

Speciation of Organic Compounds in Rainwater from León, Spain using High Resolution Mass Spectrometry.



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Introduction and AERORAIN Campaign

Many atmospheric compounds are present in both the gas and aerosol phases¹. These compounds can be incorporated into cloud droplets (in-cloud scavenging) or washed out through precipitation (below-cloud scavenging)². Identifying compounds present in rainwater can help us understand the sources of these compounds, the extent of pollution in an area and any potential health effects which may occur as a result³.

During the AERORAIN campaign (June 2015—present), rainwater and filter samples were collected at the University of León in Spain. A precipitation collector with an automated open and close system with a 3.5 L glass bottle was used to collect the rainwater which was then filtered in a sonicated device and frozen for later analysis.

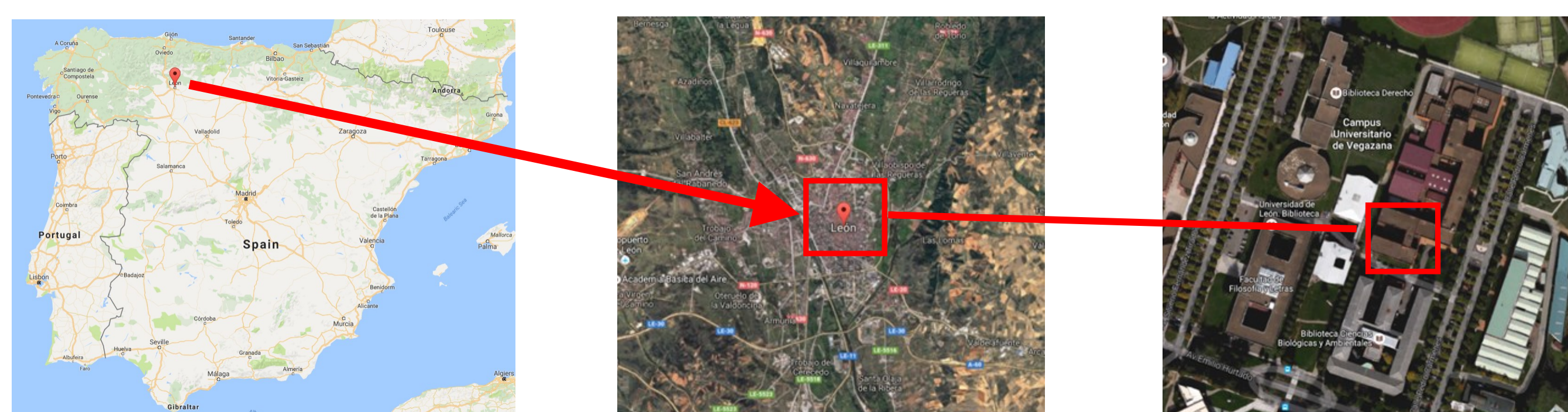


Figure 1: Sampling site on the terrace of the Veterinary Faculty at the University campus in León, Spain. Close to the National Parks of the Cantabrian mountains and the northern coast of Spain; the samples may have marine, forest and urban influence.

Solid Phase Extraction (SPE)

The filter samples were extracted in water, filtered with 0.45 µm pore size filters before SPE and then re-filtered with 0.2 µm pore size filters. Both rainwater and filter samples were prepared using SPE to remove any inorganic salts e.g. nitrates and sulphates and were then evaporated. A SPE method was developed using Reversed Phase Strata-X Polymer based sorbent mass (1 g) to remove contaminants from the ambient rainwater samples (Fig. 2) A Visiprep™ Disposable Liner Vacuum Manifold was used to allow precise flow control and prevent cross contamination between the samples.

