

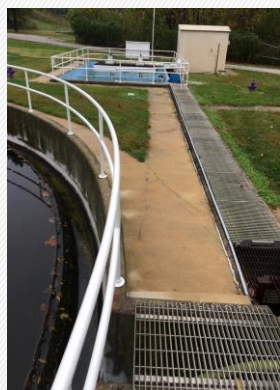


Applications of mass spectrometry imaging in the environmental sciences

SIUE

Dr. Kevin R. Tucker
Department of Chemistry

Tucker Research Lab Themes



**Water
Pollution**



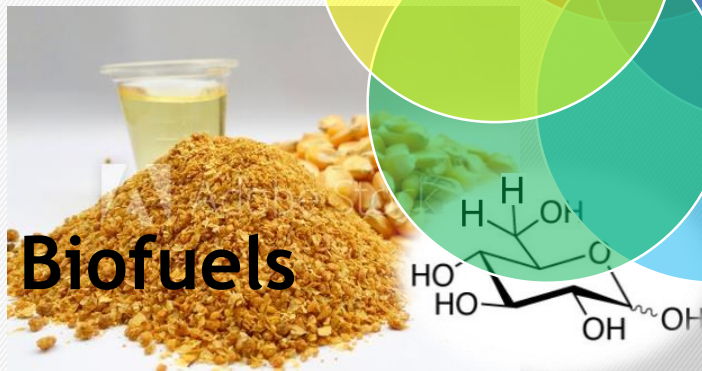
**Analytical
Chemistry**



Toxicology



Agriculture

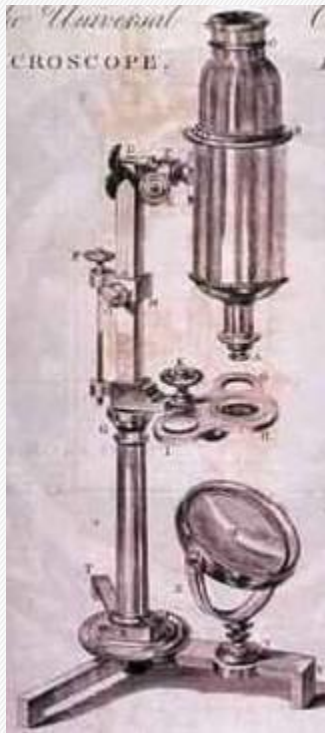


Biofuels





Anton Van Leeuwenhoek, 1632-1723
Father of Microscopy
270x Magnification



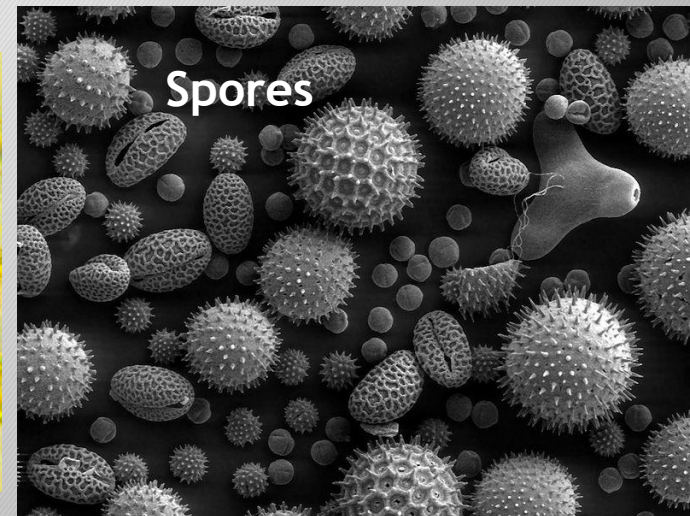
Maximum Spatial Resolution: 200 nm
1200x Magnification



Tomato Peel

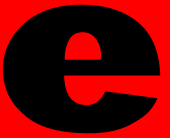


Scanning Electron Microscopy
Maximum Spatial Resolution: $<1\text{ nm}$
500,000x Magnification

