



PRECIPITATION CHEMISTRY IN NW SPAIN: THE FINGERPRINT OF SUMMER WILDFIRES

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INTRODUCTION

The summer of 2016 was a very hot and dry season. These meteorological conditions favored the occurrence of wildfires in the north and west of the Iberian Peninsula. Although the precipitation is scarce during summer, between 14 and 15 August (period **P1**) and from 13 to 15 September (period **P2**) 2016, two short but intense rain events took place, coinciding with wildfire events. Because wet deposition acts directly on the removal and transport of different pollutants from the atmosphere to the Earth's surface (Seinfeld and Pandis, 2016), it could help mitigate the negative effects of air pollutants emitted by this type of events. Thus, the aim of this study was to determine the impact of forest fire emissions that occurred in the northwest of the Peninsula during summer 2016 on the precipitation chemistry in León, Spain.

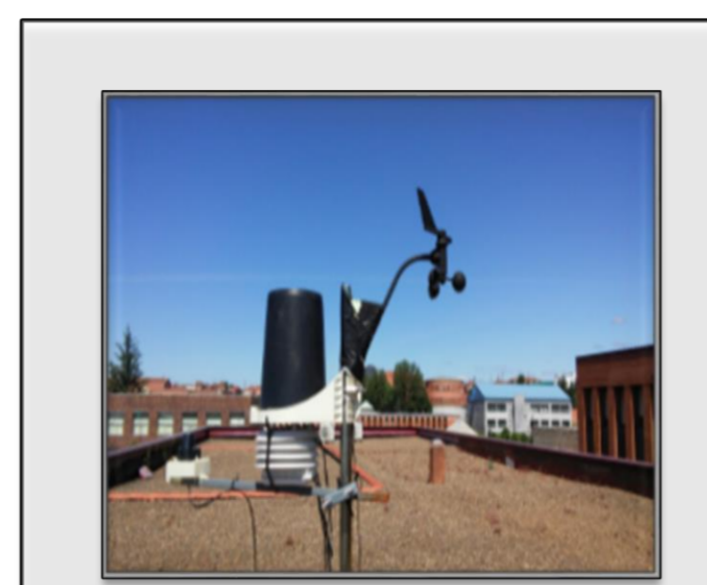
STUDY AREA

The sampling campaign was carried out in the Campus of the University of León, at León city, Spain (42° 36' N, 05° 35' W and 838 m a.s.l.) (Fig. 1), in a sampling period between 01 August and 30 September 2016.

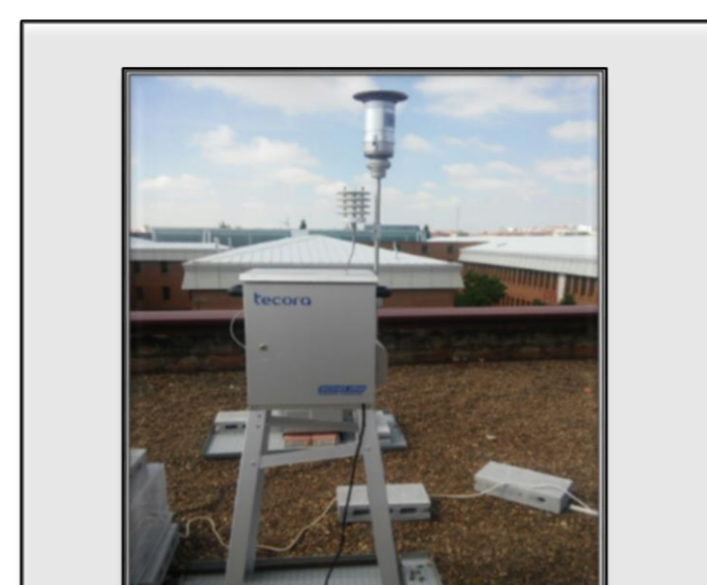


Fig. 1. Map of Iberian Peninsula and location of León.

