Atmospheric
Chemistry
and Physics

*Supplement of*

# Measurement report: A 1-year study to estimate maritime contributions to PM$_{10}$ in a coastal area in northern France

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**S1 PM₁₀ chemical characterization**

**S1.1 Organic (OC) and elemental (EC) carbon**

Carbonaceous subfractions were analysed on a punch of the filter by a thermo-optical technique following the EUSAAR-2 protocol (Cavalli et al., 2010). This method follows the recommendations of the EN16909 standard drawn up by the technical committee CEN/TC 264.

**S1.2 Elements**

Major and trace elements were analyzed following the protocol described in Ledoux et al. (2006) and Kfoury et al. (2016). Briefly, a punch of the loaded filter or the blank was digested using an acid mixture of $HNO_3/HF/HClO_4$ (4/1/0.5 V/V/V, Suprapur® grade, Merck®, Darmstadt) at 120 ˚C for 4 hours, then evaporated at 170 ˚C for 2 hours and ultrapure water was added to the residue kept at 90 ˚C for an hour. The cooled solution was diluted to 13 mL, acidified to 0.2% using $HNO_3$ before being filtered on a 0.45 µm PTFE membrane. Major elements such as Al, Ba, Fe, Mn, P, Sr, Ti, and Zn were analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, iCAP 6000 Series, Thermo Scientific, UK) while trace elements such as V, Cr, Ni, Sc, Co, Cu, As, Rb, Nb, Ag, Cd, Sn, Sb, Te, La, Ce, Tl, Pb, and Bi were analyzed by ICP coupled to a mass spectrometer (ICP-MS, Varian® 820-MS, Varian, USA). For the results validation, the standard reference material NIST-SRM 1648a was used for the elements analysis by ICP-AES and ICP-MS. Recovery rates ranged between 92 and 106% with the exception of Cr (82%).

**S1.3 Water-soluble ions**

$Cl^-$, $SO_4^{2-}$, $NO_3^-$, $Ca^{2+}$, $Mg^{2+}$, $K^+$, $Na^+$, and $NH_4^+$ were analyzed by liquid ion chromatography (Dionex® DX 100 and ICS 900, IonPac AS9 and CS12 columns, Thermo Scientific, UK) following the protocol detailed in Ledoux et al. (2006) and Fadel et al. (2022), in accordance with EN16913 recommendations. A 47 mm filter punch was extracted by sonication after adding few milliliters of ultrapure water for 30 min. This step is repeated three times with fresh ultrapure water, the leachates are then regrouped, filtered through a 0.45 µm cellulose acetate membrane, and the volume was adjusted to 20 mL. Recovery rates for the cations and anions varied between 94 and 102%.

## S1.4 Organic tracers

The analysis of organic compounds included the characterization of compounds mainly emitted from biomass burning and biogenic emissions. These compounds are anhydrosugars (levoglucosan, mannosan, and galactosan), sugar alcohols (arabitol and mannitol), and monosaccharides (glucose and mannose). A punch of the sample was extracted with ultrapure water under agitation for 30 min and then filtered using a 0.22 µm Nucleopore membrane. The analysis was done with High Performance Liquid Chromatography (HPLC) coupled to a Pulsed Amperometric Detector (PAD) (Srivastava et al., 2018).

a)



OC CGN 2013

b)



EC CGN 2013

c)