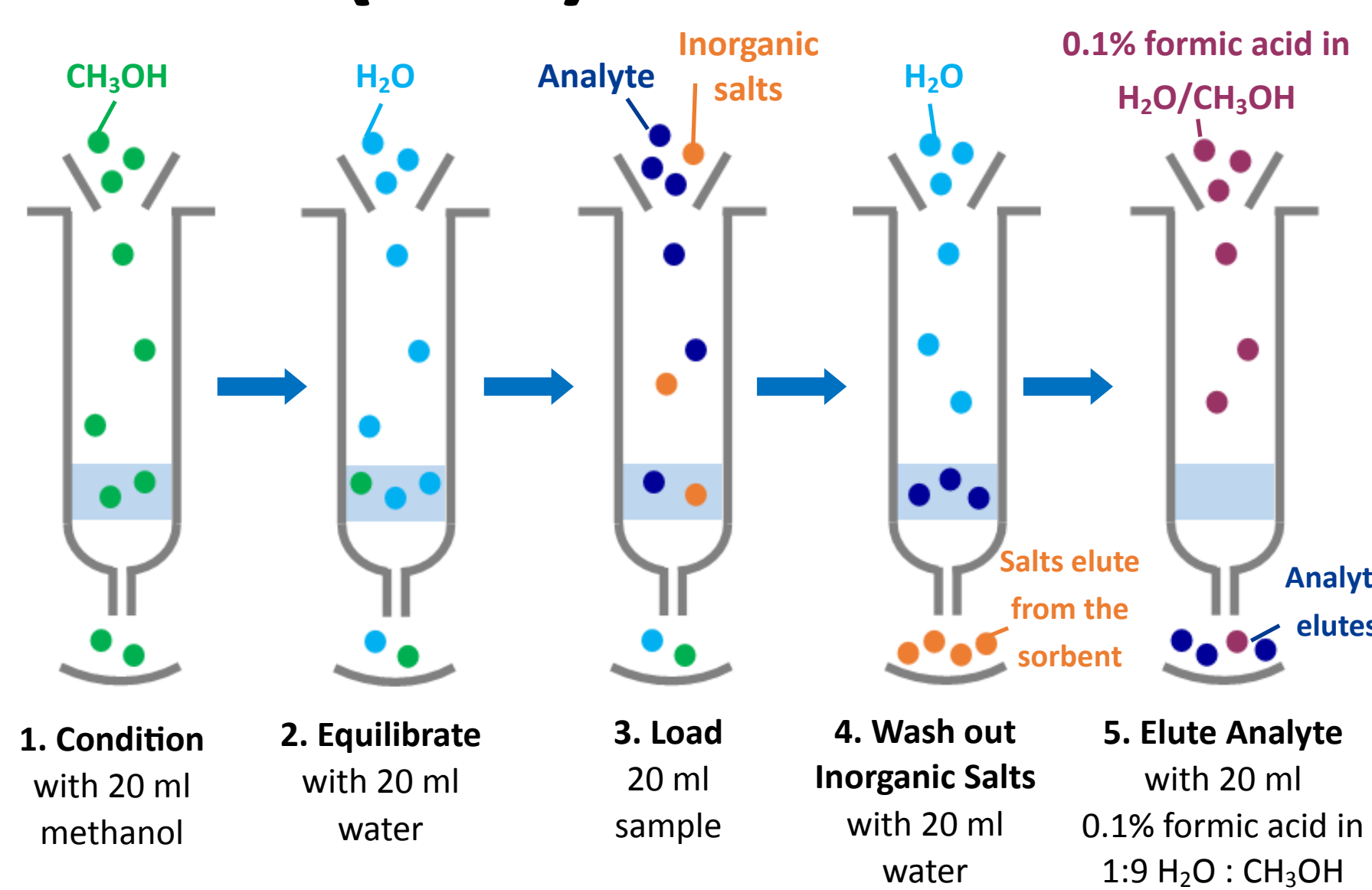


Figure 2: Solid Phase Extraction (SPE) method used for removing salts and concentrating rainwater and water-extracted aerosol filter samples

Direct Infusion and LC-MS

10 rain and 9 filter ‘Spring’ samples; 4 rain and 9 filter ‘Summer’ samples; and 12 rain and 9 filter ‘Winter’ samples were analysed.

