# Electronic Supplementary Information For:

# Rapid In-Situ Detection of Chemical Warfare Agent Simulants and Hydrolysis Products in Bulk Soils by Low-Cost 3D-Printed Cone Spray Ionization Mass Spectrometry

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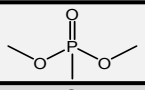
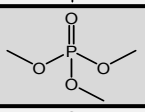
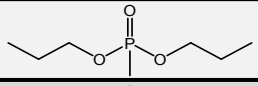
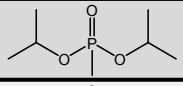
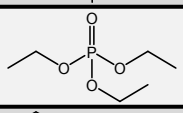
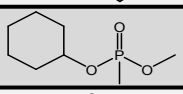
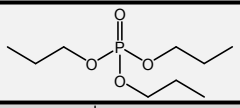
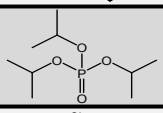
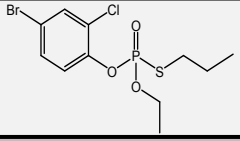
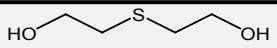
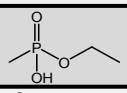
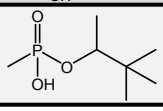
**Table S1.** CWA simulants and CWA hydrolysis products studied by 3D-PCSI-MS. Included in the table is the compound name and abbreviation, chemical structure, molecular weight, and which authentic CWA the simulant corresponds to.

| Chemical Warfare Agent Simulants | | | |
|---|---|---|---|
| **Name** | **Structure** | **Simulant[7, 9, 74-76]** | **MW (g/mol)** |
| DMMP |  | Variant for generic G-series nerve agent (phosphate group) | 124.08 |
| TMP |  | Variant for generic G-series nerve agent (phosphate group) | 140.07 |
| DEMP |  | Variant for generic G-series nerve agent (phosphate group) | 152.13 |
| DIMP |  | Structurally similar to Sarin (GB, G-series nerve agent) | 180.18 |
| TEP |  | Variant for generic G-series nerve agent (phosphate group) | 182.07 |
| CMMP |  | Structurally similar to cyclosarin (GF, G-series nerve agent) | 192.19 |
| TPP |  | Variant for generic G-series nerve agent (phosphate group) | 224.23 |
| TiPP |  | Variant for generic G-series nerve agent (phosphate group) | 224.23 |
| Profenofos |  | Simulant for generic V-series nerve agent, contains phosphate group bonded to sulfur | 373.63 |
| **Chemical Warfare Agent Hydrolysis Product** | | | |
| **Name** | **Structure** | **Hydrolysis Product (HP)** | **MW (g/mol)** |
| TDG |  | Sulfur Mustard HP (blister agent) | 122.04 |
| EMPA |  | V-series nerve agent oxidative degradation product | 124.08 |
| PinMP |  | Soman (GD, G-series nerve agent) HP | 180.18 |

