

Supplement of

Measurement report: A one-year study to estimate maritime contributions to PM₁₀ in a coastal area in Northern France

*Frédéric Ledoux^{1,a}, Cloé Roche^{1,a}, Gilles Delmaire², Gilles Roussel², Olivier Favez³,
Marc Fadel^{1,*}, Dominique Courcot¹*

¹ Unité de Chimie Environnementale et Interactions sur le Vivant, UCEIV UR4492, FR CNRS 3417, Université du Littoral Côte d'Opale (ULCO), Dunkerque, France

²Laboratoire d'Informatique Signal et Image de la Côte d'Opale, LISIC UR4491, Université du Littoral Côte d'Opale (ULCO), Calais, France.

³Institut National de l'Environnement Industriel et des Risques, INERIS, Parc Technologique ALATA, 60550 Verneuil-en-Halatte, France

*Corresponding author: marc.fadel@univ-littoral.fr

^aBoth authors equally contributed and should be considered as co-first authors.

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 HNO₃/HF/HClO₄ (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 HNO₃ 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).

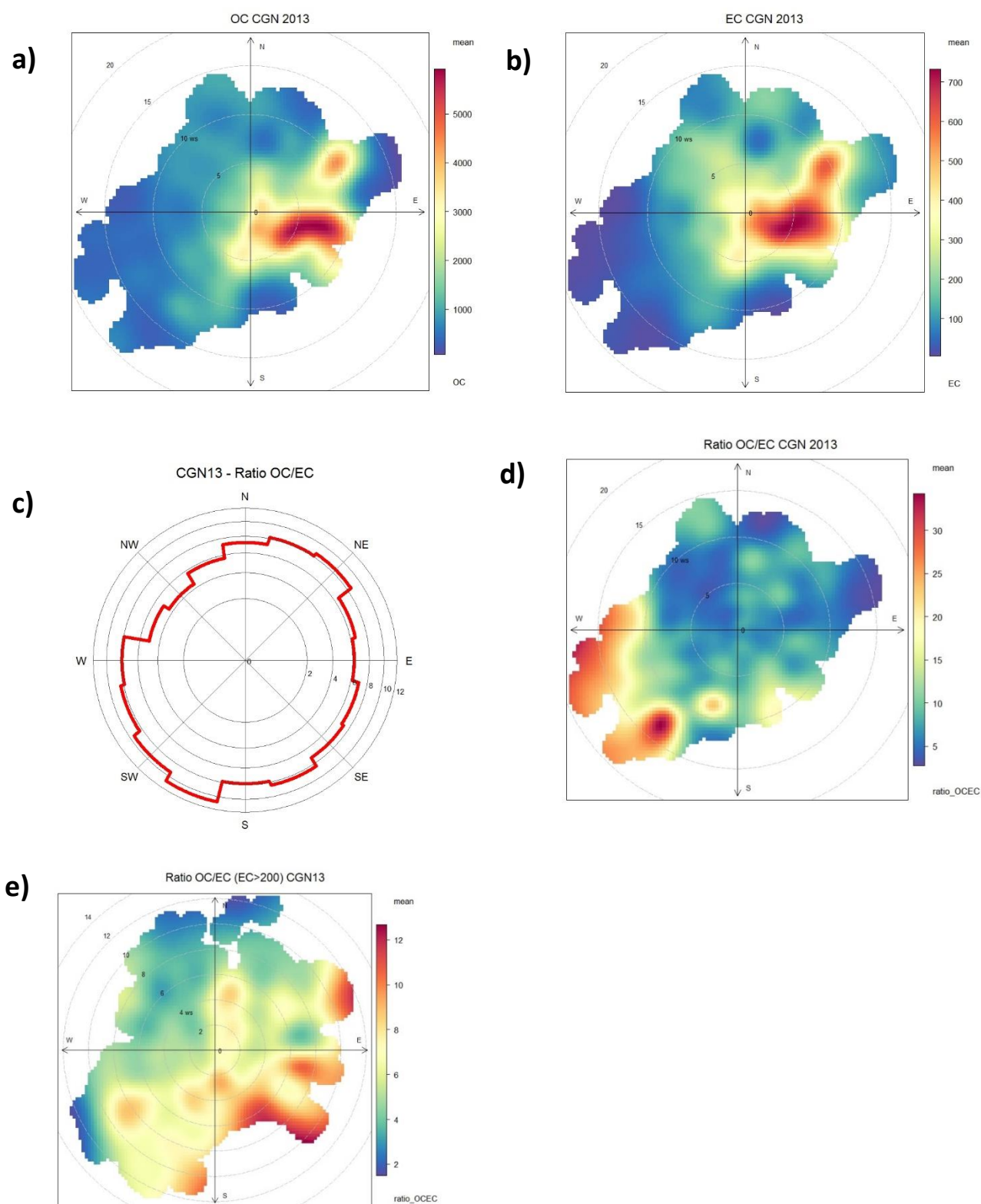


Fig. S1: Polar plots for the OC (a), EC (b), and OC/EC concentration ratio for all the samples (c) and where the concentrations of EC are higher than 200 ng/m³ (e), as well as a pollution rose for the OC/EC concentration ratio (d).

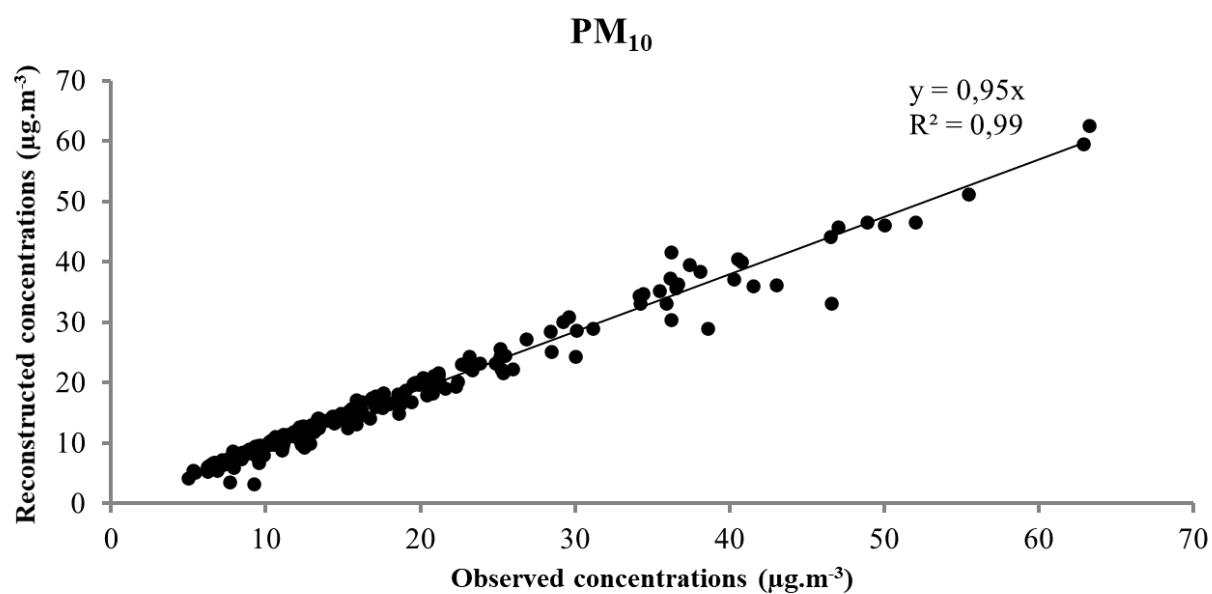


Fig. S2: Reconstructed PM₁₀ concentrations calculated using the Constrained Weighted – Non-Negative Matrix Factorization versus the observed ones.

