





1. Introduction. The AriaSaNa project, led by the Italian National Research Center (CNR), in collaboration with Parthenope University in Naples, was aimed to monitor air pollution in the main towns of the Campania Region. In the past, the contribution of fossil vs renewable C (Carbon) to elemental and organic C in atmospheric Particulate Matter (PM) was quantified by means of ¹⁴C analyses (Sirignano et al., 2019). In this study, to **identify the sources of C and N** (Nitrogen) of PM in the city center of Naples, we have used a range of techniques, including concentration and isotopic composition ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) of total C and N, analyses of major ions, air quality data, as well as characterization of the meteorology and the origin of air masses.

2. Experiment. PM samples were collected in May and December 2016. Particles with diameter < 10 μm (PM₁₀) and < 2.5 μm (PM_{2.5}) were collected for 24h on pre-cleaned (700 °C for 2 h) quartz filters (Whatman, 47 mm diameter) on top of the historical building complex in Largo San Marcellino (lat. 40.85° N; long. 14.26° E, 53 m.a.s.l., Figure 1).

2.1 C and N concentration, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$: $\delta^{13}\text{C}$, % of C, $\delta^{15}\text{N}$ and % of N were measured using an elemental analyzer (Flash HT ThermoFisher) in combustion configuration coupled with an IRMS (Delta V Advantage ThermoFisher) through the ConFlo IV interface (ThermoFisher). Half of each quartz filter was reduced in very small pieces (< 1 x 1 mm) by cutting it with a knife. Blank filter (only quartz), and quartz with reference material were measured to quantify the sampling process blank and the effect of the quartz mass in the combustion reactor. Three reference materials for N (IAEA-N2, IAEA-NO3 and IAEA 600) and three for C (IAEA-CH3, IAEA C8 and IAEA 600) were used to calibrate $\delta^{13}\text{C}$

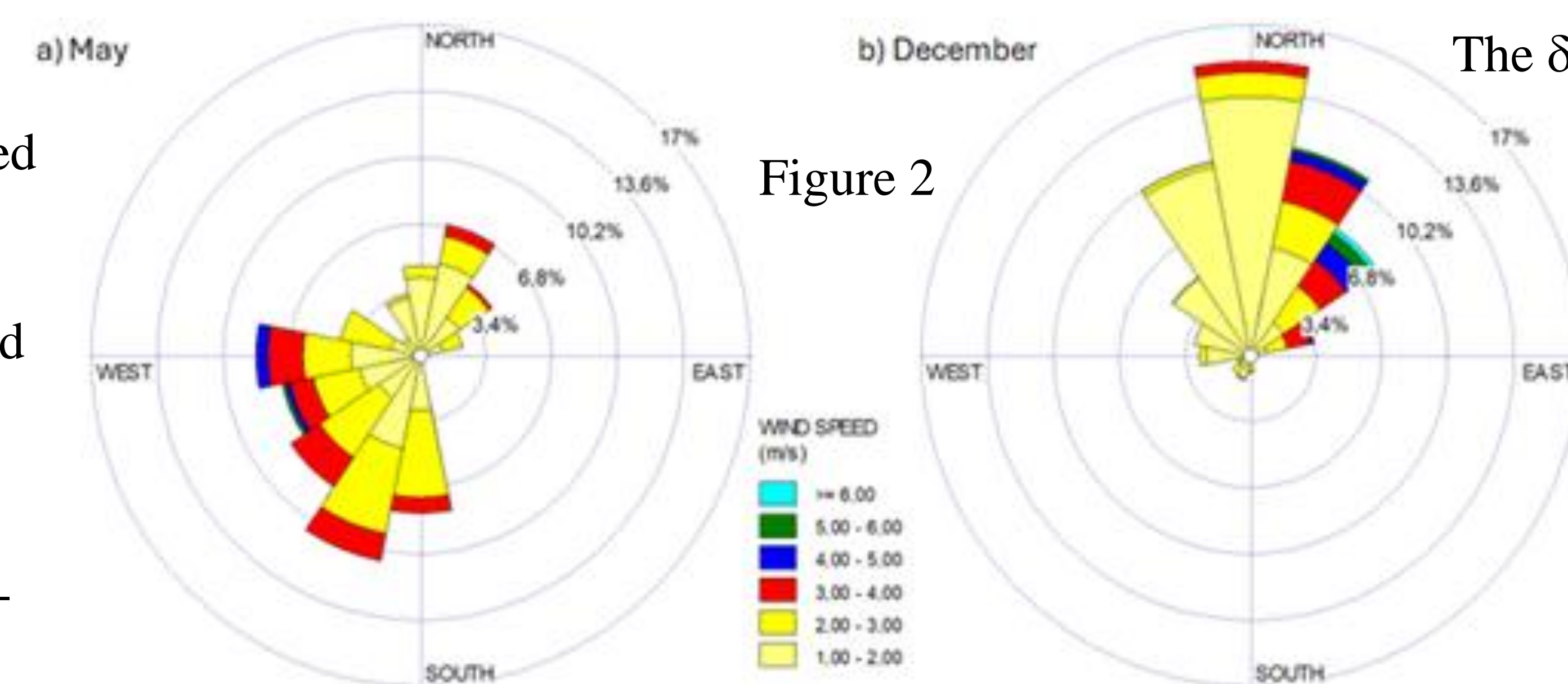
$\delta^{15}\text{N}$ measurements. Typical uncertainties were 0.2-0.4 and 0.6-0.8 per mil on $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ respectively. Acetanilide was used to calibrate % of C/N (uncertainties 0.1-0.6%).