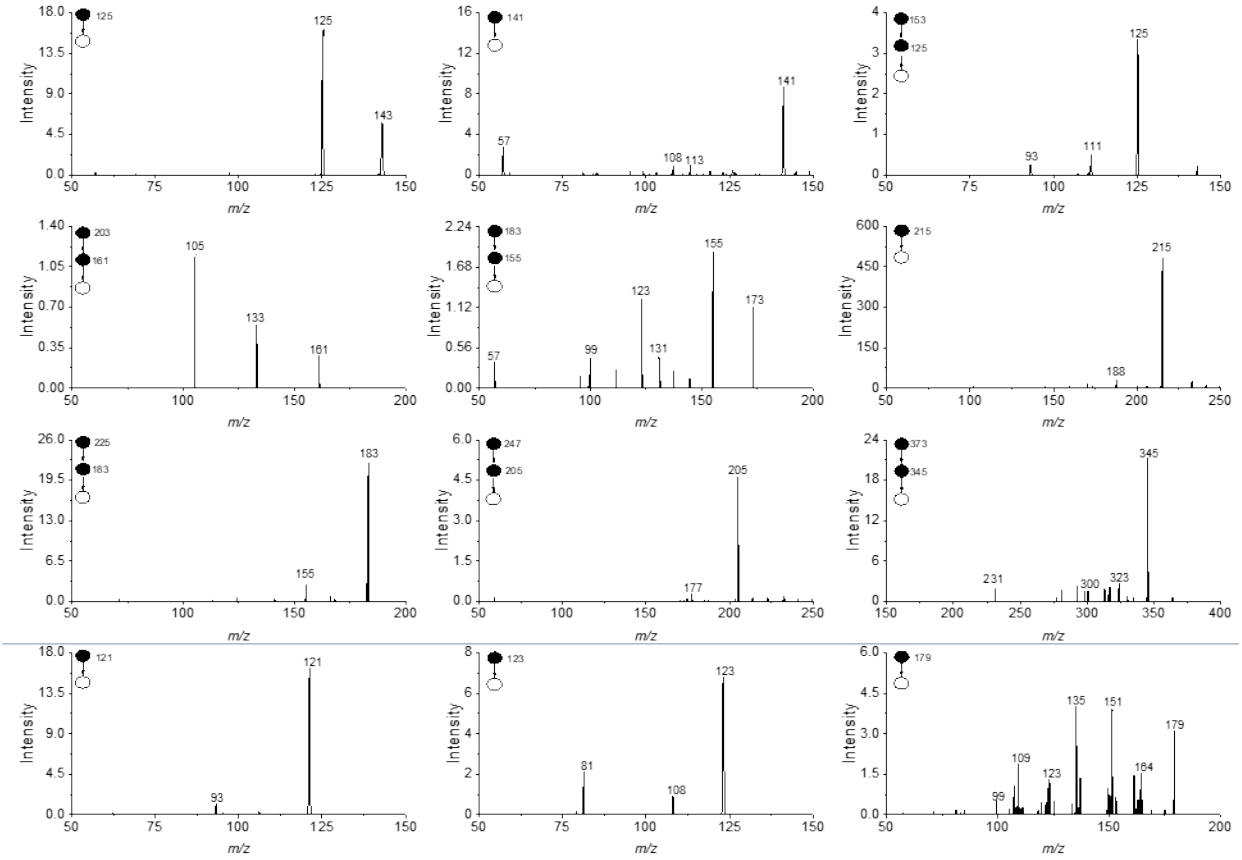



**Figure S1.** Spectra of clean topsoil at the various mass transitions of interest. No CWA simulants or hydrolysis products were added to the clean topsoil. The top nine spectra were collected in positive ionization mode, and the bottom three, below the blue line, were collected in negative ionization mode to match the corresponding CWA simulants' and hydrolysis products' transitions. No observable indicative fragments were observed in the clean topsoil. The overall signal intensities were low.

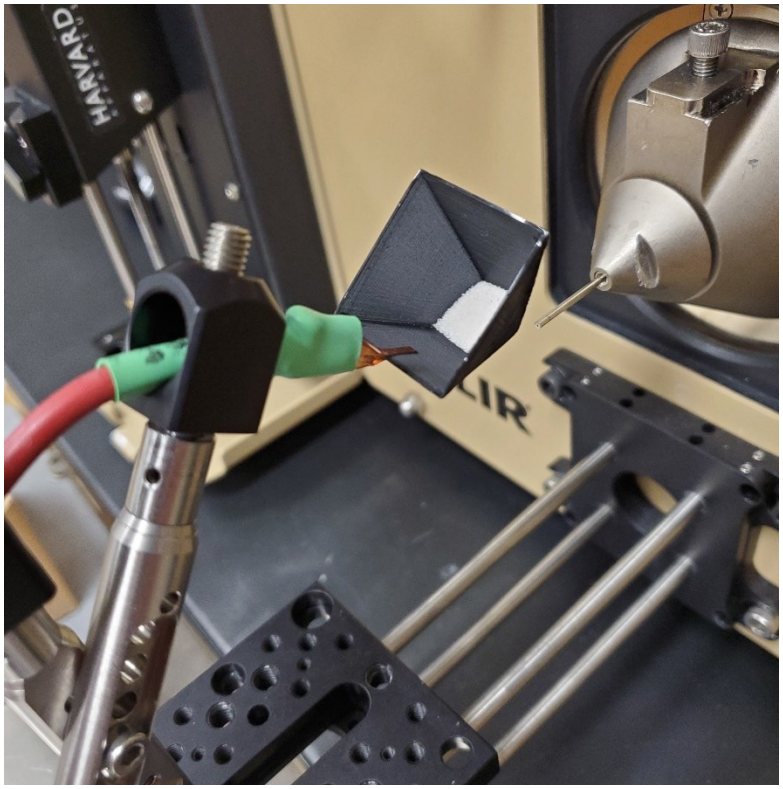



**Figure S2.** A depiction of the 3D-PCSI source coupled with the FLIR AI-MS 1.2 for soil analysis. Application of high voltage through a clamping style electrode and appropriate spray solvent allows rapid screening for contaminants (sand shown here). Generated analyte ions enter the continuous atmospheric pressure inlet for mass analysis.