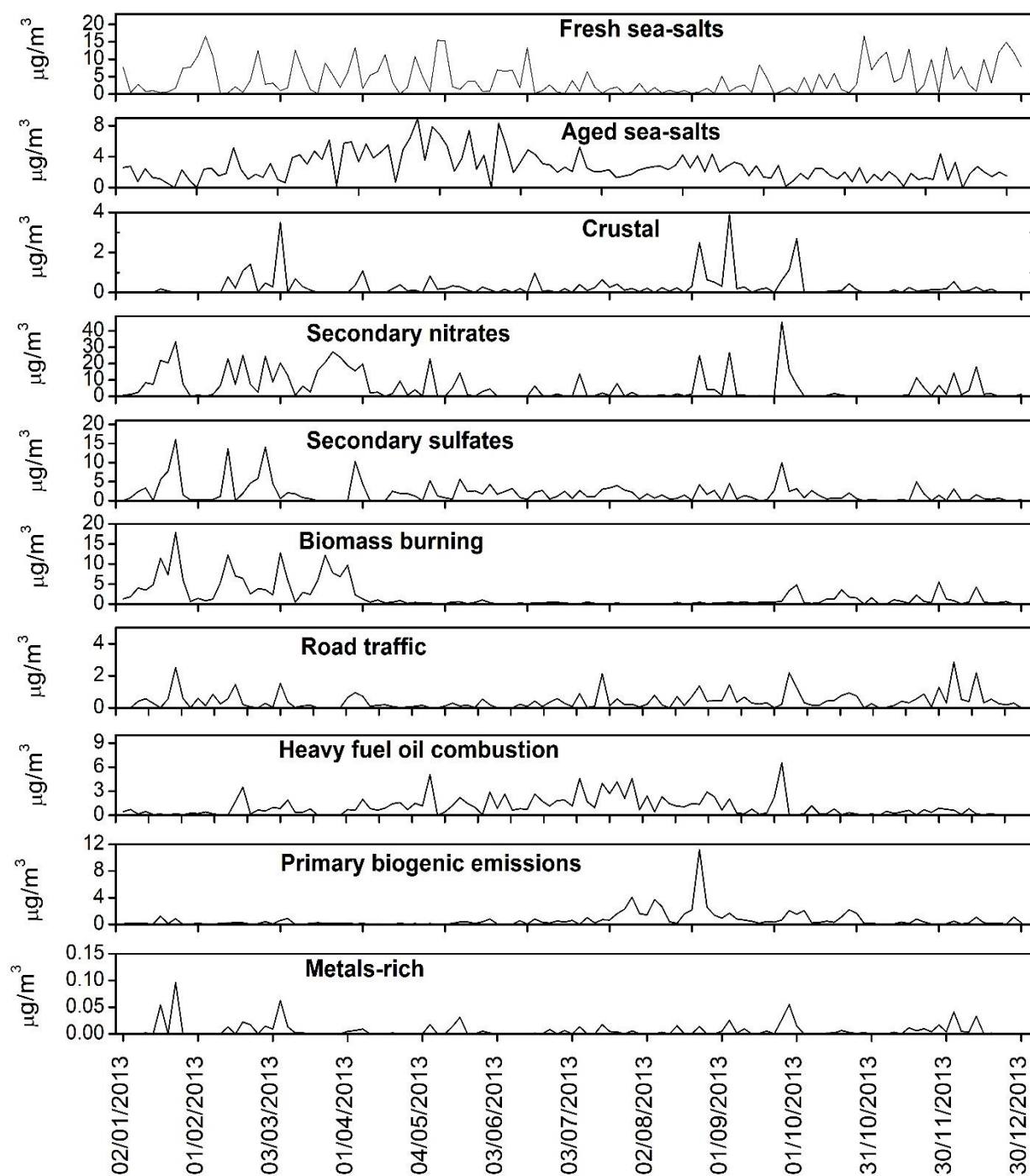


Fig. S3: Time series for the 10 identified sources of PM₁₀ at CGN during 2013