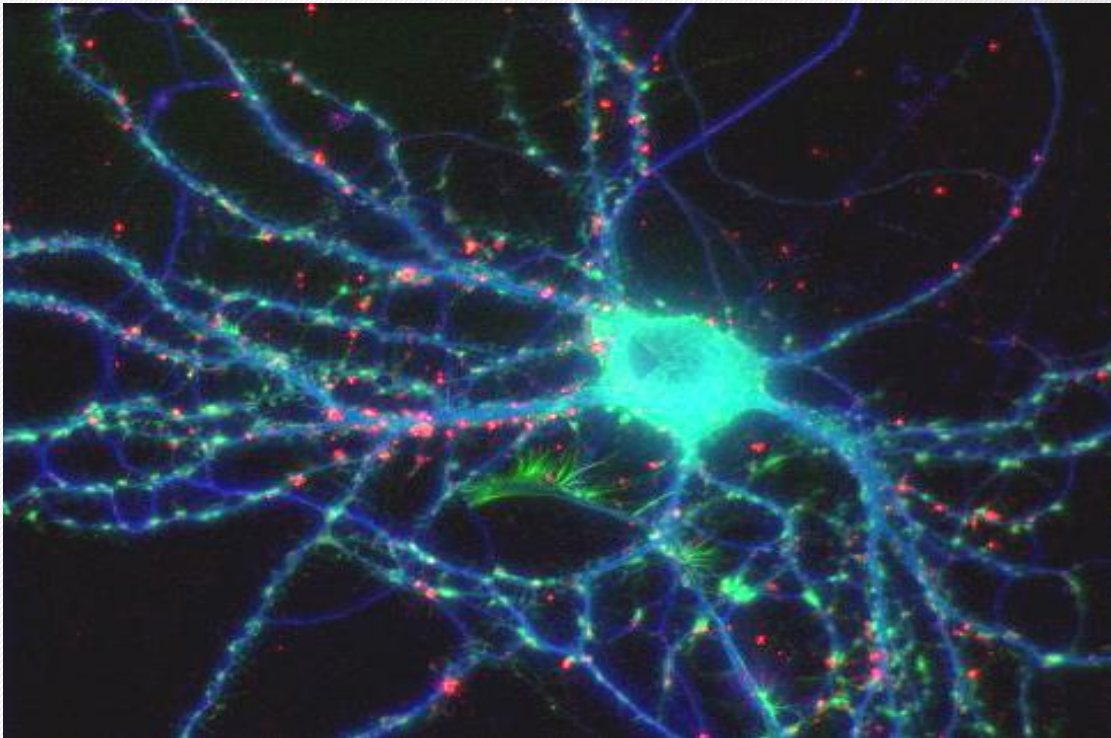


Spores

Optical Microscopy



- Traditional imaging methods (fluorescence and other optical techniques) provide specific information at better spatial resolution, but lower information content
- Mass spectrometry imaging provides a much higher information content without analyte preselection.

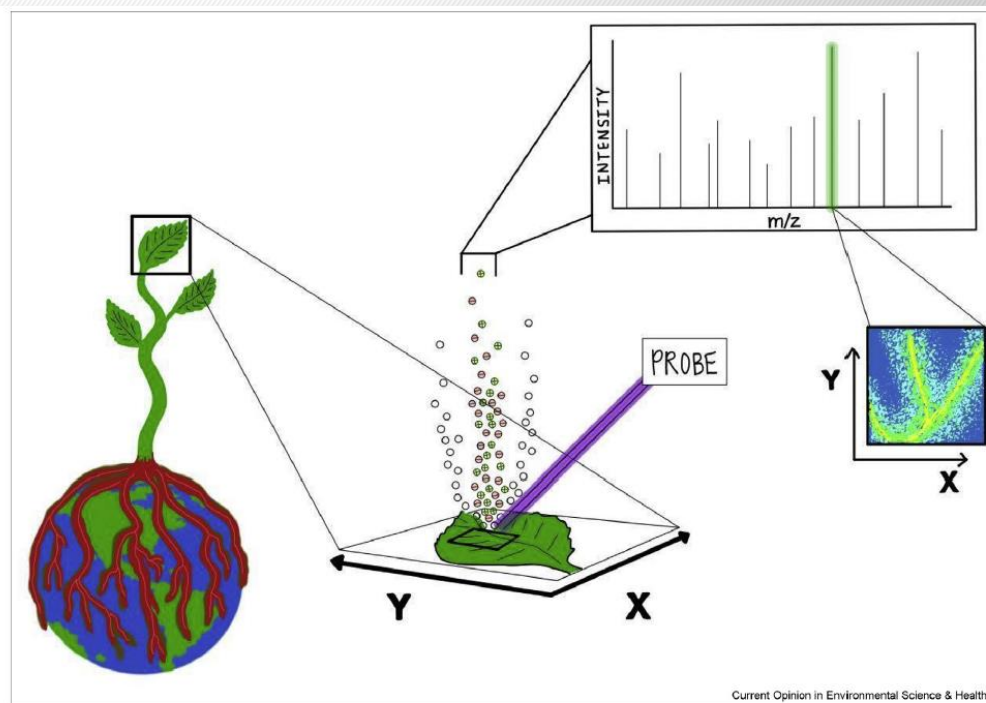


Immunofluorescence:
A multi-wavelength
image of a fixed
neuron. Cell body
labeled for **tubulin**,
F-actin, and
presynaptic protein.
[http://www.wadsworth.org/
cores/alm/gallery](http://www.wadsworth.org/cores/alm/gallery)

Mass Spectrometry Imaging



- MSI generates two-dimensional ion images by moving either the sample stage or the analytical beam in a raster pattern.
- A complete mass spectrum is taken at every position.
- The intensity of an m/z range is plotted creating an ion image.



A pictograph of mass spectrometry imaging. A piece of fresh leaf sample is sectioned onto a slide that is probed (e.g. MALDI, SIMS, etc.) to expel positive and negative ionic species into the MS detector. The neutral species are discarded and not detected. Each peak on the mass spectrum can show us a portion of the probed image in real time. MALDI, matrix-assisted laser desorption/ionization; MS, mass spectrometry; SIMS, secondary-ion mass spectrometry.

