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ABSTRACT SYMPOSIUM NAME: Accurate Mass/High Resolution Mass Spectrometry for Environmental Monitoring & Remediation (Oral)

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TITLE: Hydrogen deuterium exchange of environmental samples to improve non-target elucidation

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ABSTRACT BODY:

Abstract: Mass spectrometry is increasingly popular for the non-targeted exploration of complex sample matrices. However, mass spectra do not always contain sufficient information to unequivocally identify the correct structure from the spectrum and direct labelling techniques cannot be used to gain additional information for environmental samples. Hydrogen deuterium exchange (HDX) experiments can instead be used to provide additional information for the elucidation of unknown compounds in complex samples measured using liquid chromatography coupled with high resolution mass spectrometry (LC-HRMS) with deuterated solvents. Automated workflows were created in the R programming language to extract the data and perform the data processing. The approach and theory was tested initially on a set of 762 substances of environmental interest. The timescale of LC allowed the 100% exchange of “easily-exchangeable” hydrogens (connected to heteroatoms) and this already provided information on heteroatom-based functional groups in the full scan MS1. $[M+D]^+$ ions were generally formed in positive mode, while $[M-D]^-$ ions were observed in negative mode where an exchangeable H was present. Pairs of spectra (normal and deuterated) were found for 593 of the 762 substances (506 positive mode, 155 negative mode spectra). The presence of deuterium in MS/MS fragments was used by adding new scores to the in silico fragmenter MetFrag (<http://c-ruttkies.github.io/MetFrag/>). These included fragmentation scores for the normal and deuterated spectra, an H/D fragment pair score and an additional score to account for the number of deuterium atoms that were expected to exchange. Initial applications to non-target screening of a river water extract from Novi Sad (Serbia) revealed interesting phenomena not observed in the standard “deuterium-free” experiments, but indicate that HDX experiments can be used to gain additional information about non-target candidates in a semi-automated manner.

(No Image Selected)