Supporting Information

Communicating Confidence of Per- and Polyfluoroalkyl Substance (PFAS) Identification via High Resolution Mass Spectrometry

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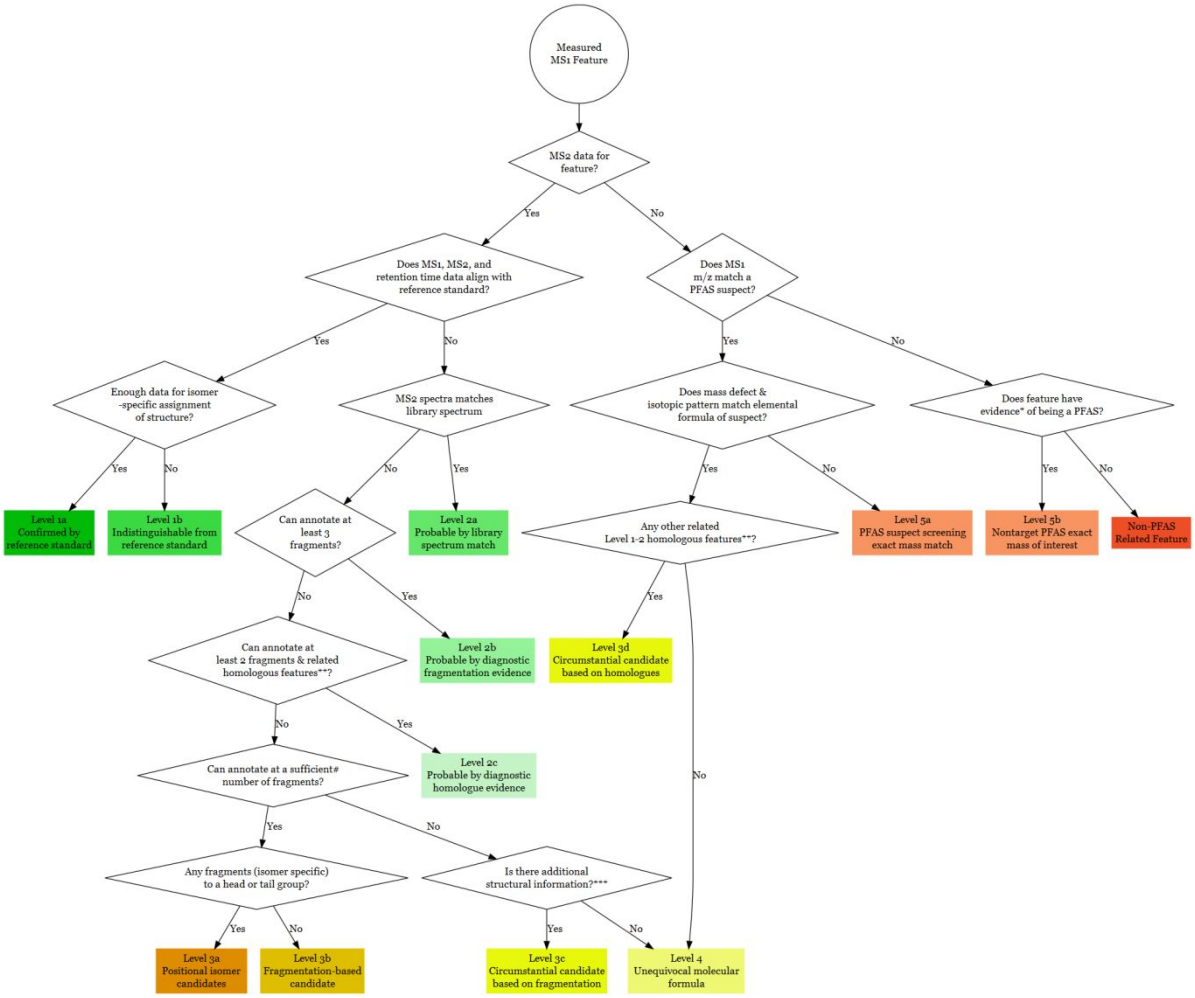

Figure S1. Confidence of PFAS identification example workflow.