Ionization Source Choices



Table 1

Ionization techniques and their characteristic properties that are used for the mass spectrometry imaging analysis of environmentally relevant samples.

| Ionization Technique | Ionization characteristics | Advantages | Disadvantages |
|----------------------|--------------------------------------|--|--|
| MALDI | Soft, atmospheric or vacuum pressure | ~10 μm spatial resolution, robust literature methodology | Costly automated matrix application systems |
| REIMS | Soft, atmospheric pressure | Easy sampling protocols, little sample preparation, characteristic peak information | Compounds are thermally decomposed leading to incomplete information for some classes of molecules |
| DESI | Soft, atmospheric pressure | Easy sampling protocols, little sample preparation, amenable to many brands of ESI instruments | Lower spatial resolution (~250 μm) |
| SIMS | Hard, ultrahigh vacuum pressure | High spatial resolution (<1 μm), little sample preparation | Very high instrument cost, limited to molecules under 500 Da, sample must be vacuum stable |
| LA-ICP | Atomizing, atmospheric pressure | Best approach for quantitative imaging of metals, little sample preparation | Not commercially available |

DESI, desorption electrospray ionization; ICP, inductively coupled plasma; LA, laser ablation; MALDI, matrix-assisted laser desorption/ionization; SIMS, secondary-ion mass spectrometry; REIMS, rapid evaporative ionization mass spectrometry.

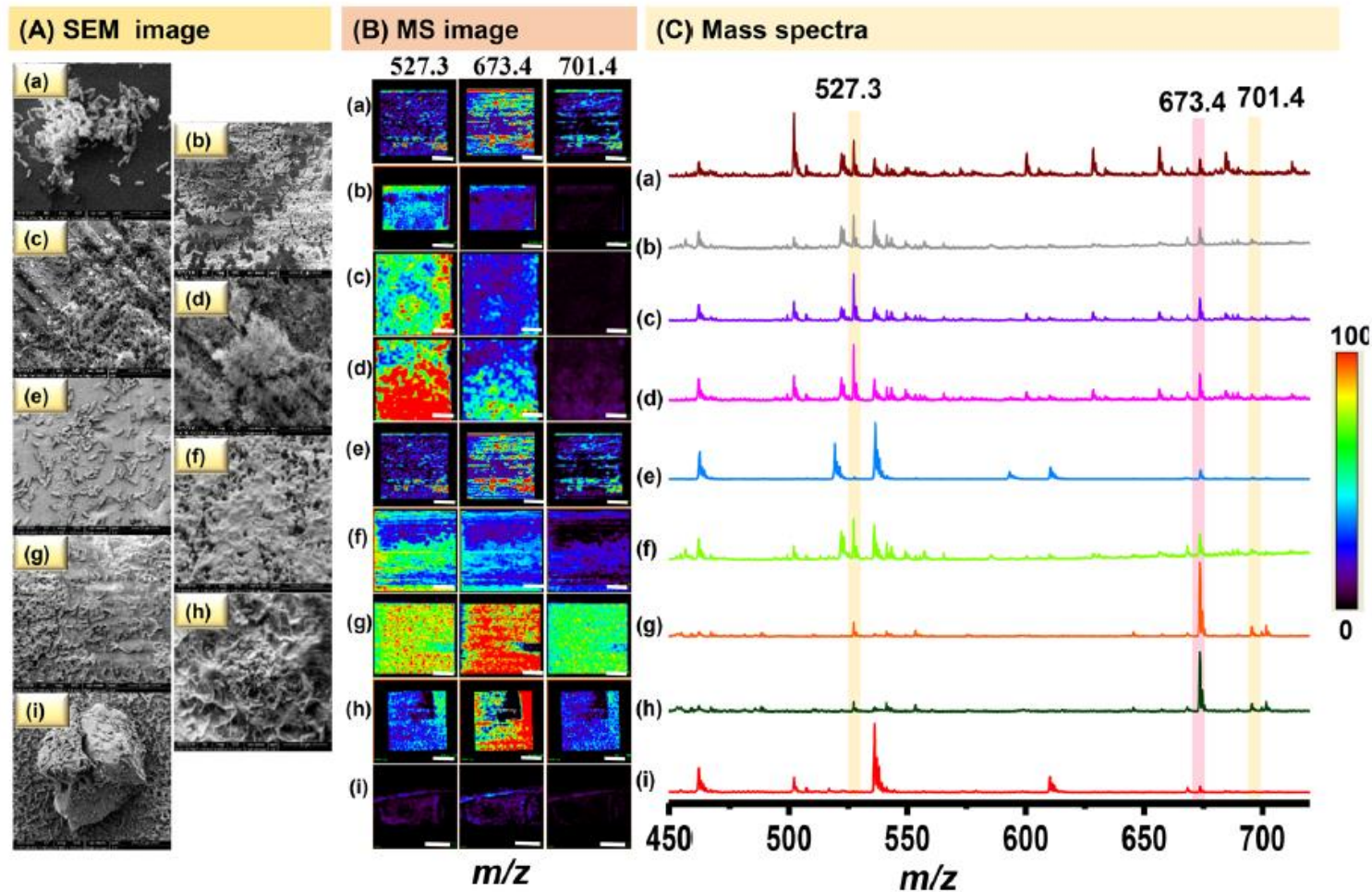


Figure 2. (A) SEM images, (B) positive mode DESI MS images, and (C) DESI mass spectra from various substrates. The substrates are (a) glass (b) polypropylene, (c) polyvinyl chloride, (d) polysulfone, (e) RO membrane, (f) nylon membrane, (g) aluminum, (h) copper, and (i) a water purification composite. Sodium adducts of different rhamnolipids are seen at m/z 527.3, 673.4, and 701.4, the spatial profiles of which are shown in part B. The scale bar in DESI MS images corresponds to 5 mm and are same in all the images. DESI MS images are color coded, and the color code is shown on the right.