2.2 Major ions: For the characterization of the soluble ion fractions, a quarter of each filter was first treated with 15 mL of ultra-pure water using a closed vessel microwave digestion system (Milestone StartE), following the multistep temperature ramp described in Chianese et al. (2019) and then filtered and analyzed using a Dionex ICS1100 system. For anion detection, we used an AS22 column and a buffer solution of 3.5 mm of sodium carbonate–bicarbonate as eluent. For cations, we used a CS12A column and 20 mm of methanesulfonic acid solution as eluent. Calibration curves were defined using certified multistandard solutions.

2.3 Meteorology and origin of air masses: We interpreted the results by analyzing changes over time of wind direction and speed as described in Hernández-Ceballos et al. (accepted in City and Environment Interactions). This was associated with the changes in back-trajectories with the Hybrid Single-Particle Lagrangian Integrated Trajectory (Hysplit). We have also analyzed changes of Planetary Boundary Layer Height (PBLH) over the town of Naples using ERA5 reanalysis dataset. We have also used temperature, relative humidity and cloud cover measured at the station of Capodichino (Naples International Airport, about 5 km from the sampling site) as well as air quality data available from 3 stations around Naples (Astronomico, Ferrovia, Museo). We have correlated all species and parameters through the Spearman's rank coefficient (r).

3. Results

3.1 Origin of air masses: the two sampling periods are characterized by substantially different meteorological conditions. In May, air masses mostly originated from South and West, that is the Tyrrhenian sea (Figure 2a). In Autumn, air masses mostly originated from North and North-East, that is land (Figure 2b).



