# Supporting Information

# "Technical Note: Gas-phase pesticide measurement using Iodide Ionization Time-of-Flight Mass Spectrometry"

Trey Murschell, S. Ryan Fulgham, Delphine K. Farmer*

Department of Chemistry, Colorado State University, Fort Collins, CO, 80523

Corresponding Author: Delphine.Farmer@colostate.edu

**Calibration System Setup**

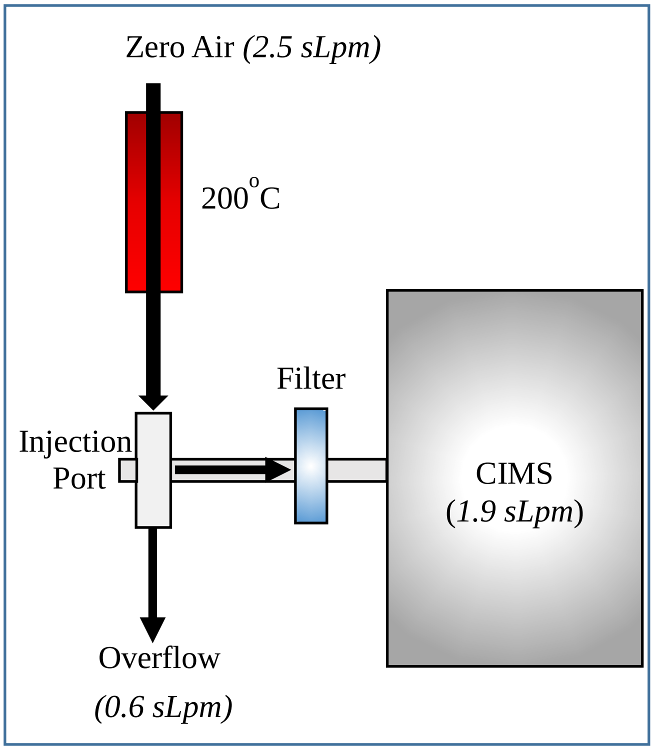

**Figure S1:** Ultra high purity zero air is flowed at 2.5 standard liters per minute (sLpm) through a heated tube filled with stainless steel wool in order to produce uniformly heated air. The air is pulled into the CIMS (1.9 sLpm) over a filter and overflow is sent out of the exhaust. The injection port is a septum placed in a Swagelok ¼” end nut.