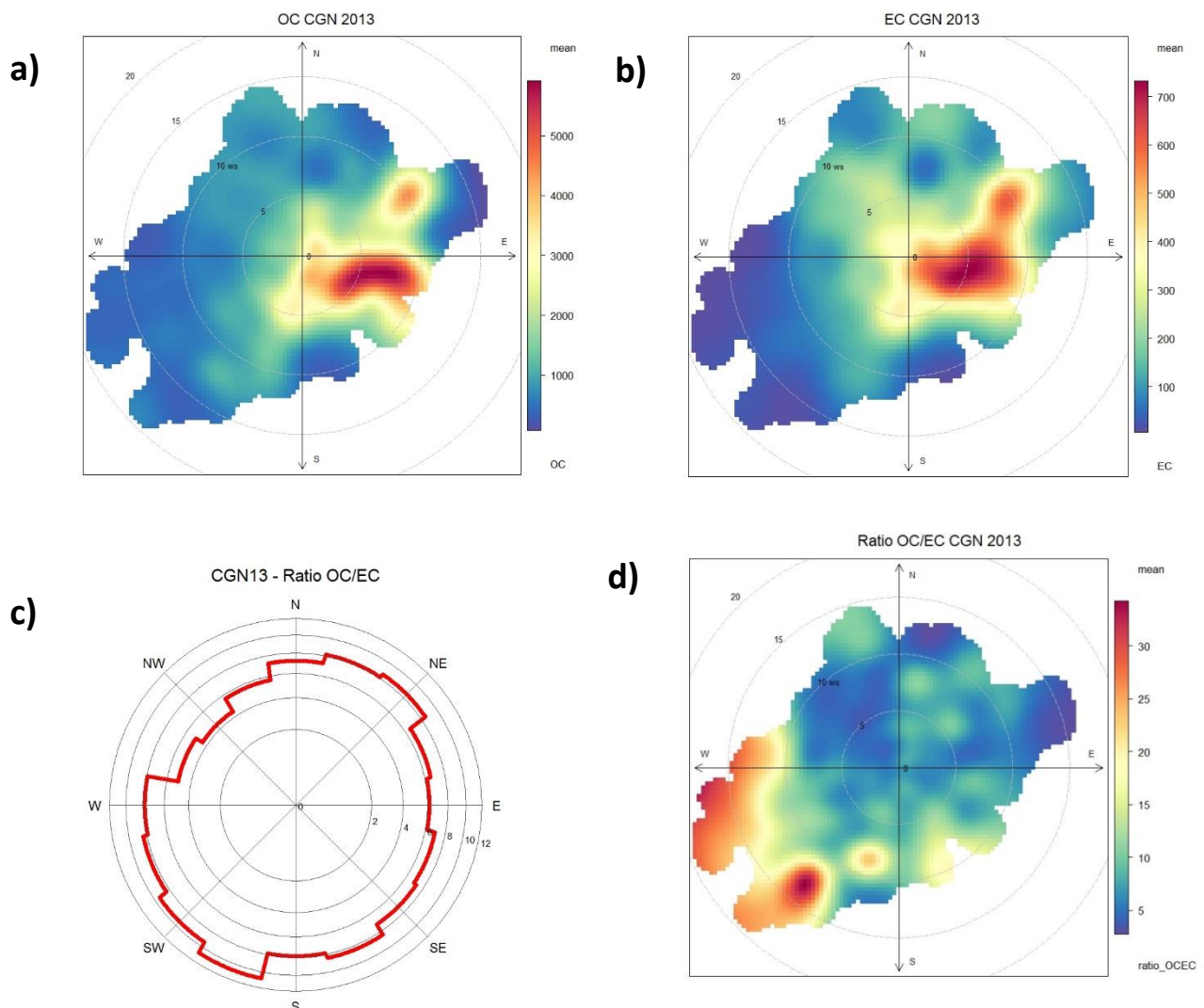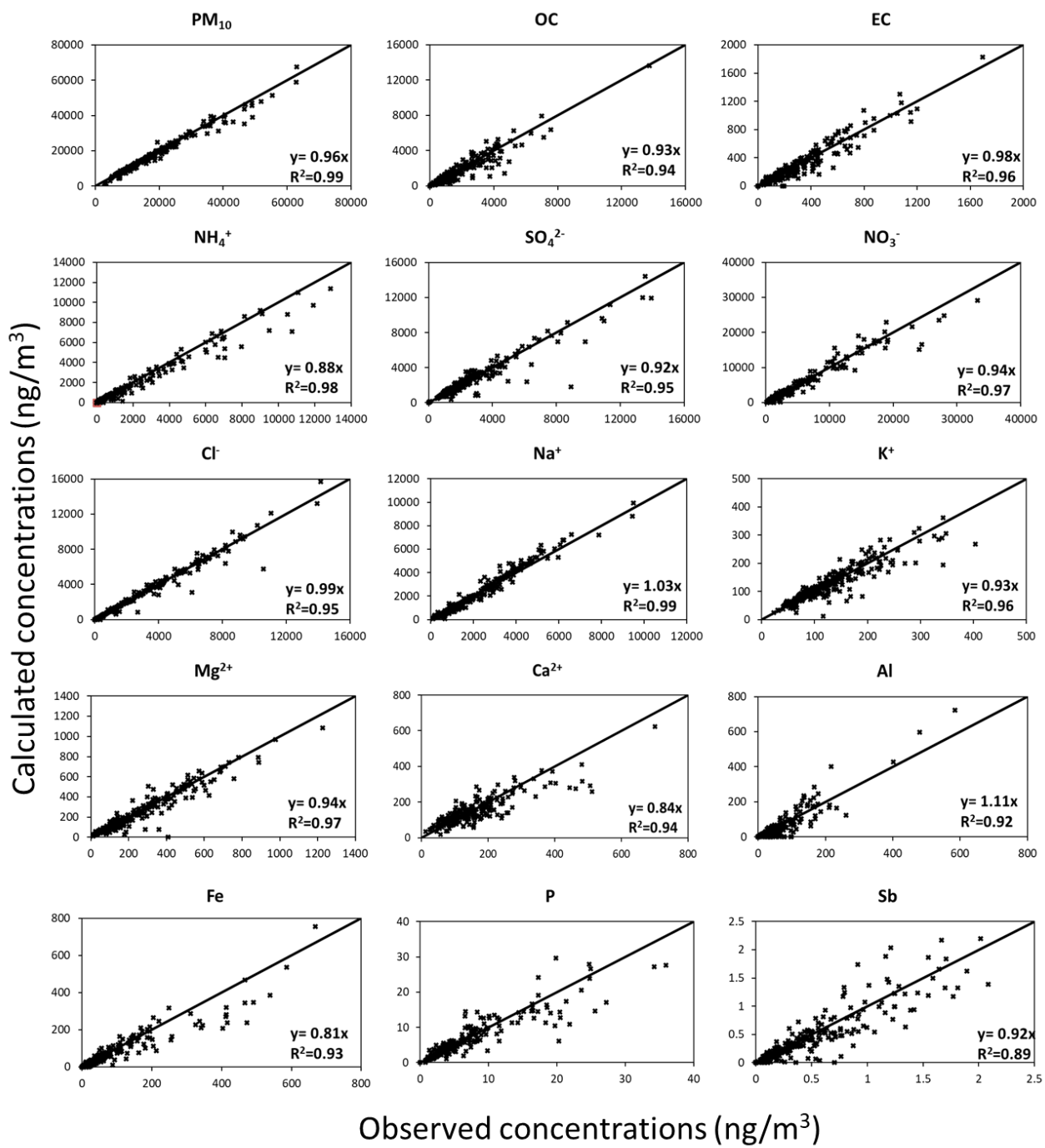CGN13 - Ratio OC/EC