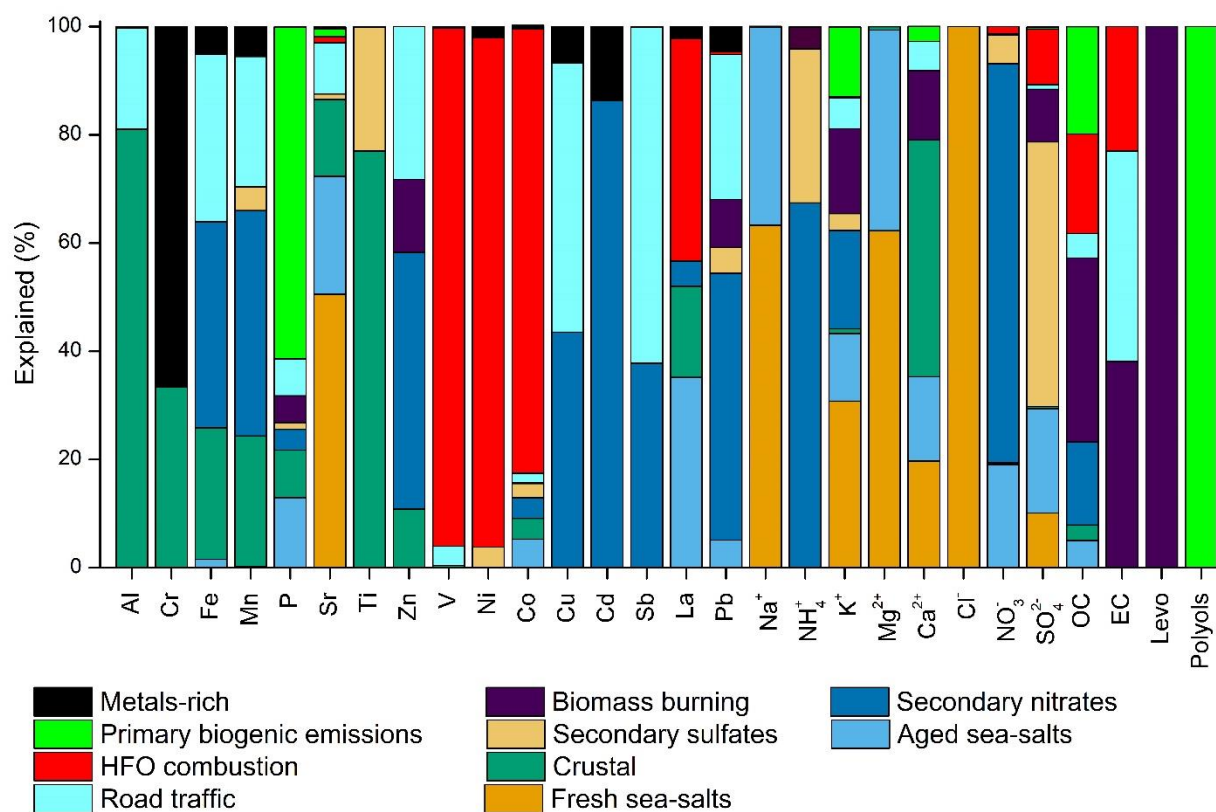


Fig. S4: Distribution of the chemical species between the 10 sources identified at CGN using the CW-NMF.