## High Resolution Peak Identification

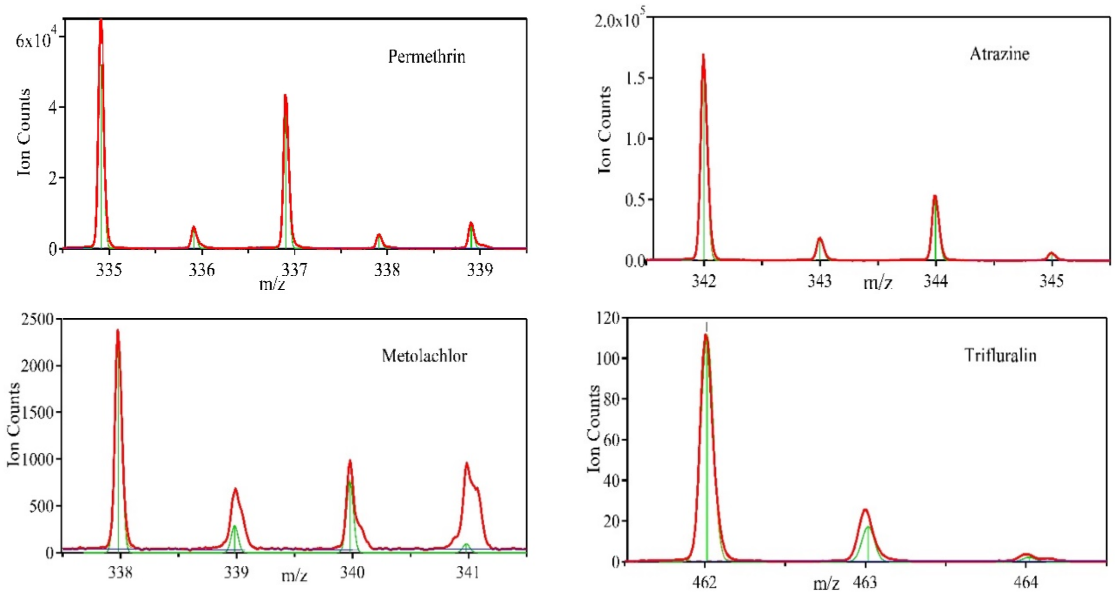

**Figure S2:** High resolution peak fits (green) of the raw signal (red) at the mass-to-charge ratios where the pesticides are detected, as well as their isotope patterns. During zero air backgrounds and solvent blanks, no other ions are present at the relevant mass-to-charge ratios which provides further confidence in identifying the pesticides and lower limits of detection. Each mass spectra are taken during 1 s at the peak of the injection period.

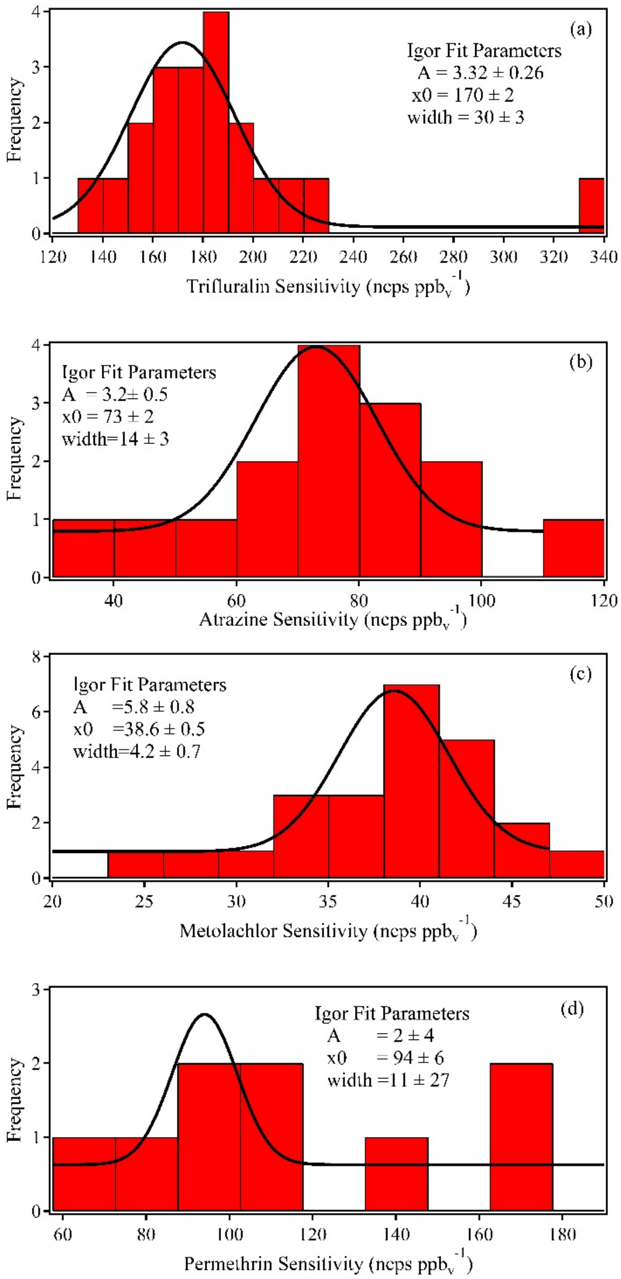

**Figure S3:** Histograms of the sensitivities (normalized counts per second per ppb$_v$) of the injections of the four pesticides using the Iodide ToF-CIMS. Fit parameters are produced from the Gaussian Fit (black trace) function in Igor, where x0 is the Gaussian center, A is the amplitude, and width is the Gaussian standard deviation.

## Permethrin Sensitivity by Injection Volume

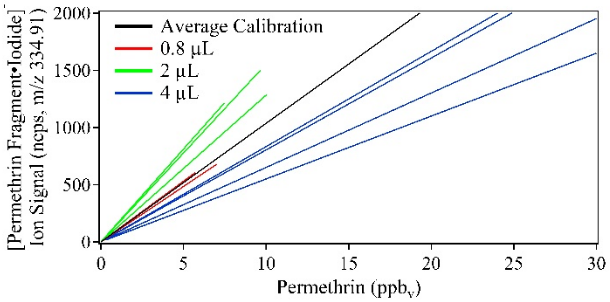

**Figure S4:** The average sensitivity for permethrin is 100 ± 40 ncps/ppb$_v$. However, the smallest injection volume (0.8 µL, red) has a greater average sensitivity (100 ± 10 ncps/ppb$_v$) than the largest volume (70 ± 10 ncps/ppb$_v$, 4 µL, blue), although the middle injection (2 µL, green) has the highest average sensitivity (150± 20 ncps/ppb$_v$).