Sampling



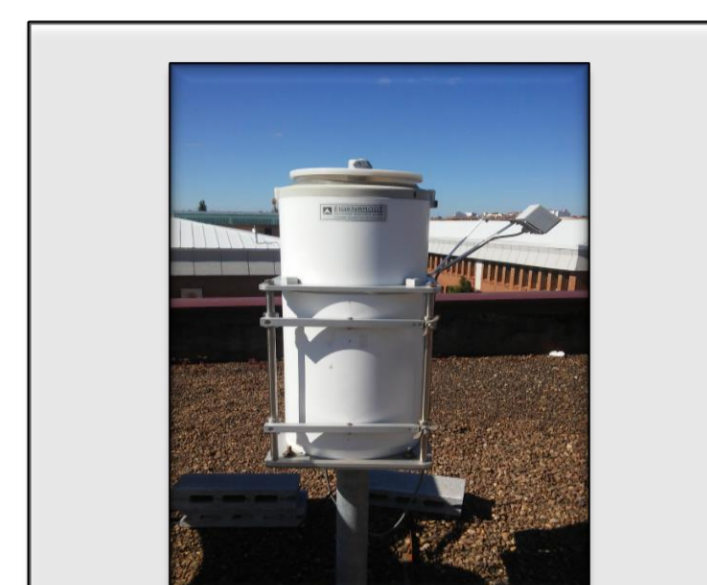
Automatic weather station recorded temperature, wind speed and direction, and relative humidity



Low volume sampler (TECORA, ECHOPM): Collection of PM₁₀ (47 mm diameter teflon filters)



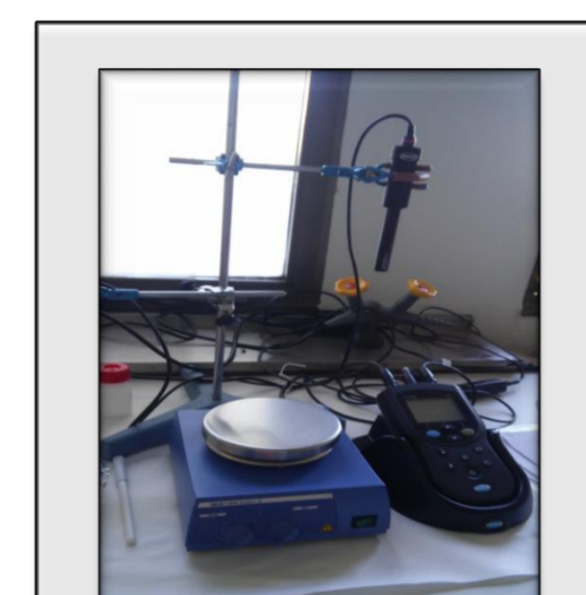
High volume sampler (CAV-A/Mb): Collection of PM₁₀ (150 mm diameter quartz filters)



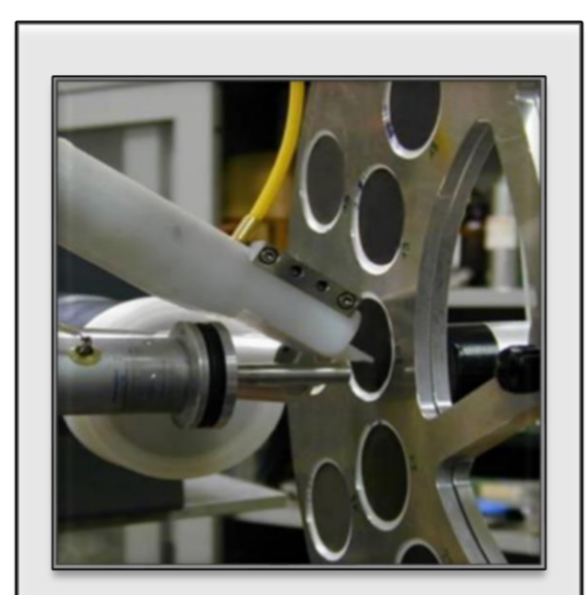
Wet-only automatic precipitation sampler (Eigenbrodt UNS 130/E)

PM₁₀ and precipitation samples were collected every 24 hours, starting at 1200 UTC every day.