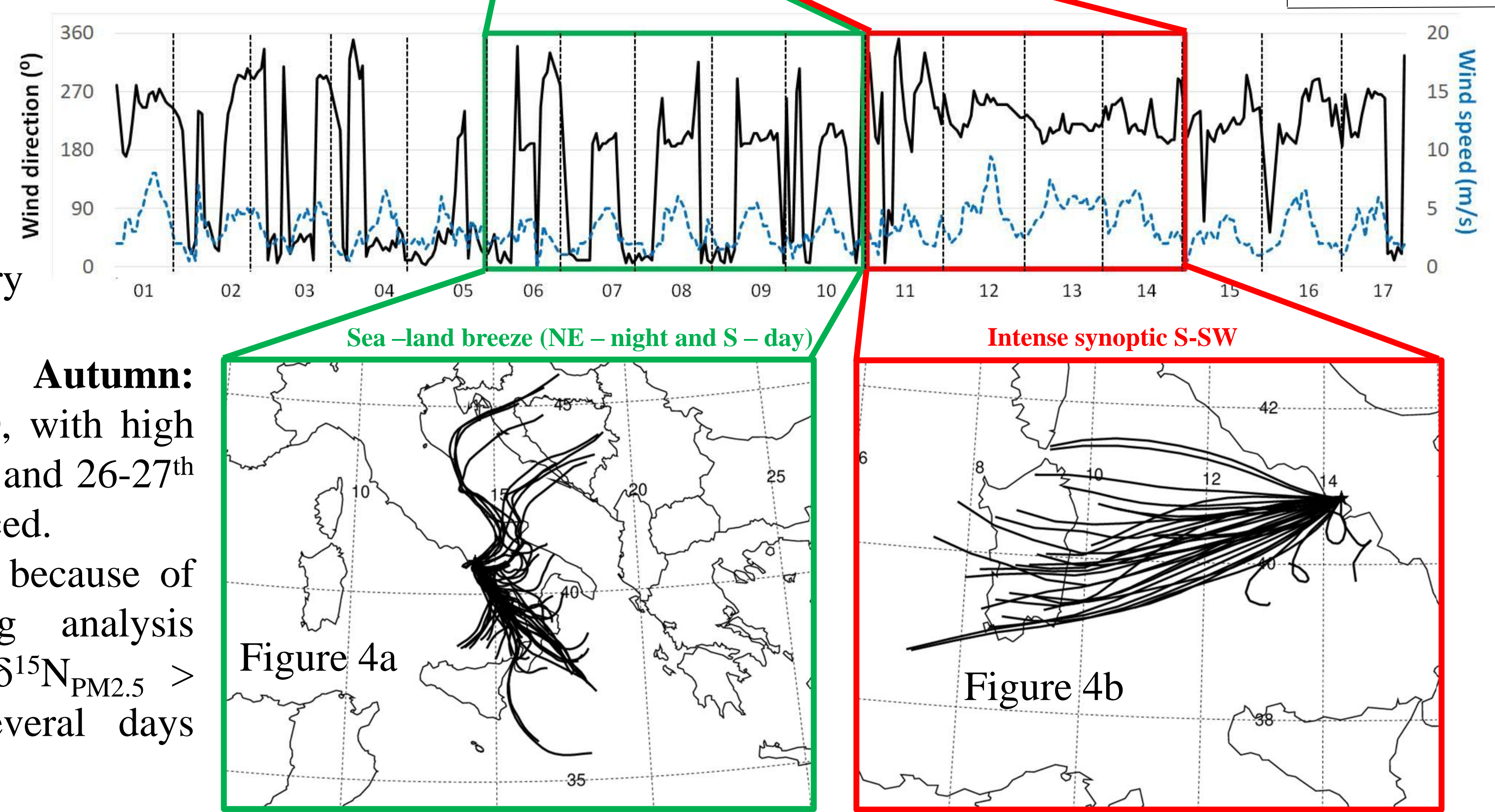
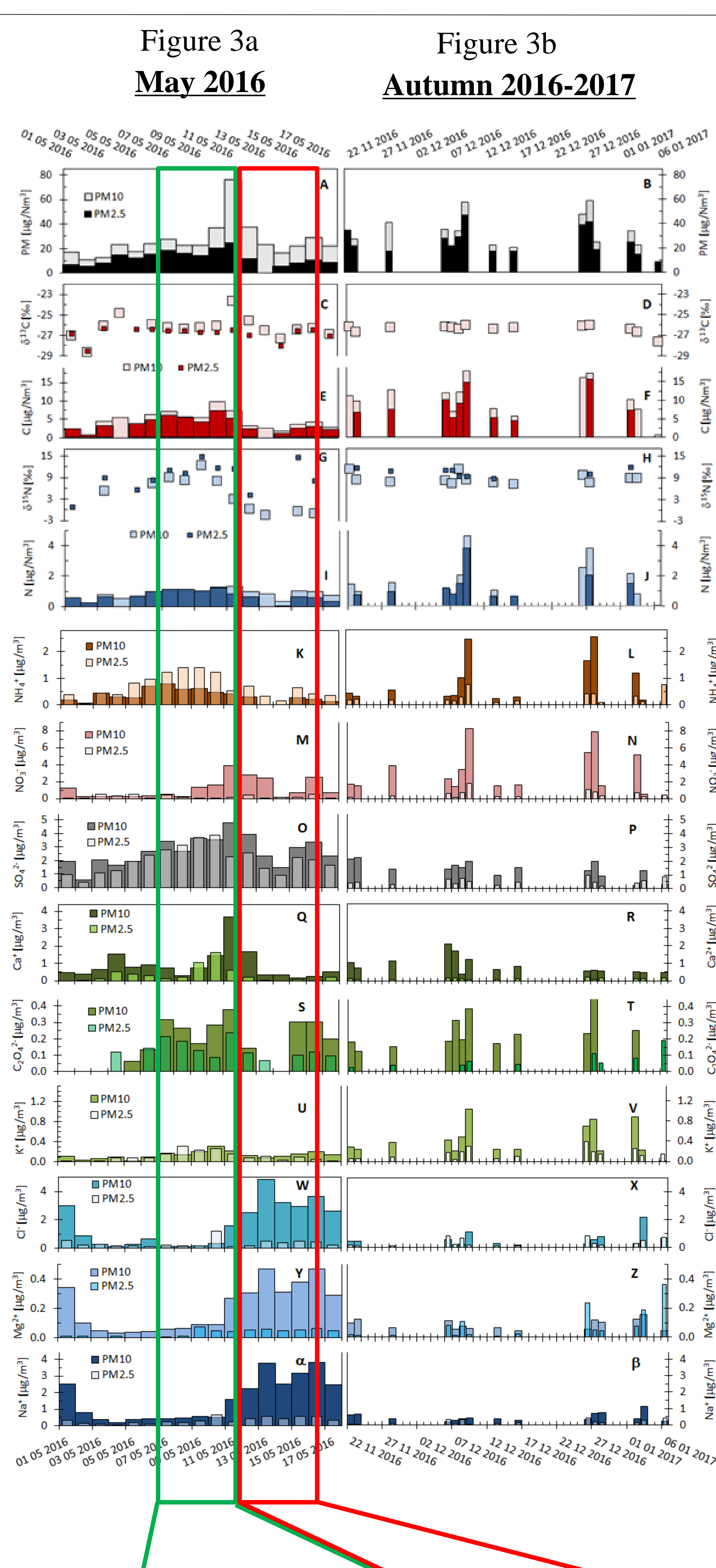
3.2 PM₁₀ in May: Many species (including total PM, C, N, $\delta^{13}\text{C}$ and some species on mainly terrestrial origin: NH_4^+ , NO_3^- , Ca^{2+} , K^+ , as well as one of the main Secondary Inorganic Ions: SO_4^{2-}) show a peak on the 10-11th May 2016 (Figure 3a). This is concurrent with a change of wind regime going from a typical sea-land breeze pattern, associated with re-circulation of air and accumulation of “pollutants” (6-10th May, green box in Figure 3a) to an intense synoptic with winds originating from South and South-West (11-14th May, red box in Figure 3a). This is consistent with the change in the origin of air masses (back-trajectories) shown in Figure 2a (North-East) and b (South-South West) determined by a change in synoptic conditions (stable vs unstable). During the unstable conditions, air from the sea brought the typical marine derived species over Naples (Cl^- , Mg^{2+} and Na^+ increase after the 11th May, Figure 3a-W, X, α). During the change (9-13th May), $\delta^{15}\text{N}$ shows a significant decrease (12-0 ‰, Figure 3a-G).