d)



Ratio OC/EC CGN 2013

Fig. S1: Polar plots for the OC (a), EC (b), and OC/EC concentration ratio for all the samples (c) and where the concentrations of EC are higher than 200 ng/m$^3$ (e), as well as a pollution rose for the OC/EC concentration ratio (d).

Figure showing scatter plots of calculated concentrations (ng/m³) versus observed concentrations (ng/m³) for PM₁₀, OC, EC, NH₄⁺, SO₄²⁻, NO₃⁻, Cl⁻, Na⁺, K⁺, Mg²⁺, Ca²⁺, Al, Fe, P, and Sb.

**PM$_{10}$**: y= 0.96x, R²=0.99

**OC**: y= 0.93x, R²=0.94

**EC**: y= 0.98x, R²=0.96

**NH$_4^+$**: y= 0.88x, R²=0.98

**SO$_4^{2-}$**: y= 0.92x, R²=0.95

**NO$_3^-$**: y= 0.94x, R²=0.97

**Cl$^-$**: y= 0.99x, R²=0.95

**Na$^+$**: y= 1.03x, R²=0.99

**K$^+$**: y= 0.93x, R²=0.96

**Mg$^{2+}$**: y= 0.94x, R²=0.97

**Ca$^{2+}$**: y= 0.84x, R²=0.94

**Al**: y= 1.11x, R²=0.92

**Fe**: y= 0.81x, R²=0.93

**P**

**Sb**: y= 0.92x, R²=0.89

Calculated concentrations (ng/m$^3$)
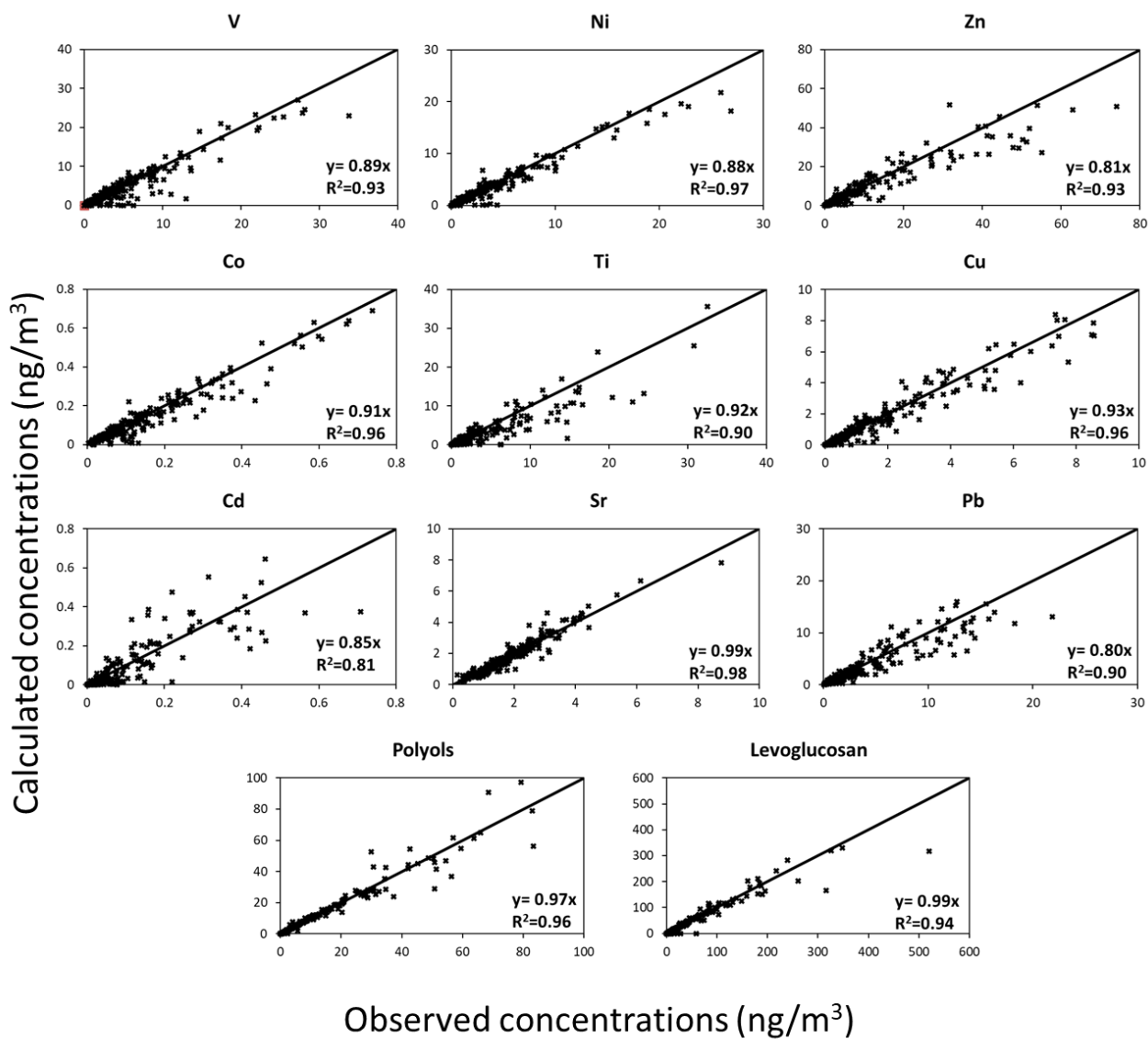
Observed concentrations (ng/m$^3$)