Analysis



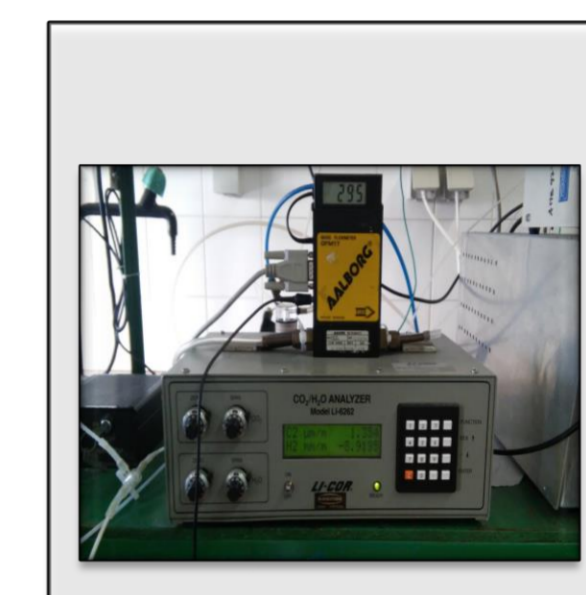
Determination of Conductivity and pH (Hach, HQ 40d multi)



PIXE (Particle-Induced X-ray Emission): analysis of major and trace elements



Thermo Scientific Dionex™ ICS-5000 Ion Chromatography: water soluble ions and levoglucosan



Water insoluble organic (WIOC) and elemental (WIEC) carbon analysis by thermal-optical technique



Total Organic Carbon Analyzer Shimadzu (TOC-VCPH): analysis of dissolved organic carbon (DOC)

Fig. 2. Sampling and analytical instrumentation

RESULTS AND CONCLUSIONS

On 14 August (Fig. 3a) and 13 September 2016 (Fig. 3b), NAAP images showed a high smoke concentration at the northwest of the Iberian Peninsula, and the air mass trajectories confirmed that the smoke from wildfires reached León city.