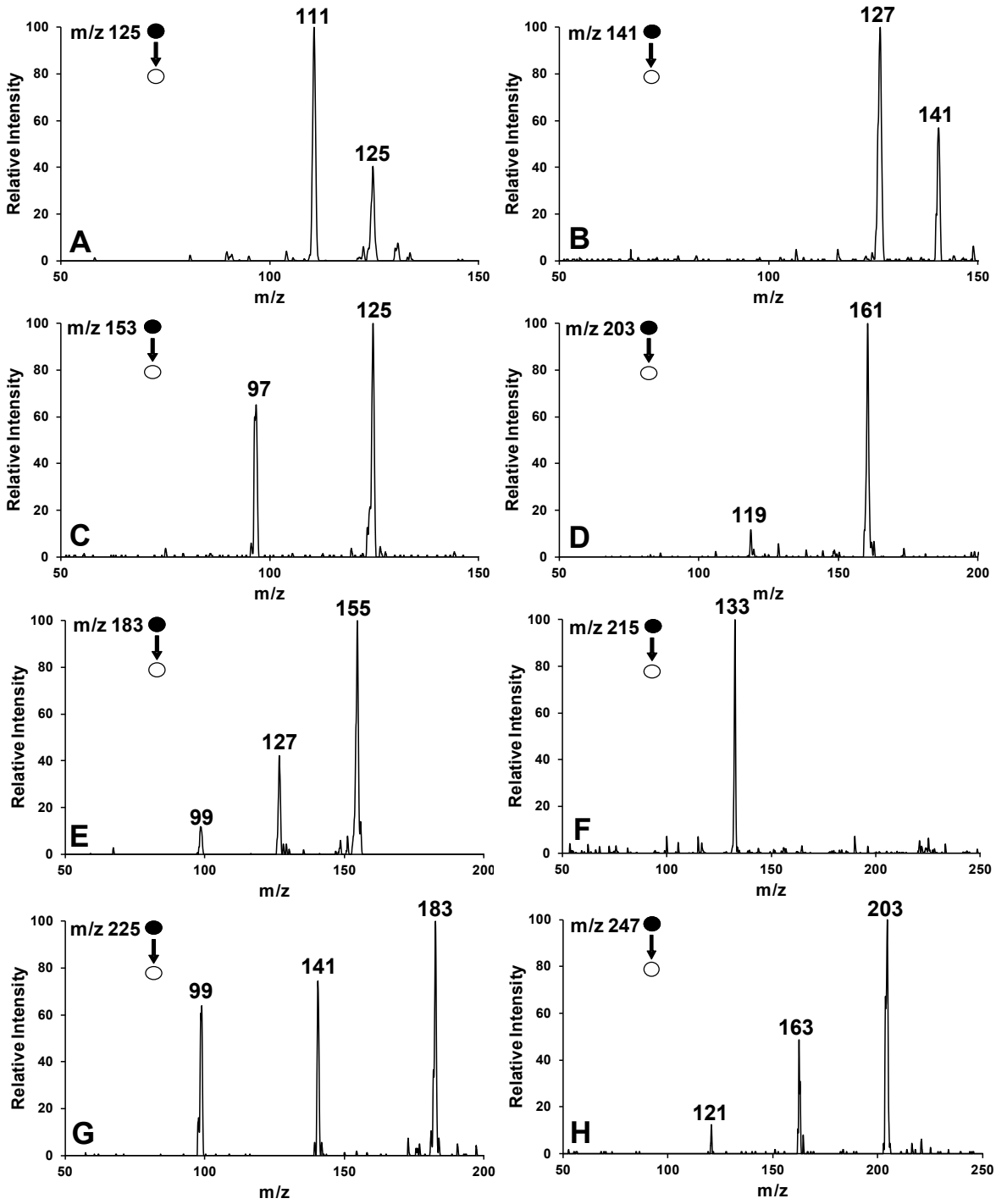



**Figure S3.** 3D-PCSI-MS/MS spectra collected on the FLIR AI-MS 1.2 portable mass spectrometer for (A) DMMP, (B) TMP, (C) DEMP, (D) DIMP, (E) TEP, (F) CMMP, (G) TPP, and (H) TiPP. Characteristic fragmentation patterns are observed, similar to those obtained in the benchtop MS system utilized in this study.

**Table 2**. The empirical limits of detection based on triplicate measurements, for eight CWA simulants in sand matrix on the field deployable AI-MS. LOD concentrations reported in parts per million (ppm).

| Chemical Warfare Agent Simulant | |
|---|---|
| **Name** | **LOD in Sand (ppm)** |
| DMMP | 0.9 |
| TMP | 2 |
| DEMP | 1 |
| DIMP | 1 |
| TEP | 1 |
| CMMP | 0.95 |
| TPP | 2 |
| TiPP | 1 |