3.3 PM_{2.5} in May: Like PM₁₀, but with a limited number of species peaking on the 10-11th May (including total PM, C, N, and NO_3^- , Ca^{2+} , K^+ , as well as SO_4^{2-}). Marine derived species (Cl^- , Mg^{2+} and Na^+) do not show any increase after the 11th May (Figure 3a-W, Y, α). Suspiciously, NH_4^+ PM_{2.5} is higher than NH_4^+ PM₁₀ for most days in May (Figure 3a-K), while Total N_{PM2.5} = Total N_{PM10} within uncertainties (Figure 3a-I). $\delta^{13}\text{C}_{\text{PM2.5}}$ = $\delta^{13}\text{C}_{\text{PM10}}$ in most days (Figure 3a-C) except those when the wind regime changed (11-12th May) when $\delta^{13}\text{C}_{\text{PM2.5}} < \delta^{13}\text{C}_{\text{PM10}}$ and $\delta^{15}\text{N}_{\text{PM2.5}} > \delta^{15}\text{N}_{\text{PM10}}$ in most days (Figure 3a-G).

3.4 PM₁₀ in Autumn: High values are measured for some species (Total PM, C, N and those of mainly terrestrial origin NH_4^+ , NO_3^- , K^+) on the 9th and the 26-27th December (Figure 3b).

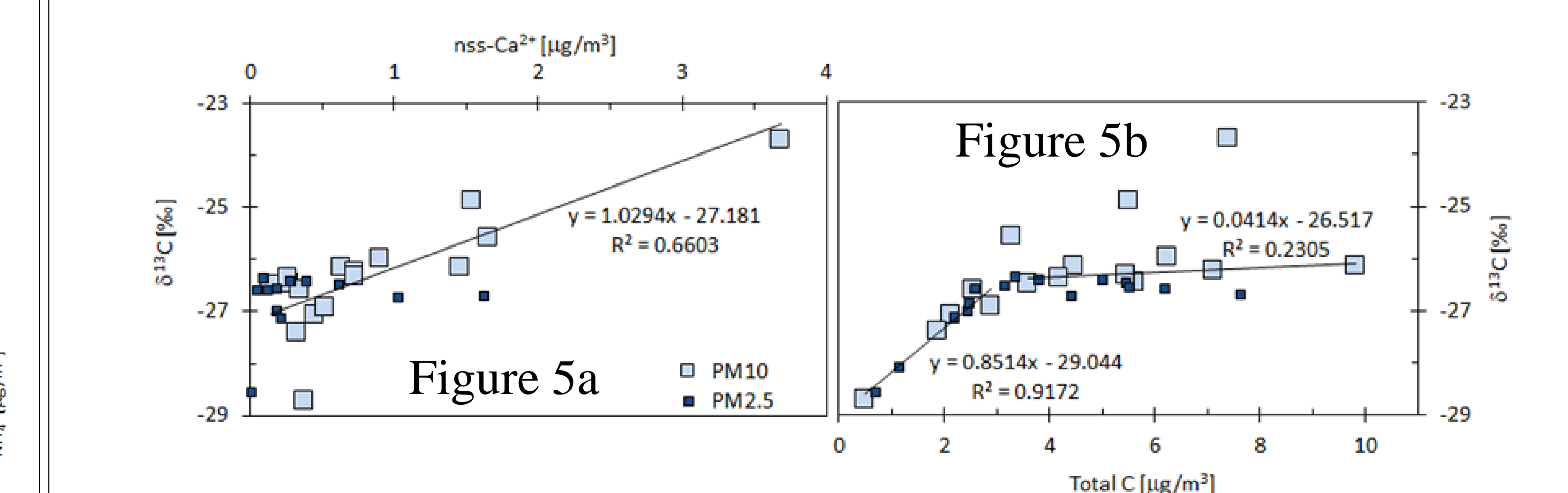
The $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ are very stable instead.