Fig. S2: Calculated species and PM$_{10}$ concentrations using Constrained Weighted - Non-Negative Matrix Factorization versus observed concentrations for all the species considered in the calculation (with the identity line as reference).
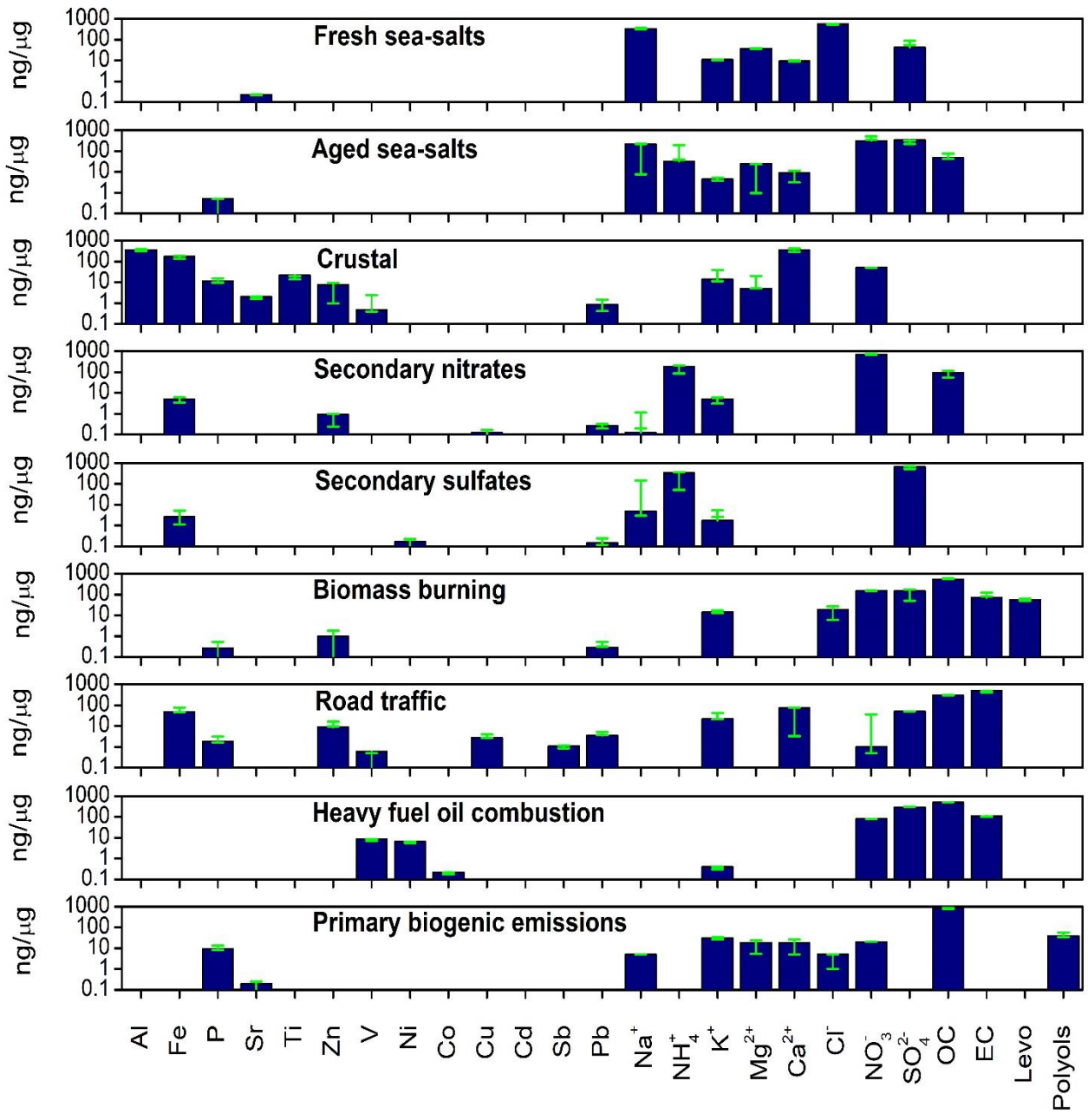