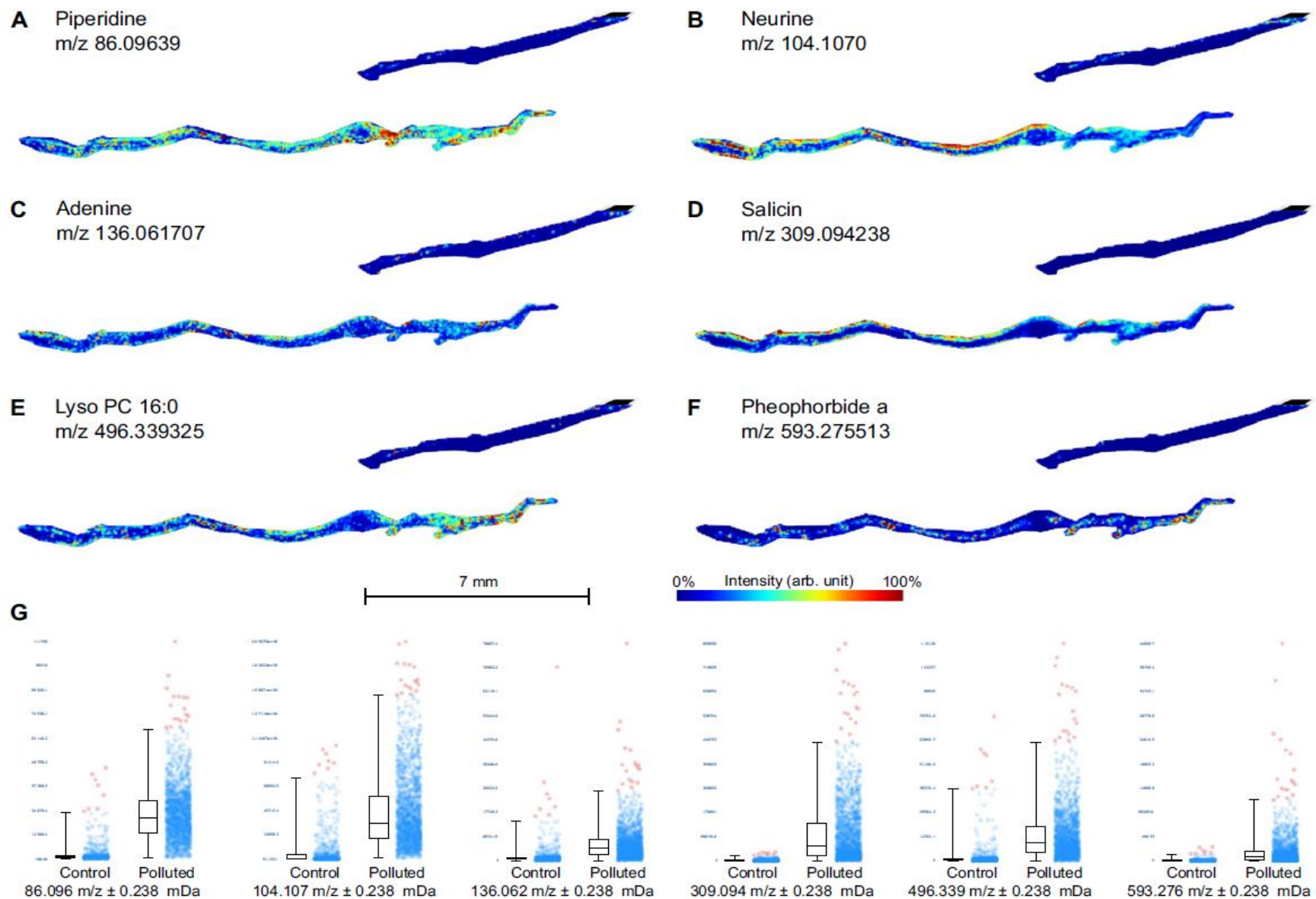


Fig. 4. Plant metabolites annotated in poplar leaves. Plant metabolites were annotated in poplar leaves and appear to be more generally distributed. Neurine (B) and salicin (D) are mostly found in peripheral tissues, pheophorbide a (F) is localized in inner tissues, and other metabolites are found in the whole leaves. Boxplots (G) confirm that these metabolite features are differential between control and polluted leaves. Intensity is presented as an arbitrary unit and represented by a color gradient. The chemical properties of piperidine, neurine, adenine, salicin, lyso PC 16:0 and pheophorbide a are presented in Table S2. Replicates are shown in Fig. S4.