3.5 PM_{2.5} in Autumn: Similar to PM₁₀, with high values on the 9th and 26-27th but less pronounced. $\delta^{13}\text{C}_{\text{PM2.5}}$ misses because of problems during analysis (Figure 3b-D). $\delta^{15}\text{N}_{\text{PM2.5}} > \delta^{15}\text{N}_{\text{PM10}}$ for several days (Figure 3a-G).

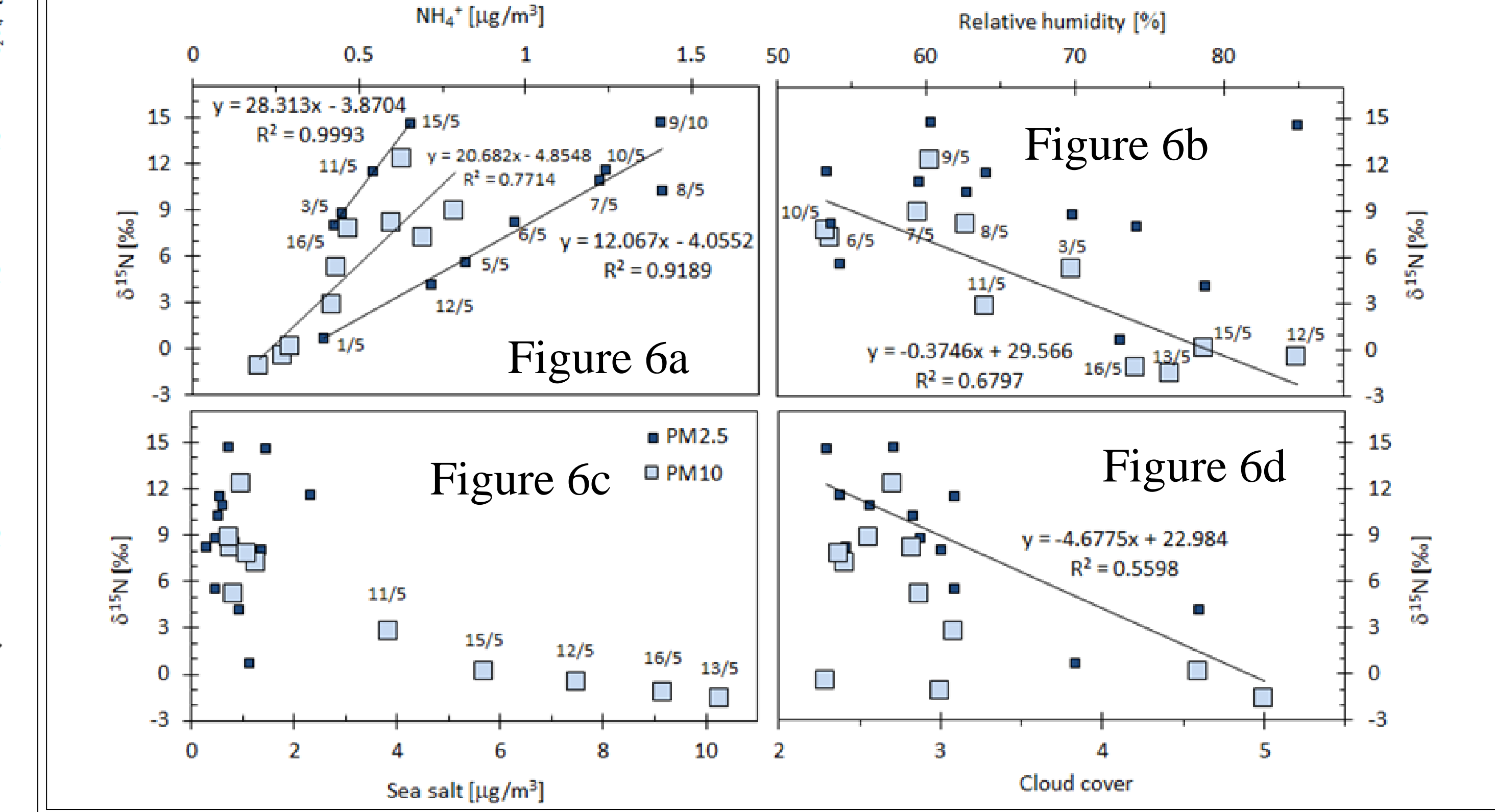


4. Discussions

4.1 C in PM₁₀ in May: The $\delta^{13}\text{C}$ shows high correlation with nss- Ca^{2+} (r = 0.81, p < 0.01, Figure 5a) and there is a clear shift of $\delta^{13}\text{C}$ towards more negative values as total C decreases (see values below 3 $\mu\text{g m}^{-3}$ in Figure 5b). Since the sources that are best resolved by $\delta^{13}\text{C}$ analyses are C₃ plants ([-20 -30] ‰), with fossil C typically depleted in ¹³C, C₄ plants ([-10 -20] ‰) and carbonates (CO_3^{2-} = [-5 +5] ‰), we suggest that the baseline C is mainly composed of fossil C, while the peaks found at the end of the sea-land wind regime are caused by resuspension of CO_3^{2-} -carrying dust (Shen et al., 2013; Vodička et al., 2024).



4.2 N in PM₁₀ in May: $\delta^{15}\text{N}$ best correlates with NH_4^+ (r = 0.90, p < 0.01, Figure 6a), suggesting that variations of $\delta^{15}\text{N}$ of total N are mainly caused by changes of $\delta^{15}\text{N}$ - NH_4^+ . $\delta^{15}\text{N}$ is negatively correlated with relative humidity (r = -0.77, p < 0.01, Figure 6b). These correlations suggest kinetic isotope fractionation associated with the reaction: $\text{NH}_4^+ \leftrightarrow \text{NH}_3$ (Heaton et al., 1987, 