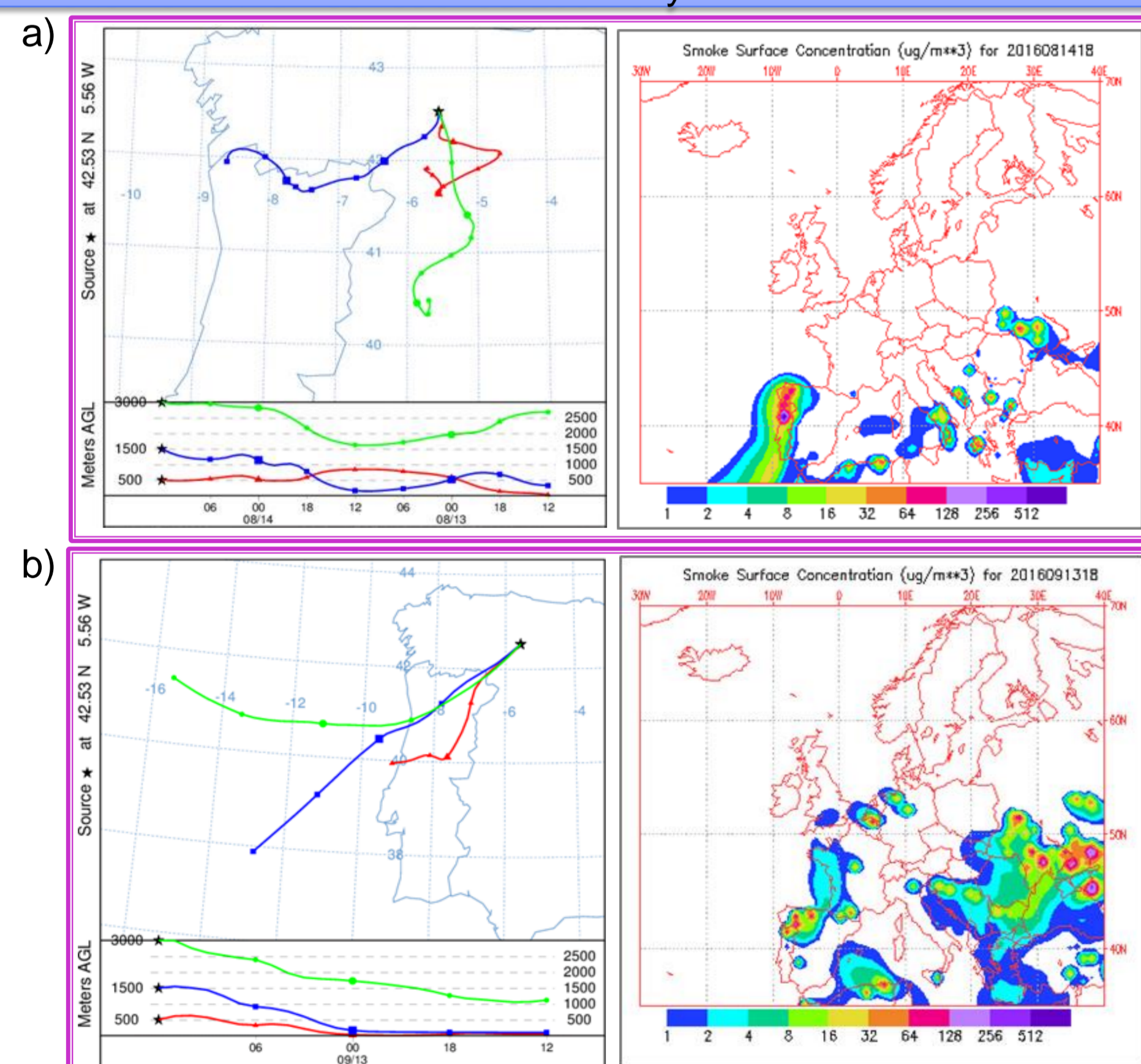


Fig. 3. HYSPLIT back trajectories at 500, 1500 and 3000 m and NAAPs images of smoke concentration for 14 August (a) and 13 September (b) 2016.

The PM₁₀ chemical composition showed a significant increase of the main biomass burning tracers (K and levoglucosan), OC and EC concentrations during both events, confirming the contribution from wildfire emissions to the airborne aerosol in León during these days.