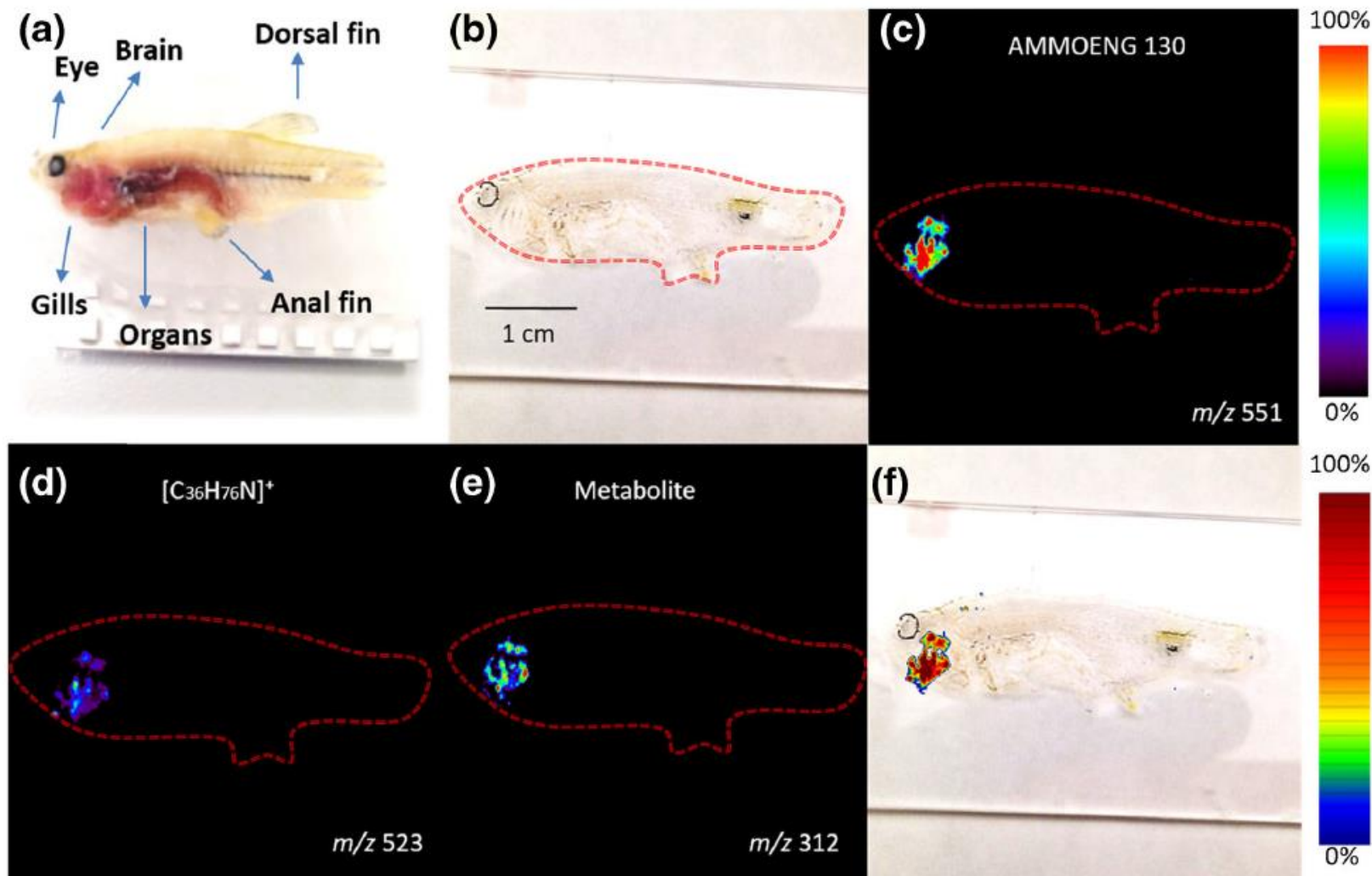
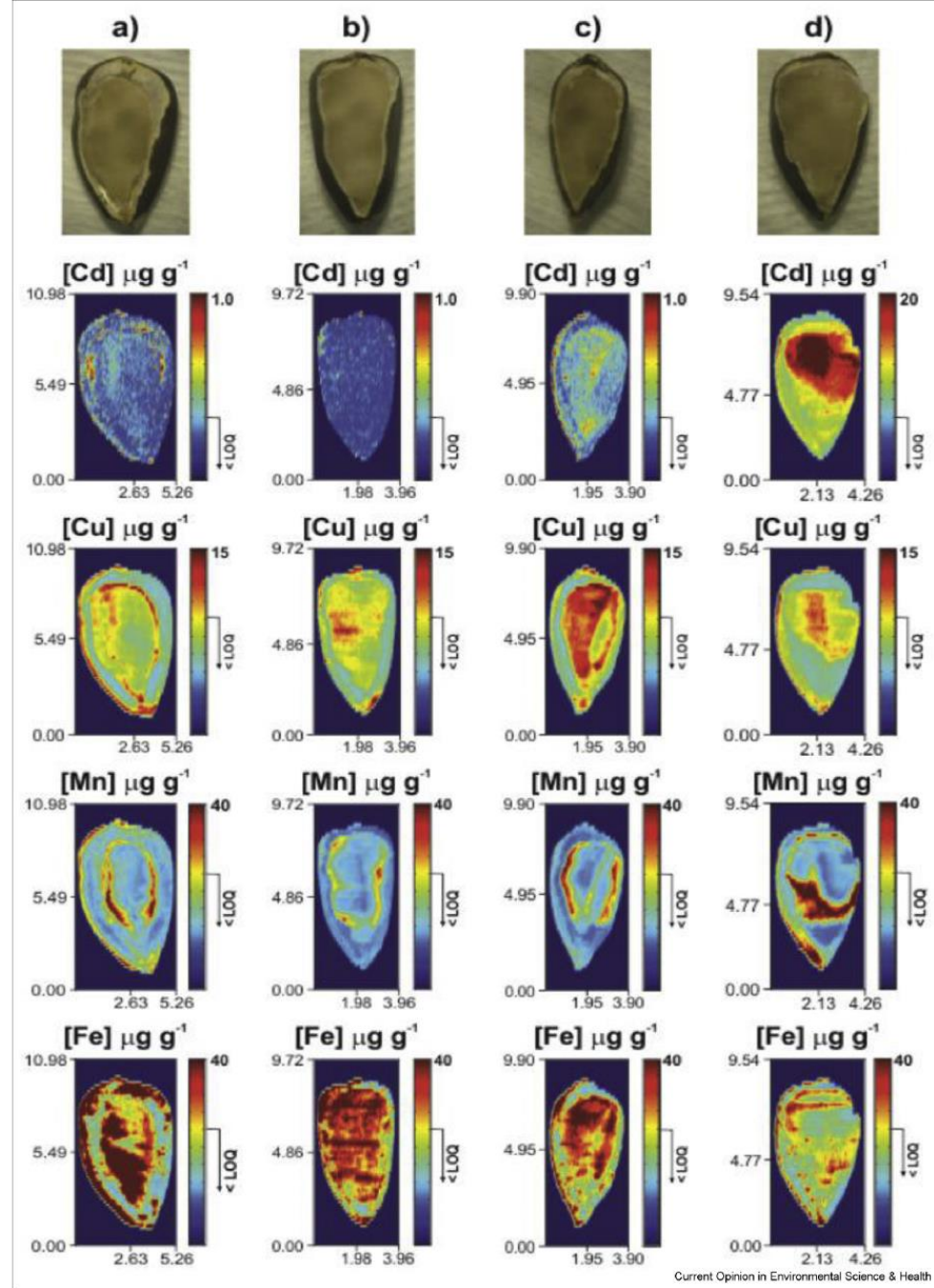