Fig.S3: PM$_{10}$ source profiles at Cape Gris-Nez (CGN) identified using the CW-NMF model along with the percentiles 25$^{th}$ and 75$^{th}$ calculated via the bootstrap analysis.
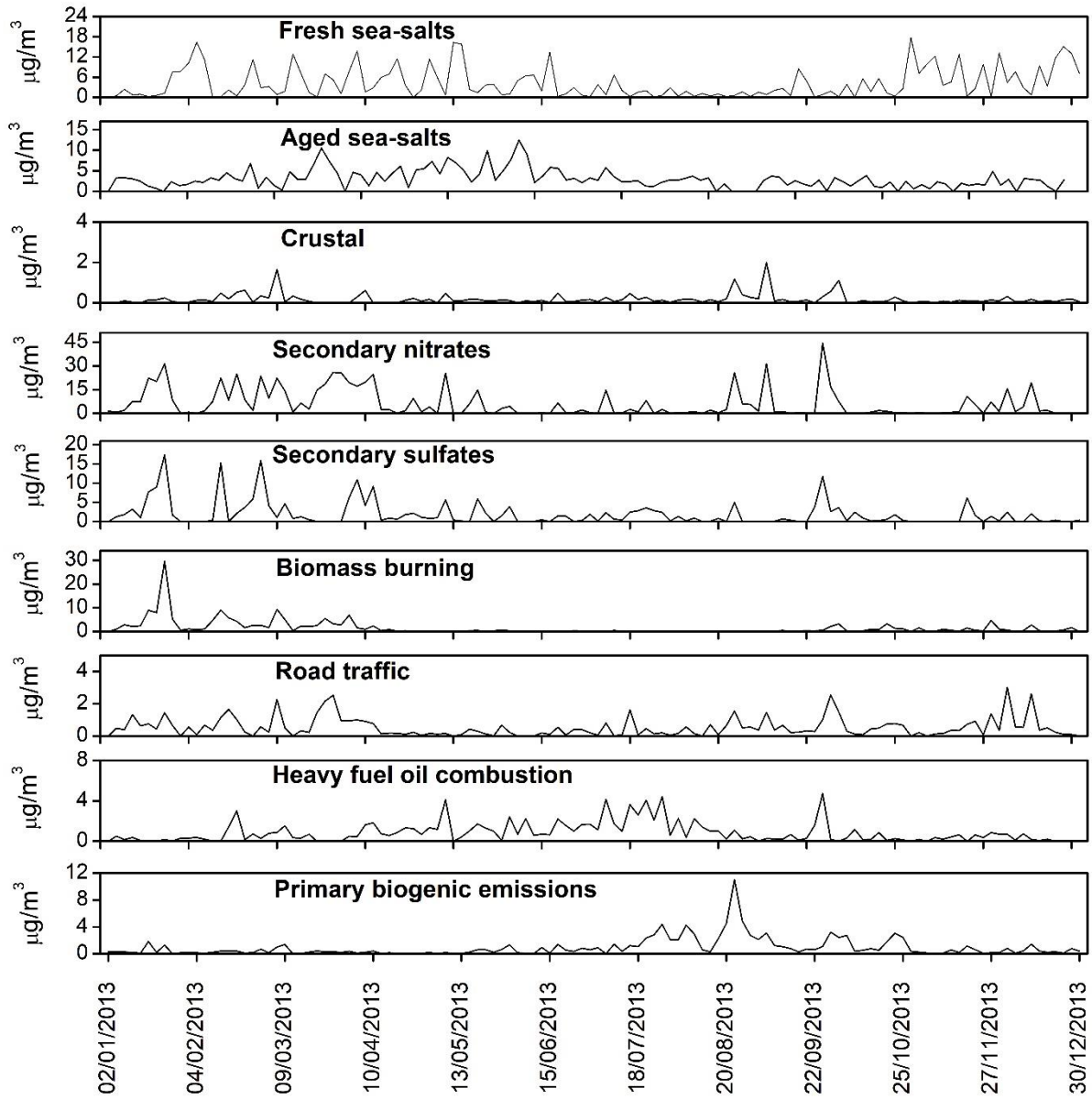