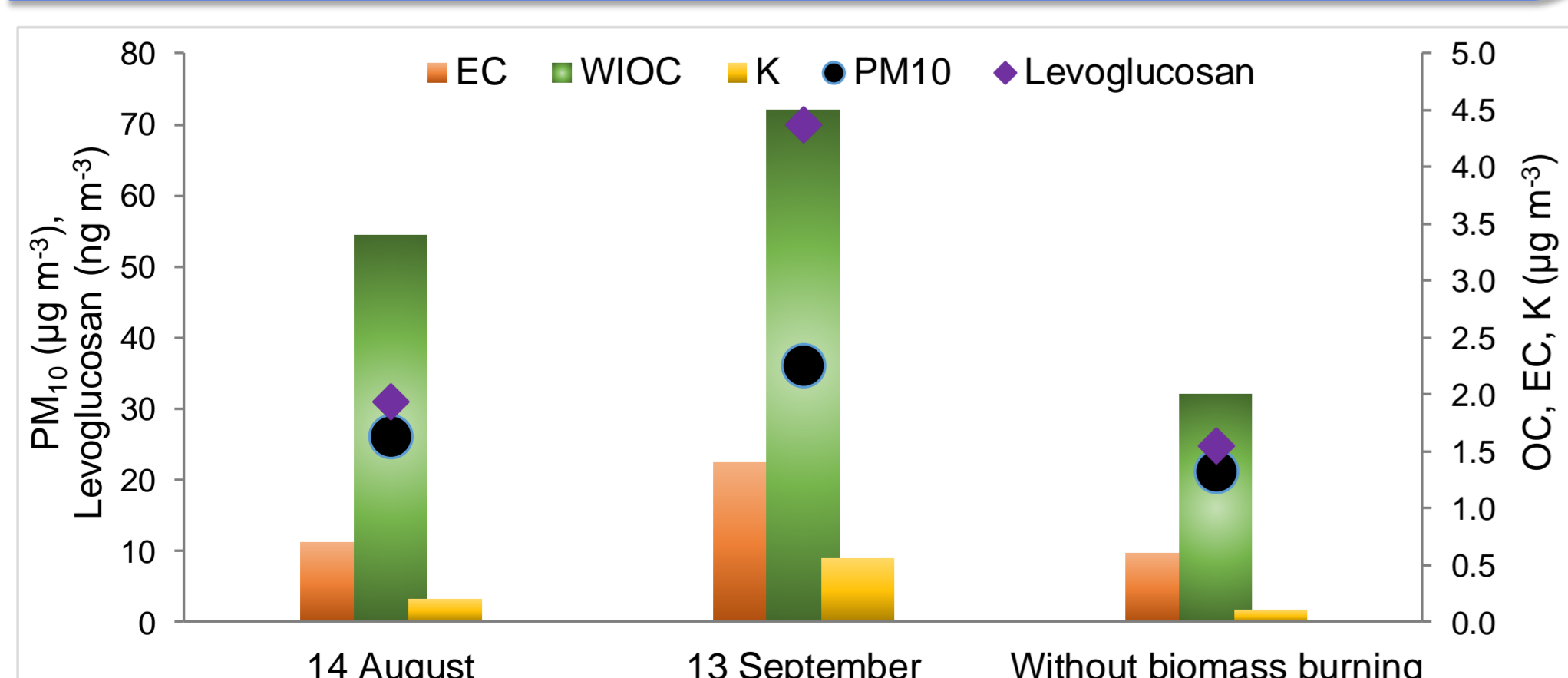


Fig. 4. Daily PM₁₀, EC, OC, K and levoglucosan concentrations in air for 14 August, 13 September and in days without biomass burning events (daily measure between 01 and 30 May 2016).

The mean precipitation intensity was 1.6 mm h⁻¹ and 0.85 mm h⁻¹ for **P1** and **P2**, respectively, and the accumulated precipitation was 3.72 mm in **P1** and 4.63 mm in **P2**. The **P1** rain sample was collected in one fraction on 15 August (**F1**) of 0.03 L, while **P2** was sampled in two fractions of 0.04 L (**F2**) and 0.11 L (**F3**), collected on 14 and 15 September, respectively.

The chemical composition of F1, F2 and F3 showed high concentrations of K⁺, NH₄⁺, Ca²⁺, SO₄²⁻ and NO₃⁻ (Fig. 5a). These ions are commonly related to smoke particles.