Figure 5. Accumulation of AMMOENG 130 in whole body zebrafish exposed to concentrations of 5.0 mg/L analyzed by DESI-MS imaging. (a) Zebrafish image outlining organ systems. (b) Optical image of the zebrafish tissue section under analysis. (c) Accumulation of AMMOENG 130 (m/z 551). (d) Accumulation of hexadecylstearyldimethylammonium (m/z 523). (e) Metabolite accumulation (m/z 312). (f) Overlay of the optical image with the DESI-MS image of AMMOENG 130. All images and overlays produced in both scale bars were normalized with Biomap

LA-ICP-MS

Pessôa, G. de S.; Lopes Júnior, C. A.; Madrid, K. C.; Arruda, M. A. Z. A Quantitative Approach for Cd, Cu, Fe and Mn through Laser Ablation Imaging for Evaluating the Translocation and Accumulation of Metals in Sunflower Seeds. *Talanta* **2017**, *167*, 317-324. <https://doi.org/10.1016/j.talanta.2017.02.029>.



MSI of sunflower seeds. Cd, Cu, Mn, and Fe distributions in sunflower seeds for the groups: (a) precursor, (b) control, (c) Cd-low (50 mg), and (d) Cd-high (700 mg). The picture of each seed is shown on the top of each column [46].