Fig. S4: Time series for the 9 identified sources of $PM_{10}$ at CGN during 2013
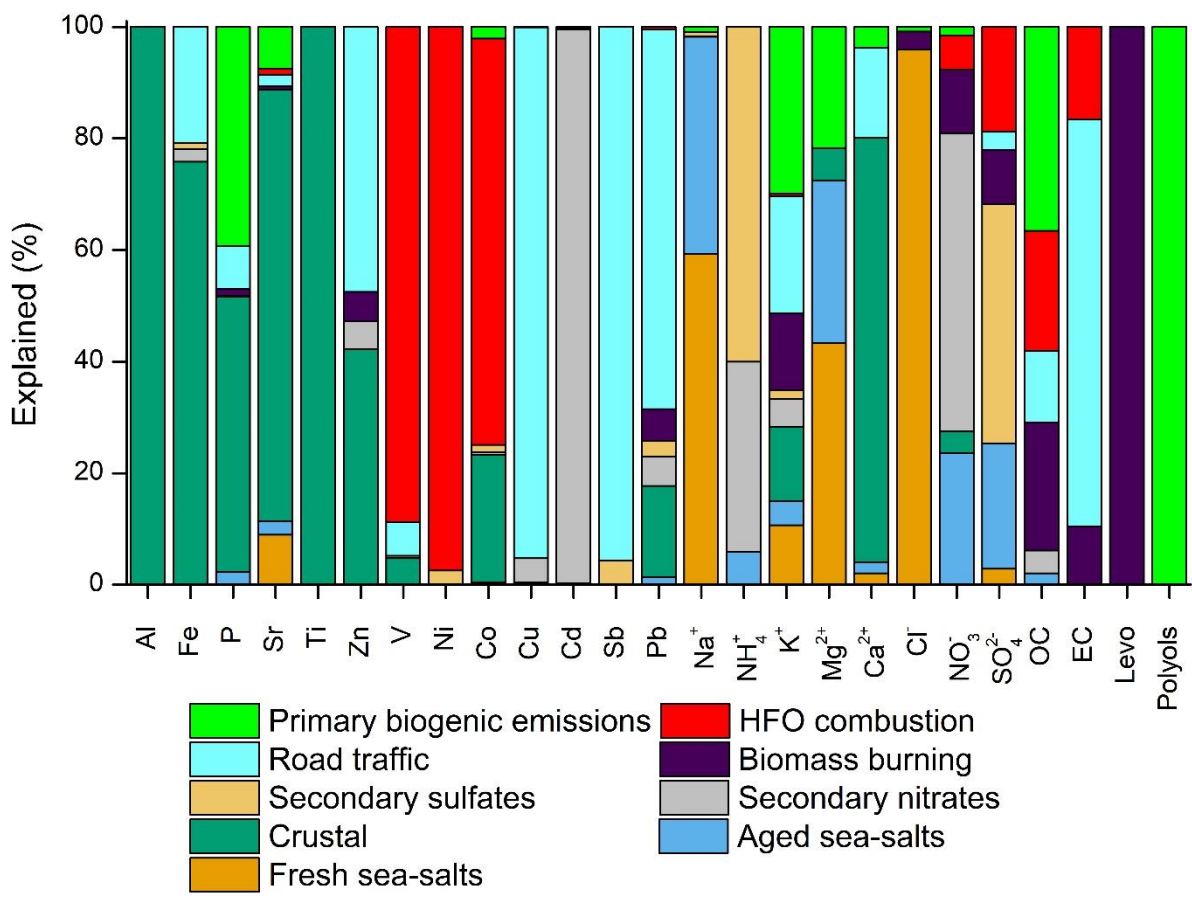
Fig. S5: Distribution of the chemical species between the 9 sources identified at CGN using the CW-NMF.
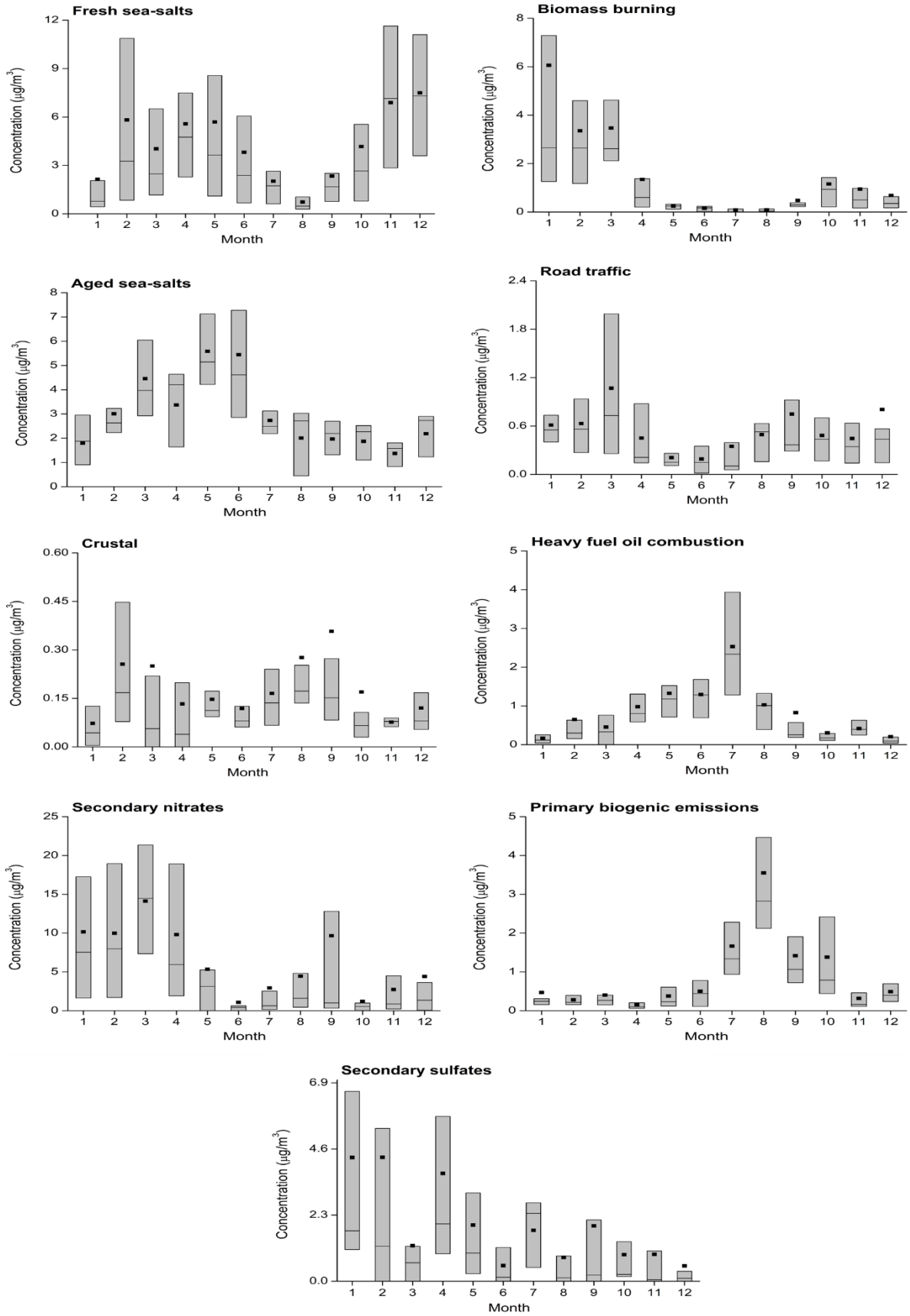
