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Complementary atmospheric pressure electrospray and photoionization high-resolution mass spectrometry unravel the molecular complexity of soil humeomes

GIOVANNI VINCI[1], ALESSANDRO PICCOLO[1] AND **MAXIME BRIDOUX**[2]

[1]Università di Napoli Federico II
[2]CEA

Presenting Author: maxime.bridoux@gmail.com

High-resolution mass spectrometry (HRMS) can resolve thousands of compounds in complex mixtures such as natural organic matter. However, HRMS is seldom sufficient to fully resolve the molecular heterogeneity of Humus in the soil matrix, especially if no preliminary simplification of Humus complexity is applied and if a single ionization technique is used. Here we show that HRMS, when applied with both photoionization (APPI) and electrospray ionization (ESI) and combined with the extensive molecular simplification provided by a humeomic fractionation [1] , significantly increases identification of the molecular composition of soil Humus [2]. Different sequential extractions separate the soil Humeome in three organosoluble fractions (ORG1-3) and two hydrosoluble fractions (AQU2 and RESOM), which showed distinct molecular characteristics. The ORG fractions were particularly homogeneous and rich in alkyl compounds including unsaturated hydrocarbons and lipid compounds found mainly in ORG 1 and ORG 3, but also aromatic compounds comprising lignin-like molecules and condensed structures mainly detected in ORG2. The AQU2 fractions revealed greater complexity and heterogeneity due to the simultaneous detection of sugars, amino sugars, tannins and N-containing compounds not detectable in appreciable concentrations in other fractions. The most recalcitrant RESOM fraction contained highly reduced molecules and condensed structures. The combined use of APPI and ESI showed a marked selectivity in the detection of chemically different molecules separated in each fraction, thereby enhancing their molecular characterization. Specifically, APPI tended to ionize less oxidized and N-containing molecules, and compounds with high concentrations of unsaturation or aromatics, while ESI was more prone to detect highly oxidized compounds consisting of large O/C ratios. Our findings indicate that the combination of a soil Humeome fractionation with a detailed high-resolution characterization of differently ionized molecules in the separated fractions enables a far deeper understanding of the molecular composition of soil Humus and the comprehension of its environmental reactivity.

[1] Nebbioso & Piccolo (2011), *Biomacromolecules* 12, 1187-1199.

[2] Vinci, Piccolo & Bridoux (2022) *Anal. Chim. Acta.* 1194, 339398.