The prepared samples were analysed via Direct Infusion using a chip-based Nano-Electrospray Ionisation (nano-ESI) source coupled to a LTQ Velos Orbitrap high resolution Mass Spectrometer (MS). The mass spectra were recorded in negative mode over mass ranges of m/z 60-550 and m/z 150-900. The samples were also analysed using High Performance Liquid Chromatography (HPLC) coupled to the MS (LC-MS). Methanol and 0.1 % formic acid in water were used as the polar mobile phase to separate the analytes according to retention time on the non-polar stationary phase.

HYSPLIT air mass trajectories

Air mass backward trajectories were plotted for each sample from the sampling location using the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory’s (ARL) Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) with the GDAS1 meteorological dataset. Start time of 10:00 UTC coincided with sample collection time and run time was 72 hours at heights of 100, 500 and 1000 m AGL. Rainfall data (mm/hr) was also plotted along the 100 m trajectory.

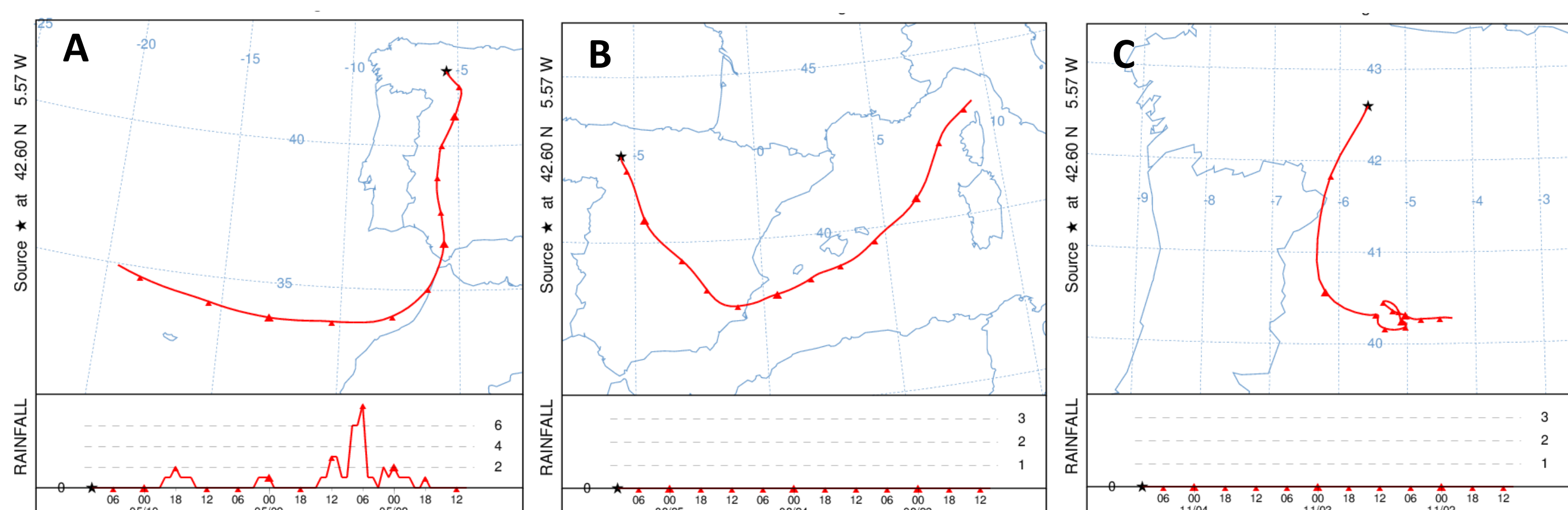


Figure 3: NOAA HYSPLIT backward trajectories for rain events across different seasons. Start time: 10:00 UTC, run time: 72 hours. Above: westerly trajectory for one Spring rain sample at 100 m AGL (A), Summer rain sample with ‘Other’ (mixture of continental and marine) trajectory (B) and winter rain sample with continental trajectory (C). Rainfall data plotted along 100 m trajectories for 72 hours is also shown.

