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

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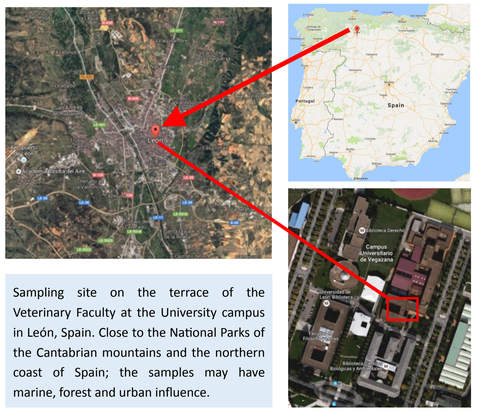
Introduction

Many atmospheric compounds can be incorporated into cloud droplets (in-cloud scavenging) or washed out through precipitation (below-cloud scavenging)[1]. The chemical composition of rainwater can help us understand the sources and transport of pollutants, persistence of organic compounds and any potential health effects which occur as a result [2,3]. Presented here is a molecular characterisation of a subset of rainwater samples collected from León, Spain during the AERORAIN Campaign (2015-2016).

The AERORAIN Campaign *(June 2015 - Dec 2016)*

One aim of this campaign is to parametise the action of rain on aerosols and aerosol impact on human health and on climate.

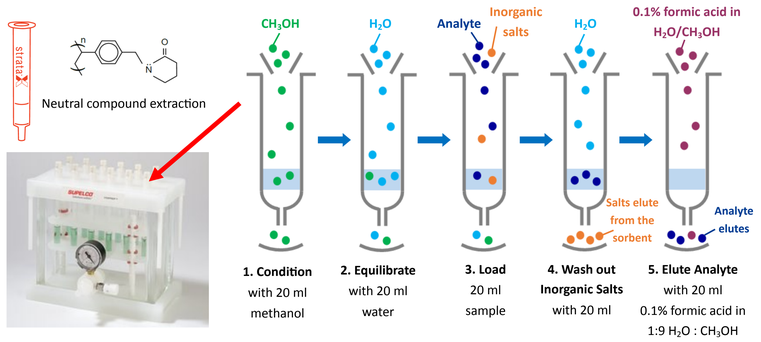
The sampling location is at the University of León in Spain. A precipitation collector with an automated open and close system with a 3.5 L glass bottle was used to collect the rainwater. The collected rainwater is filtered in a sonicated device and frozen for later analysis.



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.

Sample Preparation—Solid Phase Extraction

The rainwater samples were prepared using Solid Phase Extraction (SPE Reversed Phase Strata-X Polymer based sorbent mass, 1g) to remove any inorganic salts e.g. nitrates and sulphates and were concentrated and evaporated to 100 µl. A Visiprep™ Disposable Liner Vacuum Manifold was used to allow precise flow control and prevent cross contamination.



Method and Data Analysis

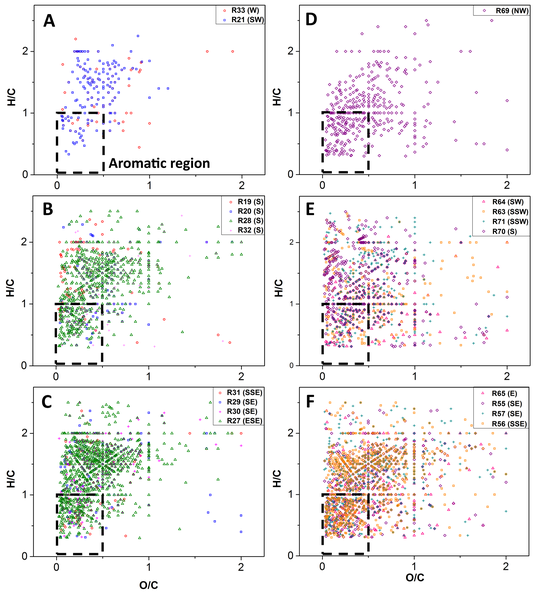
10 rainwater samples collected during "Spring" (April-May), 4 from "Summer" (July-August) (*not presented here*) and 12 from "Winter" (October –December) of 2016 were analysed. Initial sample volumes ranged from 7-25 ml and average pHs of 6.63 for Spring samples, 5.67 for Summer samples and 5.83 for Winter samples.