Footnotes:

*Evidence of being a PFAS described in Level 5b text

**Related homologous features are ± m/z 50 or 100 and expected retention time interval from a level 1-2 feature

***Including:

- Observation of sufficient number of fragments to exclude other structural isomers, based on *in silico* predicted MS/MS fragments for the proposed structure.
- Fractionation of species by positive or negative charge through anion or cation exchange solid-phase extraction.
- Detection of possible zwitterionic PFASs in both positive and negative ionization modes.
- Chromatography indicative of electrochemical fluorination. In such cases, often a branched isomer peak (or peaks) is followed by a linear isomer peak.
- The abundance of homologues that are separated by -(CF2CF2)- (i.e., 99.9936 Da). Elevated concentrations of only even- or odd-length homologues are indicative of fluorotelomerization. The lengths of homologues are more uniformly distributed in typical electrochemical fluorination-based mixtures.
- A positive mass defect for candidate PFASs, which may indicate the presence of non-fluorinated functional groups in the structure.

#Sufficient defined as the number of fragments needed to align a structure with a particular PFAS subclass (see section titled "High-Resolution MS/MS Spectra" for more information)'

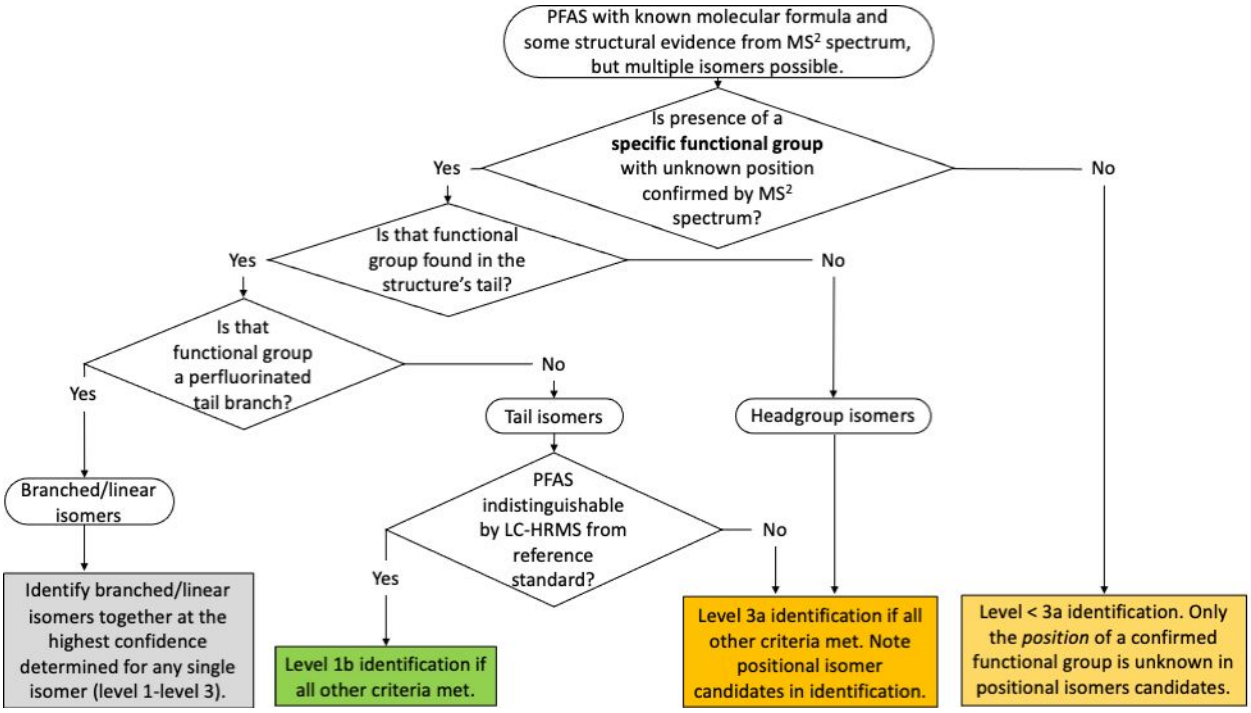

Figure S2. Guidance for classification and identification of PFASs with some evidence of structure from MS/MS spectrum, but multiple isomers possible. Isomer candidates may be determined entirely from structural evidence or from structural evidence and PFAS suspect lists.