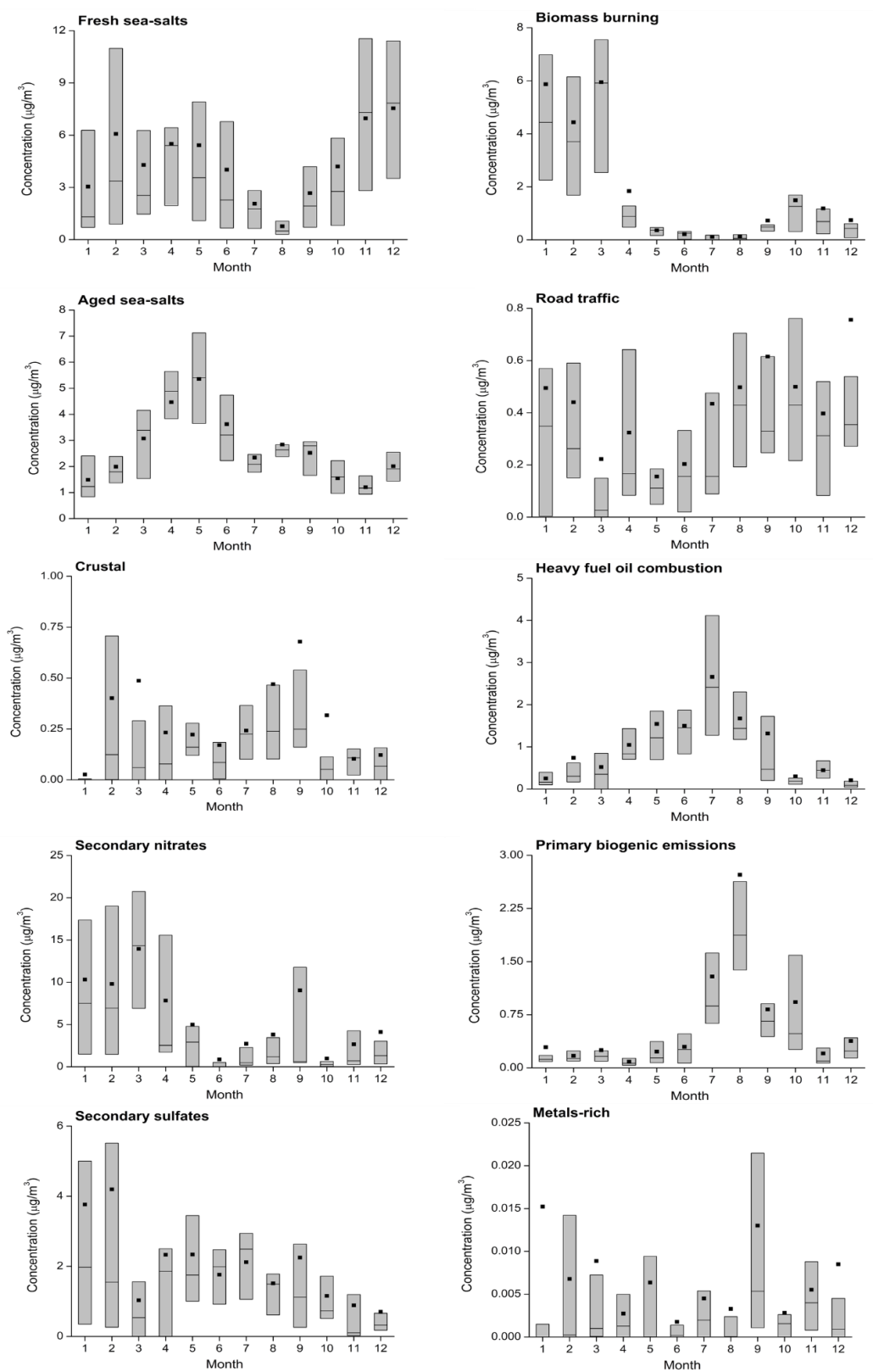


Fig. S5: Monthly average, median, percentiles 25th and 75th of the contributions in $\mu\text{g}/\text{m}^3$ of the sources at CGN in 2013

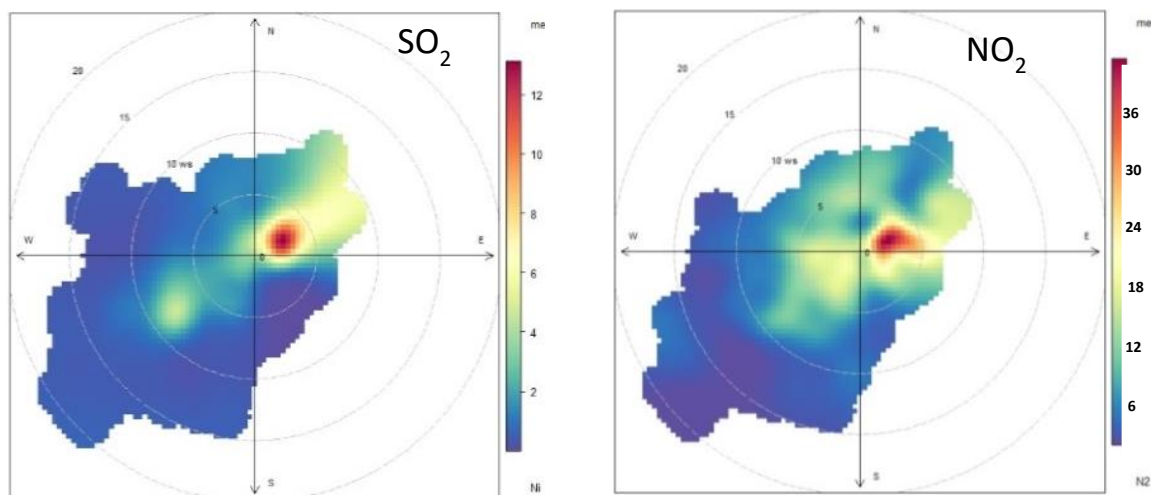


Fig. S6: Concentration roses of SO_2 and NO_2 at CGN during 2013