Research Plan



Exposure

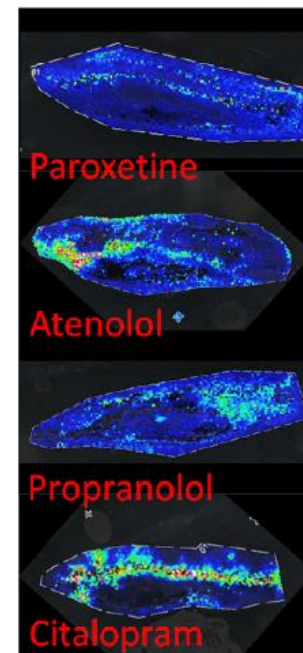
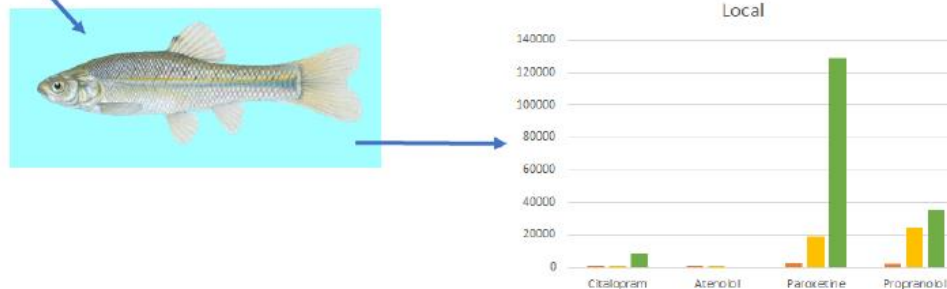
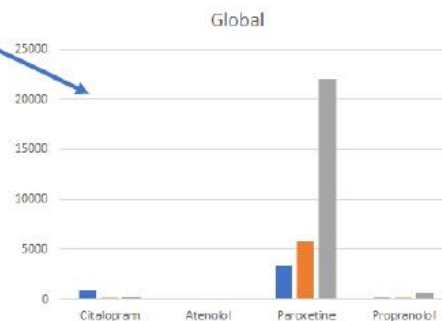
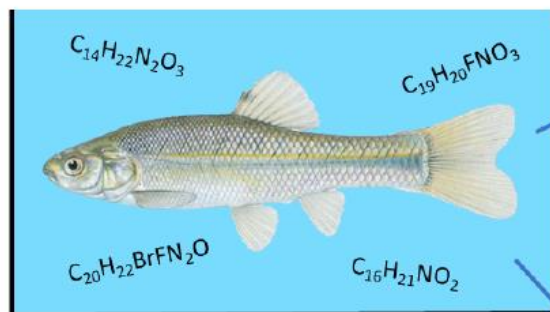
Analysis

