Portrayal of organic aerosol sources in Western European and South American locations using ¹H NMR spectroscopy

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Organic aerosols (OAs) represent an important fraction of atmospheric particulate matter and, consequently, may exert a significant impact on climate and human health (Mauderly *et al.*, 2008). During the last 15 years, much of the work on the detailed structural characterization of this fraction has been focused on the water-soluble organic matter (WSOM) component, which represents a highly variable fraction (~10-80%) of particulate organic matter (Duarte and Duarte, 2012). Despite its importance in several atmospheric processes, the multitude of molecular forms, sources, and atmospheric reactivity makes a complete characterization of aerosol WSOM extremely difficult. Nevertheless, determining the structural composition of this component is needed both to increase the current understanding of its role in various atmospheric processes, and to better constrain its major sources. In this context, solution-state proton nuclear magnetic resonance (¹H NMR) spectroscopy has proved to be a very useful tool for both unravelling the functional group composition of aerosol WSOM, and aerosol source identification.

In this work, ¹H NMR spectroscopy was applied for assessing the major organic functional groups present in WSOM extracted from aerosol samples collected in different Western European (Portugal – Aveiro and Lisbon) and South American (Brazil – São Paulo, Rio de Janeiro, and Amazonia, Argentina – Buenos Aires, Colombia – Bogotá, and Peru – Lima) locations. Despite the limited variability of functional group compositions, the studied aerosol samples are less oxidized than those observed elsewhere (Decesari *et al.*, 2007), with smaller relative contributions of carbon-oxygen double bonds. Furthermore, these samples do not fit the already established ¹H NMR source apportionment fingerprints of marine, secondary, and biomass burning OAs (Decesari *et al.*, 2007). The qualitative and quantitative differences of ¹H NMR profiles suggested the existence of a possible new fingerprint associated with the contribution of biological particles (Chalbot *et al.*, 2014) and urban aerosols (Cleveland *et al.*, 2012). These results indicate that the boundaries of the signature "boxes", especially of secondary and biomass burning OAs, might be different for the studied aerosol samples, and that the relative distribution of nonexchangeable organic hydrogen functional groups appear to be distinctively unique for urban and biological particles.

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