The prepared samples were analysed with 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.

Data analysis:

- Mass tolerance set to 5 ppm, 40 formulae assignments allowed
- Only allowed formulae with $^{12}C \leq 100$, $^{13}C \leq 1$, $^{1}H \leq 200$, $^{16}O \leq 50$, $^{14}N \leq 20$, $^{32}S \leq 2$, $^{34}S \leq 1$
- Nitrogen and Double Bond Equivalent (DBE) check
- Blank Subtraction and Common Ion Removal

Results

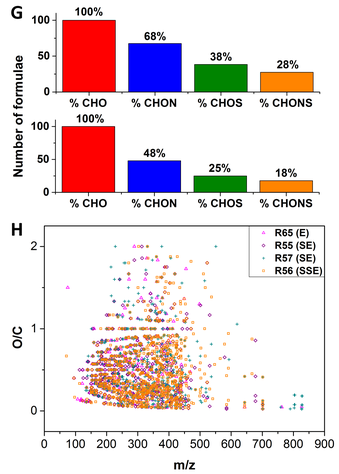


Van Krevelen plots for rainwater samples following direct infusion in negative ionisation mode. Spring rainwater samples from rain events brought by winds from the west (A), south (B) and south-east (C). Also shown are Winter rainwater samples from rain events brought by winds from north-west (D), south-west (E) and south-east (F). All samples have significant proportion of aromatic compounds (dashed area).

Van Krevelen plots for Spring and Winter rainwater samples show that Winter samples overall contain more compounds than Spring samples which could be due to Winter rain events having higher maximum rain intensities on average.

Both Spring samples (A,B,C) and Winter samples (D,E,F) show a high fraction of compounds (dashed area) with O/C ratios of 0-0.5 and H/C ratios of 0-1 which are consistent with substituted aromatic compounds.

Rain events brought to the sampling site by winds from a south-easterly direction (C and F) contain the most compounds, for both Spring and Winter samples. This could be due to close proximity to road pollution from nearby motorway.



Composition of Winter (G top) and Spring (G bottom) rainwater samples showing more nitrogen and sulphur containing compounds in Spring samples. Plot H shows m/z vs O/C ratio for Winter samples with heavy compounds with m/z > 450 Da (also observed in Spring samples).

Carboxylic acids and potentially, some nitrogen and/or sulphur containing compounds have been identified. Overall, the winter samples contained on average ~200 more compounds than the spring samples. Distributions of compounds for Winter (G - top) and Spring (G - bottom) samples show that Winter samples contain more nitrogen and sulphur containing compounds. This may be due to lower boundary layer conditions for the winter rain events causing more mixing and dissolving of more compounds in the cloud droplets which then get rained out of the atmosphere.

Plot H of m/z vs O/C ratio for Winter rainwater indicates presence of heavy compounds with m/z >450 which are likely to be primary compounds either of natural or anthropogenic origin. This was also observed for the Spring samples, to a slightly lesser extent.

Conclusions and Future Work

- These Winter rainwater samples on average contained ~200 more compounds than the Spring rainwater and also more CHO, CHON, CHOS and CHONS compounds than Spring samples.
- Meteorological factors for these samples are very important. Rain events from South-East of León contain more compounds than rain from the South directly, West and North. Air mass back trajectories will be used to learn more about the significance of this.
- The same rainwater samples were also analysed using High Performance Liquid Chromatography (HPLC) coupled to the MS (LC-MS). Analysis of this data will indicate concentrations of specific compounds present in rainwater across the different seasons.
- Aerosol was collected during the same rain events and extracted in water and prepared using similar SPE method as described. Analysis of the filters show some similar trends to those observed in the rainwater but further analysis is required to fully assess the relationship between rainwater and aerosol composition.

References

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3. Kawamura, K. and Kaplan, I. R. 1983. *Organic Compounds in the Rainwater of Los Angeles.* Environmental Science and Technology, 17, 497-501.
4. Phenomenex. 2015. *Solid Phase Extraction (SPE) Method Development Guide*.