Fig. S6: Boxplot of the monthly contribution of the sources expressed in µg/m$^3$ (25$^{th}$, 50$^{th}$, and 75$^{th}$ percentiles) along with the monthly average concentrations (black squares)
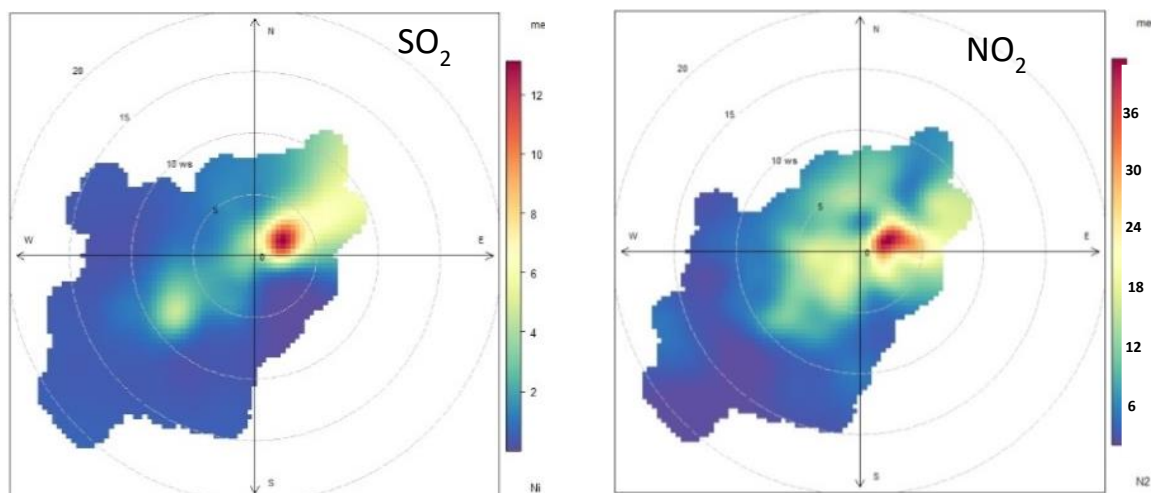
Fig. S7: Concentration roses of SO₂ and NO₂ at CGN during 2013

