in France ranged from **4.8 µg m^{-3} to 11.6 µg m^{-3}** for the period **2014 – 2020**, with the **majority of sites / years ex**ceeding the annual **WHO limit value** (5 µg m^{-3})
- **Better $PM_{2.5}$ 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 $PM_{2.5}$** all year long
- **SIA** contributed mostly in **spring**
- The **contribution of OM** to $PM_{2.5}$ was **larger at the southern sites** whereas the contribution of **SIA** was **larger at the northern sites.**

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Conclusions

- **Better reproduction of $PM_{2.5}$** concentrations **by random-forest modelling** when using **3-hourly** met and long-range transport information ($R^2 > 0.90$ and RMSE < 1.5 µg m^{-3})
- **Temporal variables had greater** role in explaining the **variability in $PM_{2.5}$ concentrations** (15 – 45%); followed by the **cluster variable** (~15%) representing the long-range transport
- De-weathered time series for $PM_{2.5}$ and the main components were built using the RF modelling
- All sites observed **downward trends in $PM_{2.5}$**, at a rate of **-4 to -9% $year^{-1}$** for the period **2014 - 2020**
- Downward trends in $PM_{2.5}$ were coincidental with the **downward trends in nss-SO_4^{2-} (-4 to -8 % $year^{-1}$)** associated with the decrease in SO_2 emissions (mean decrease of -8% $year^{-1}$ between 2014 – 2019 in France)
- **Reduction in NO_3^-** concentrations from reduced NO_X emissions **less evident** at the French EMEP sites: **3 out of 5 sites observed significant downward trends** (REV, SND and VER: -3% $year^{-1}$ to -6% $year^{-1}$). For 2014-2020, NO_X emissions in France decreased at a rate of -5% $year^{-1}$.
- **Reduction in biomass burning** was observed with downward trends in **nss-K^+ at three sites** (VER, SND and PEY: -3 to -7 % $year^{-1}$). One site observed a **significant upward trend (GUI)** (2% $year^{-1}$)

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Many thanks for your attention

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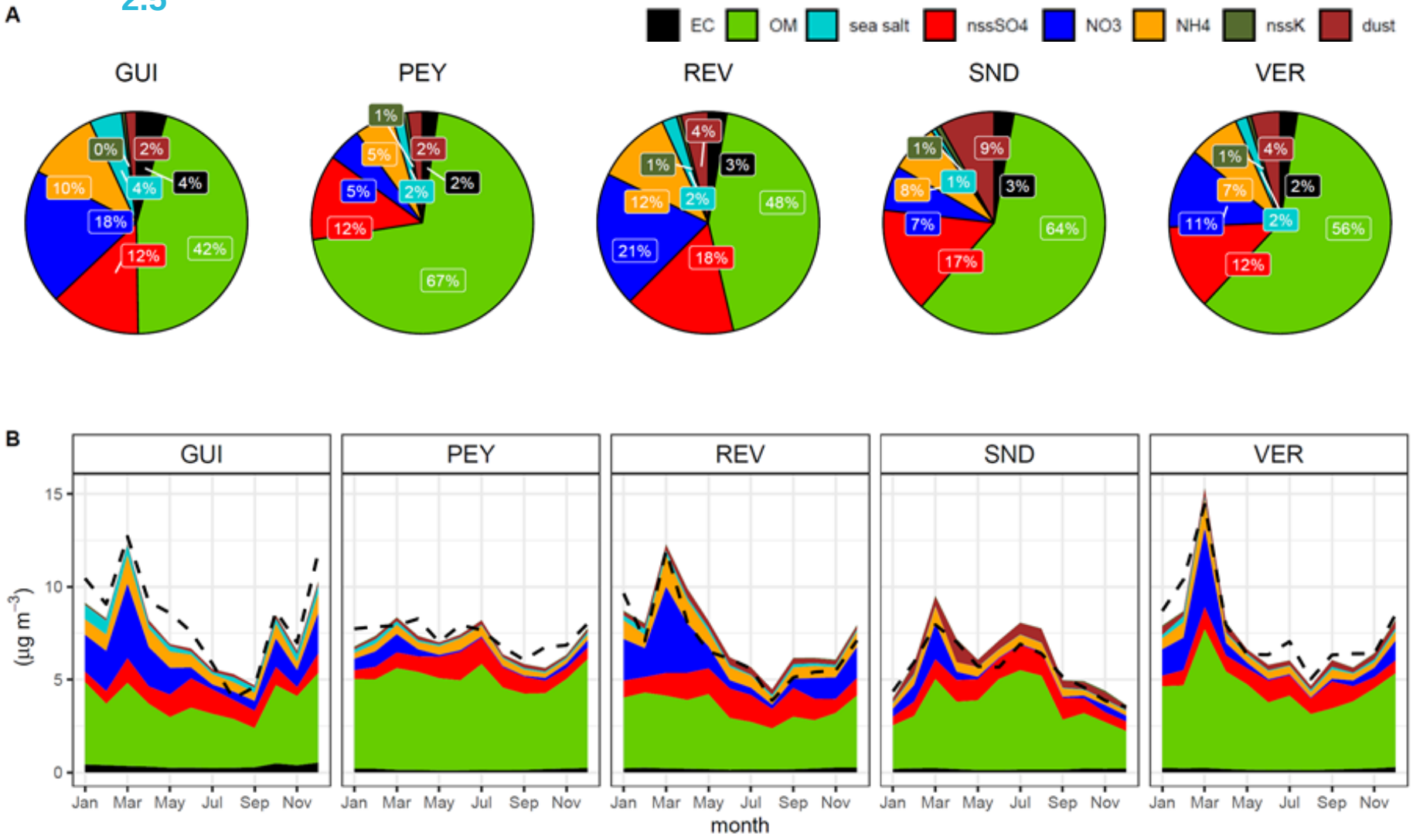
$PM_{2.5}$ mass closure



--- $PM_{2.5}$

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Results: partial dependency plots for the cluster variable