Most of the spring rain samples had a marine, westerly backwards trajectory across the Atlantic Ocean (Fig. 3 A). Contrastingly, most of the summer and winter samples had a (mostly) continental back trajectory with little marine influence (Fig. 3 C). There were some samples which had ‘other’ trajectories with mixed continental and marine influences (Fig. 3 B).

Rainwater and Filter Composition

- Carboxylic acids and nitrogen and sulphur-containing compounds have been identified. Summer filter samples contained the largest number of total compounds, likely due to increased photochemistry and biological activity (Table 1).
- On average, 14% of formulae assigned in spring filters were also present in the rainwater collected on the same day. In summer, 36% of rain compounds were present in the filters and for winter it was 29%.
- Some of the longer rain events (> 3 days), showed washout of the atmosphere by the rain where the number of compounds decreased over time, almost by a factor of 5.
- There were many compounds in both rain and filter samples with high Double Bond Equivalent (DBE) values, consistent with Polycyclic Aromatic Hydrocarbons (PAHs) (Fig. 4).

	Spring	Summer	Winter
Rain	244 (78—799)	1065 (426—2224)	396 (177—808)
Filters	893 (583—1231)	1425 (426—2224)	691 (207—1079)

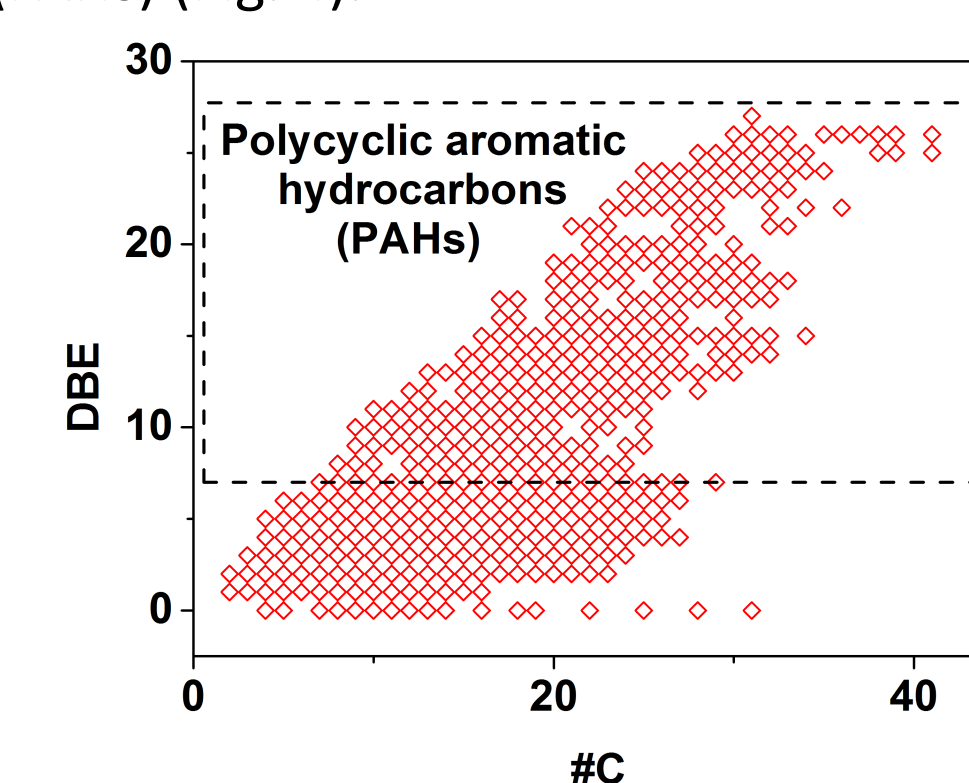


Table 1 (above, left): Average number of compounds in rain and filter samples across different seasons in 2016. Range of number of compounds are shown in brackets. **Figure 4** (above, right): Number of carbon atoms versus Double Bond Equivalent (DBE) for one summer rainwater sample. Many compounds had DBE values ≥ 7.0 , consistent with oxidised polycyclic aromatic hydrocarbons (PAHs).