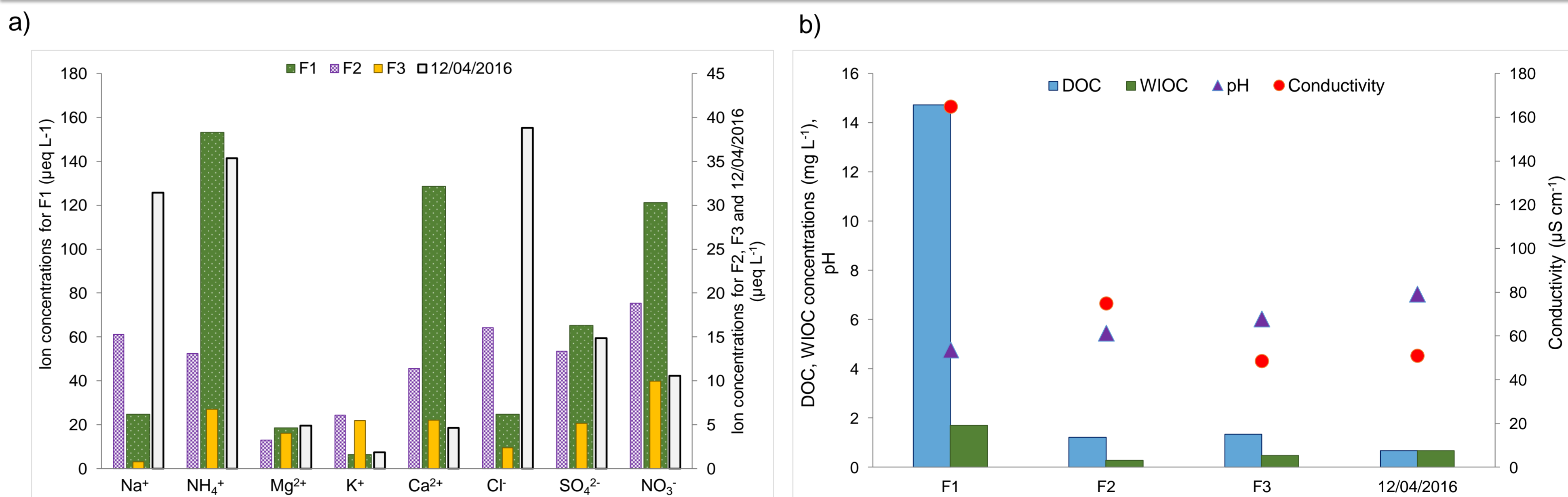


Fig. 5. For each rainwater fractions, collected on 15 August (F1), 14 September (F2) and 15 September (F3), 2016 and on a day without wildfire emissions (12/04/2016): a) Ion concentrations and b) DOC and WIOC concentrations, pH and conductivity.

F1 sample had a pH of 4.8 and a concentration of DOC and WIOC of 14.7 and 1.7 mg L⁻¹, respectively, indicating an excess of acidic species, probably organic compounds (Fig. 5b). Regarding F2, the pH was 5.5, and the NC was 0.8, showing that the alkaline constituents prevented the acidification of rainwater in this event. The highest conductivity value was obtained in F1, which had the highest concentration of ions of both studied events.

Calculations:

- Neutralization Capacity (NC):