SO$_2$ and NO$_2$ were continuously measured using an AF21M SO$_2$ analyzer (Environnement SA, France) and an AC32M NO-NO$_2$-NO$_X$ *analyzer* (Environnement SA, France), respectively. The calibration of the analyzers was done at the beginning of the campaign and were routinely check by the regional air quality network atmo Hauts-de-France. The temporal resolution was 15 minutes for gas concentrations. More details related to the measurement campaign of the gases at Cape Gris-Nez can be found in Ledoux et al. (2018).

<u>Bootstrap analysis:</u>

The Bootstrap analysis show the effects from random errors and include partially the effects of rotational ambiguity. It is used to find if there is a small set of observations that can largely influence the solution. This method creates sets of bootstrap data constructed by randomly selecting blocks of observations from the initial dataset. The size of the block was taken as 5 samples for this study. The solution was bootstrapped 100 times to ensure the robustness of the results. Mapping over 80% of the factors indicates that the bootstrap uncertainties can be interpreted, and the number of factors may be appropriate.

<u>Table S1:</u> Bootstrap mapping results for CW-NMF results at CGN site

| **Bootstrap mapping Min. correlation coefficient r = 0.6** | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Unmapped |
| Boot Factor 1 (Fresh sea-salts) | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Boot Factor 2 (Aged sea-salts) | 0 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Boot Factor 3 (Crustal) | 0 | 0 | 99 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| Boot Factor 4 (Secondary nitrates) | 0 | 0 | 0 | 100 | 0 | 0 | 0 | 0 | 0 | 0 |
| Boot Factor 5 (Secondary sulfates) | 0 | 0 | 0 | 0 | 100 | 0 | 0 | 0 | 0 | 0 |
| Boot Factor 6 (Biomass burning) | 0 | 0 | 0 | 0 | 0 | 99 | 0 | 0 | 0 | 1 |
| Boot Factor 7 (Road traffic) | 0 | 0 | 0 | 0 | 0 | 0 | 100 | 0 | 0 | 0 |
| Boot Factor 8 (HFO combustion) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 100 | 0 | 0 |
| Boot Factor 9 (Primary biogenic emissions) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 100 | 0 |

Table S2: Average contribution and standard deviation in μg/m³ and percentages of the factors to $PM_{10}$

| Source | Contrib. at CGN ($\mu g.m^{-3}$) | Standard deviation ($\mu g.m^{-3}$) | Contrib. at CGN to $PM_{10}$ (%) |
|---|---|---|---|
| Fresh sea-salts | 4.24 | 4.57 | 21.9% |
| Aged sea-salts | 3.0 | 2.31 | 15.4% |
| Crustal | 0.18 | 0.28 | 0.9% |
| Secondary nitrates | 6.27 | 9.03 | 32.3% |
| Secondary sulfates | 1.91 | 3.24 | 9.8% |
| Biomass burning | 1.49 | 3.25 | 7.7% |
| Road traffic | 0.54 | 0.61 | 2.8% |
| HFO combustion | 0.85 | 1.01 | 4.5% |
| Primary biogenic emissions | 0.92 | 1.40 | 4.7% |