From April—July, CHO compounds dominate the rain and aerosol composition but from July—December, CHON compounds increase (Fig. 5) which could be due to increased photochemistry in summer and biomass burning from residential heating in Spain and Portugal during winter.

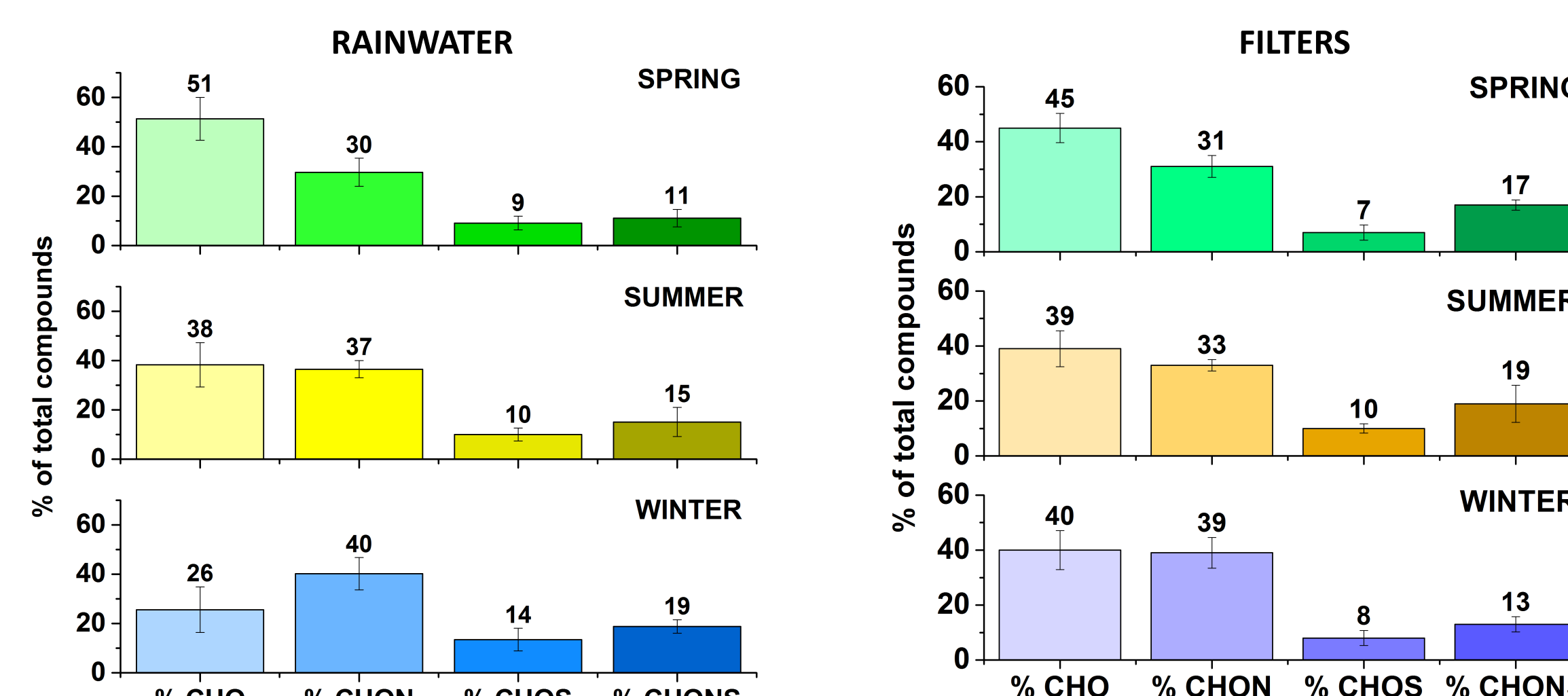


Figure 5: Composition sub groups expressed as percentages of the total number of compounds in the rain (above, left) and filter samples (above, right).