$$NC = [C_{Ca^{2+}} + C_{NH_4^+}] / [C_{SO_4^{2-}} + C_{NO_3^-}]$$

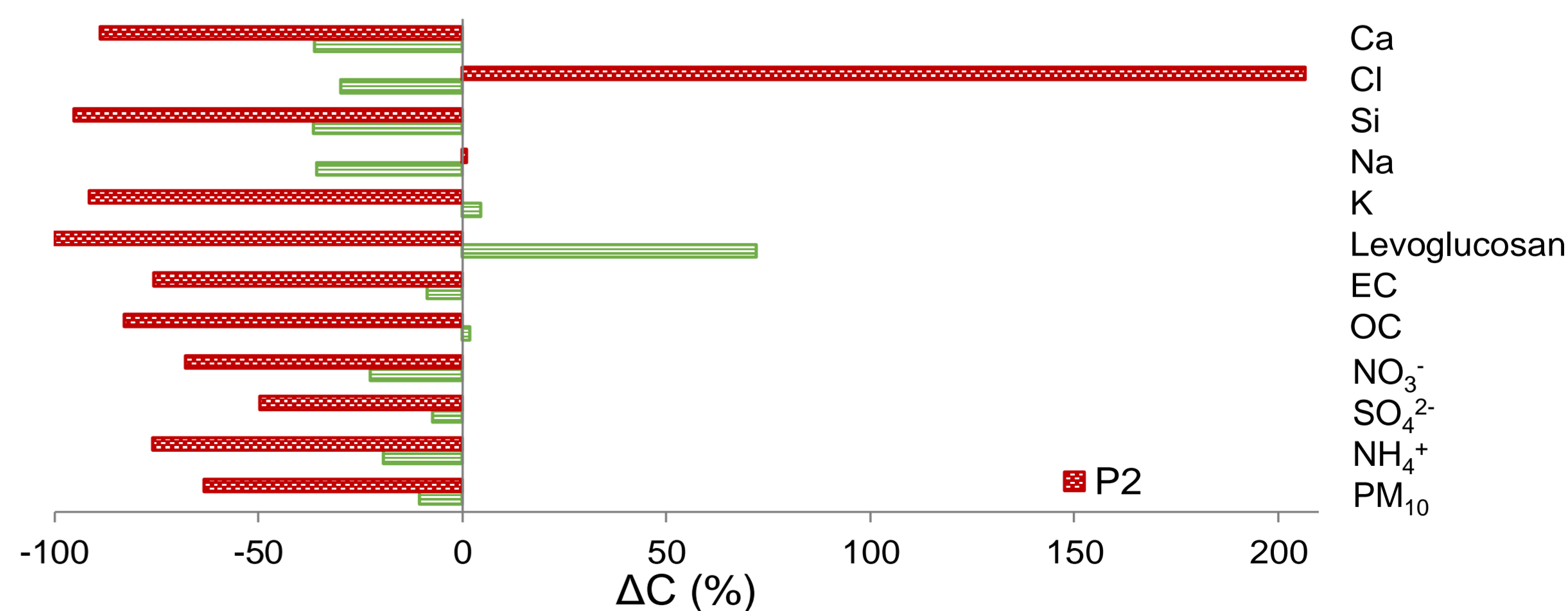
where $C_{Ca^{2+}}$, $C_{NH_4^+}$, $C_{SO_4^{2-}}$ and $C_{NO_3^-}$ are the concentrations, in $\mu\text{eq L}^{-1}$ of the ions calcium, ammonium, sulfate and nitrate, respectively.

- Removal coefficients (ΔC):

$$\Delta C = \frac{C_i - C_f}{C_i} \times 100$$

Where C_i and C_f are the aerosol concentrations before and after rain event, respectively.

Fig. 6. Removal coefficients (ΔC) for the precipitation event of 15 August (P1) and 15 September (P2).



The scavenging effect of the rain was also observed through a decrease in the air pollutant concentrations (Fig. 6) and a slight increase in the pH of rainwater samples F2 and F3 (Fig. 5b), showing that the rainfall amount and intensity are key factors for cleaning up the atmosphere. The coefficient of removal of levoglucosan and K during P1 is positive because the event of forest fire continued after the rain, increasing the concentration of these elements. A similar behavior was observed in P2 with Cl, showing an input of aerosols of sea salt after precipitation.

ACKNOWLEDGEMENTS

This work was partially supported by the Spanish Ministry of Economy and Competitiveness (Grant TEC2014-57821-R), the University of León (Programa Propio 2015/00054/001 and 2018/00203/001) and AERORAIN project (Ministry of Economy and Competitiveness, Grant CGL2014-52556-R, co-financed with FEDER funds). F. Oduber acknowledges the grant BES-2015-074473 from the Spanish Ministry of Economy and Competitiveness. C. Blanco-Alegre acknowledges the grant FPU16-05764 from the Spanish Ministry of Education, Culture and Sport. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (<http://www.ready.noaa.gov>) used in this study. The authors would also like to express their gratitude to the Naval Research Laboratory for providing the NAAP aerosol maps.

REFERENCES

Seinfeld, J.H., Pandis, S.N. (2016). Atmospheric chemistry and physics: from air pollution to climate change. John Wiley & Sons.