1997). The correlation with sea salt in the days 11-16th (Figure 6c) suggests that the increase of $\delta^{15}\text{N}$ during the sea-land breeze (3rd-10th May) might be due to a shift from volatilization to combustion derived N.



4. Conclusions

- Total C_{PM10} and C_{PM2.5} in May are mostly of C₃ origin, with a fossil baseline and a significant contribution of CO_3^{2-} in days with a wind shift and dust resuspension.
- $\delta^{15}\text{N}_{\text{PM10}}$ and $\delta^{15}\text{N}_{\text{PM2.5}}$ in May are influenced by kinetic isotope effects. The correlations found suggest a shift from volatilization to combustion NH_3 sources during the sea-land breeze regime (Chen et al., 2022)
- In Autumn, there are high values of Total PM, C, N and of terrestrial derived species like NH_4^+ , NO_3^- and K^+ , which are tentatively interpreted as biomass burning events. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ do not change significantly and are not useful to identify the sources in that case.
- In the future, to quantify the contribution of different sources, we will use the insight gained to constrain an isotope mass balance for source apportionment.

5. References

Sirignano et al. (2019) Atmosphere, 10: 451; Chianese et al. (2019) J Atmos Chem 76: 151-169; Shen et al. (2013) Radiocarbon 55(2-3): 1790-1800; Vodička et al. (2025) Atmos Chem Phys: 3656; Heaton (1987) Atmos Env 21(4): 843-852; Heaton et al. (1997) Oecologia 109: 600-607; Chen et al. (2022) Nat Comm 13: 7710

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