Samples from rain events which had (mostly) continental air mass backwards trajectories contained more compounds than those from marine, westerly trajectories from across the Atlantic Ocean. This may be due to the higher biogenic terrestrial terpene emissions and anthropogenic emissions occurring over land compared with the ‘cleaner’ air over the ocean. Samples which had a mixture of (non-westerly) marine and continental influences had the highest number of compounds (Fig. 6).

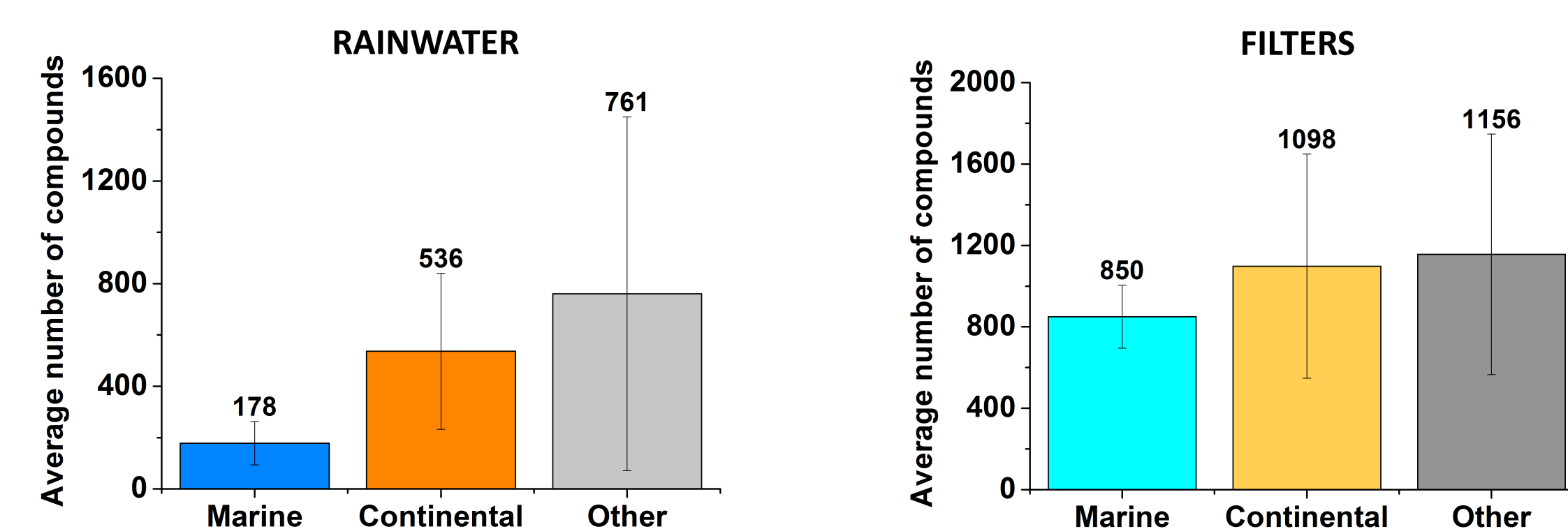


Figure 6: Average number of compounds for rain (above, left) and filter (above, right) samples from marine, continental and ‘other’ trajectories. Note: ‘other’ refers to a mixture of marine and continental influence, producing the highest number of compounds.

Conclusions and Future Work

- Aerosol collected on filters during rain events has higher number of compounds than the rainwater from the same event.
- Total number of compounds in rain: Summer >> Winter > Spring. In filters: Summer >> Spring > Winter.
- From April—July, CHO compounds dominate rain and filter samples. From July—December, CHON compounds increase due to increased photochemistry during summer and biomass burning for residential heating during the winter.
- More compounds are present in both rain and filters in Winter (29%) than Spring (14%) and Summer (36%). This coincides with increased N and S containing compounds in Winter which are more soluble in rainwater.
- Analysis of LC-MS data for the rain and filter samples will help identify specific compounds in the samples.

References

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