Results

Global

Local

Imaging



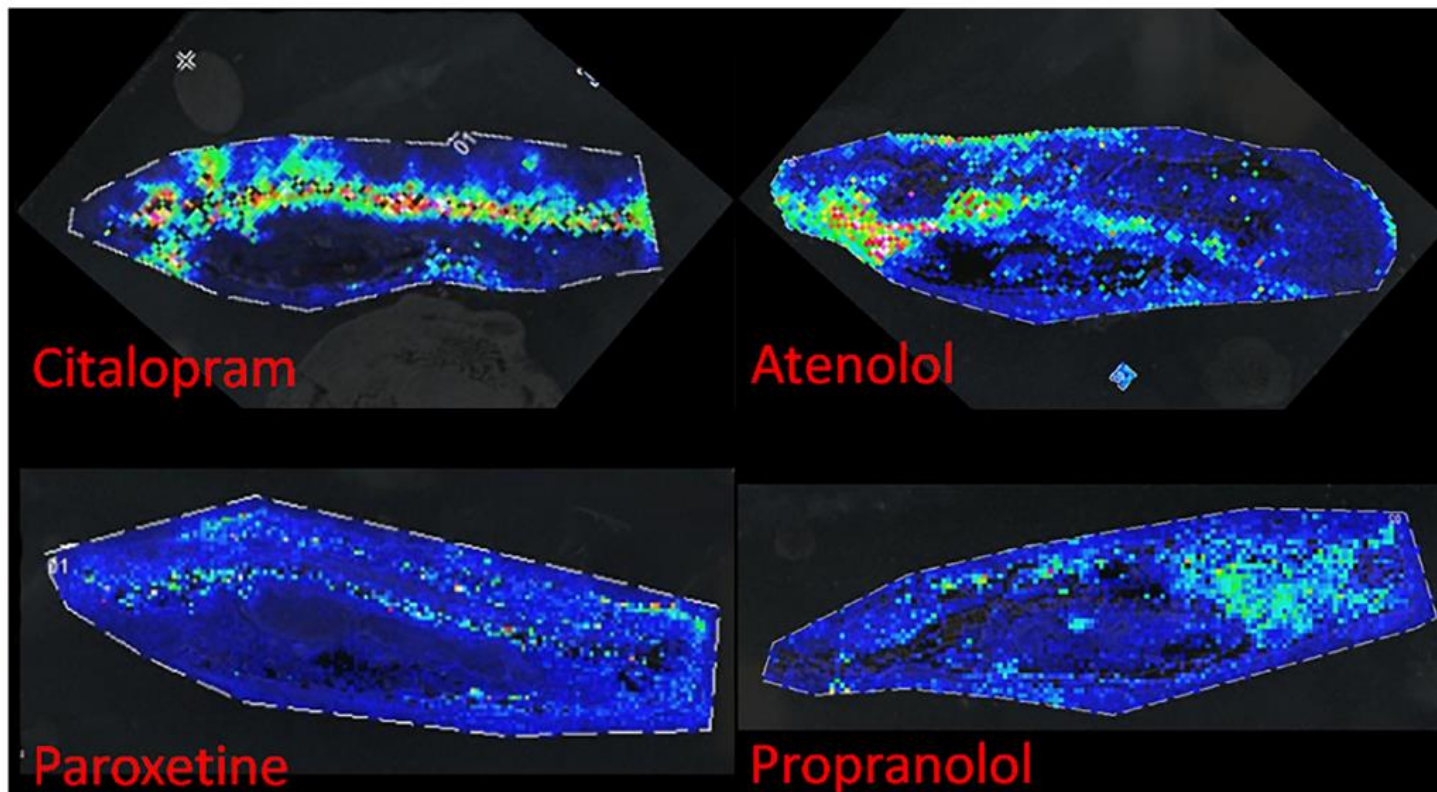


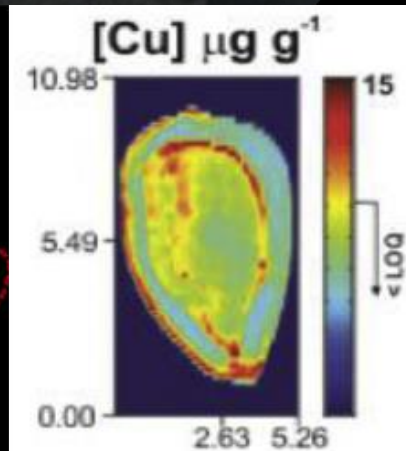
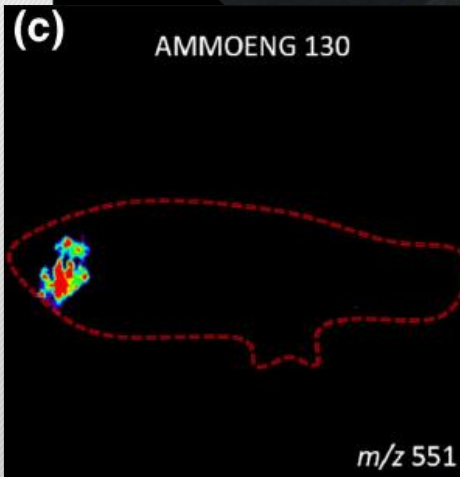
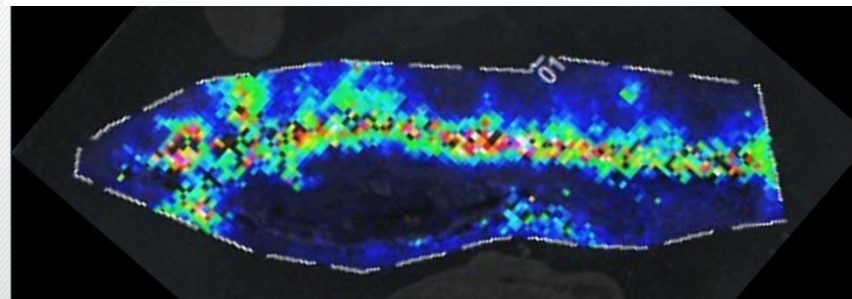
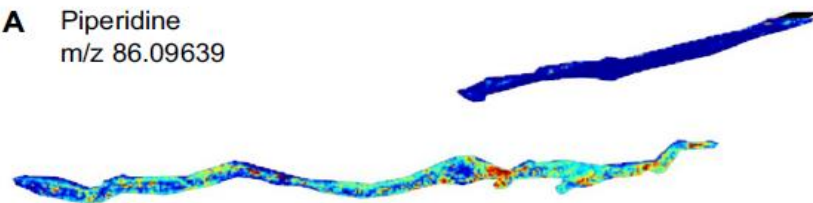
Fig. 1. MALDI mass spectrometry images in thermal color (signal increases from black<blue<green<yellow<orange<red<pink<white) from fathead minnows exposed to citalopram, atenolol, paroxetine, and propranolol at environmentally relevant concentrations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

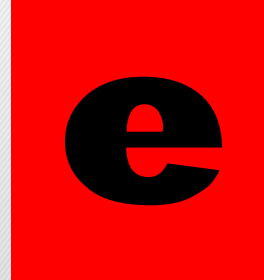
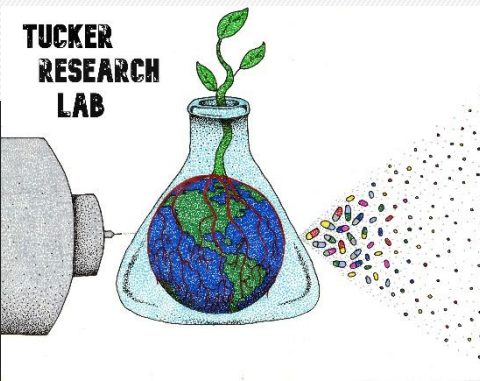
Mass Spectrometry Imaging Conclusions



- MSI can be used for substrates ranging from microbes to plants and animals.
- MSI targets analytes including organic, inorganic, and polymeric - large and small molecules.
- Different ionization sources are required depending on the substrate and the analytes of interest.

A Piperidine
 m/z 86.09639





SIGMA XI
THE SCIENTIFIC RESEARCH SOCIETY



Illinois Corn Marketing Board



• My research group:

- Back row: Nicholas Grunloh, Sarah Rizzo, Jackson Hoang, Dr. Kevin Tucker, Cole Hoffmann, Lexi Reinders, and Dalia Hassan.
- Front Row: Nicholas Howard, Karolina Chmielewska, Jillian Rhomberg, Jacob Smith, Samantha Olendorff, Emily Hubecky, and Sophia Melzer.
- Not Picture: Alayna Stephens, Jayda Hatten, Katie Maloof, Youssef Hassan, Emily Wiggins, and Valeria Zerda Pinta.





Thank You!