## Relative Humidity Effects

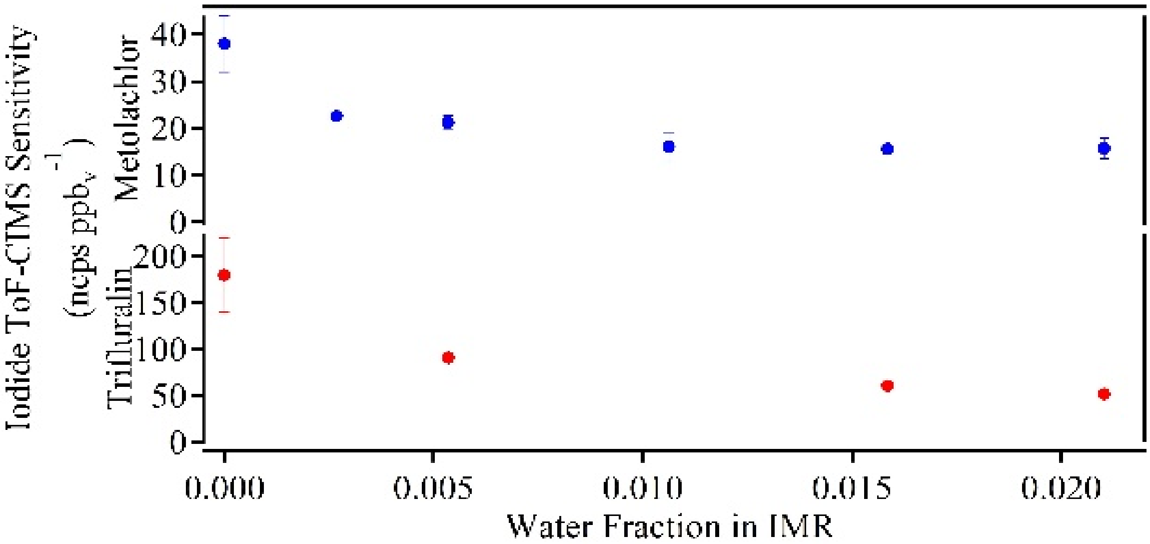

**Figure S5:** Relative humidity may impact the sensitivity of the instrument to analytes as iodide is thought to ionize compounds by a ligand exchange reaction with water.[3]

$[I\cdot H_2O]^- + M \rightarrow [I\cdot M]^- + H_2O$ (R2)

Increasing RH (or water fraction in the IMR, molecules of $H_2O$ in total molecules) will increase the concentration of $[I\cdot H_2O]^-$ and thus sensitivity to analytes if R2 is the correct mechanism. However, neither trifluralin nor metolachlor showed this expected behavior. In Supplemental Figure S5 replicate injections of trifluralin (detected as the iodide adduct with the parent molecule, blue), and metolachlor (detected as the iodide adduct with the $C_{11}H_{14}ClNO$ fragment, red) in humidified zero air exhibit decreasing sensitivity with increasing water content. Trifluralin would be underestimated by 67% for a field measurement at 60% RH relative to a 0% RH calibration. We note that no other changes in the pesticide relevant peaks were observed during the RH experiments, nor did other peaks appear.

$M + I^- \rightarrow [M\cdot I]^-$ (R3)

The observation of decreasing sensitivity for trifluralin and metolachlor fragments with increasing water content in the carrier gas is consistent with this mechanism as concentrations of the $I^-$ reagent ions decrease, while the $[I\cdot H_2O]^-$ reagent ions increase. We note that this is not due to the presence of halogens, as Lee et al. reported increased sensitivity of two halogenated compounds, $Cl_2$ and $Br_2$, with increasing RH.[27] Instead, the large size of the pesticide analytes relative to more commonly studied small molecules, or the presence of nitrogen groups, may be responsible for the preference towards iodide clustering (R3) over ligand switch (R2) ionization mechanisms.

## Mass Spectra Resolution

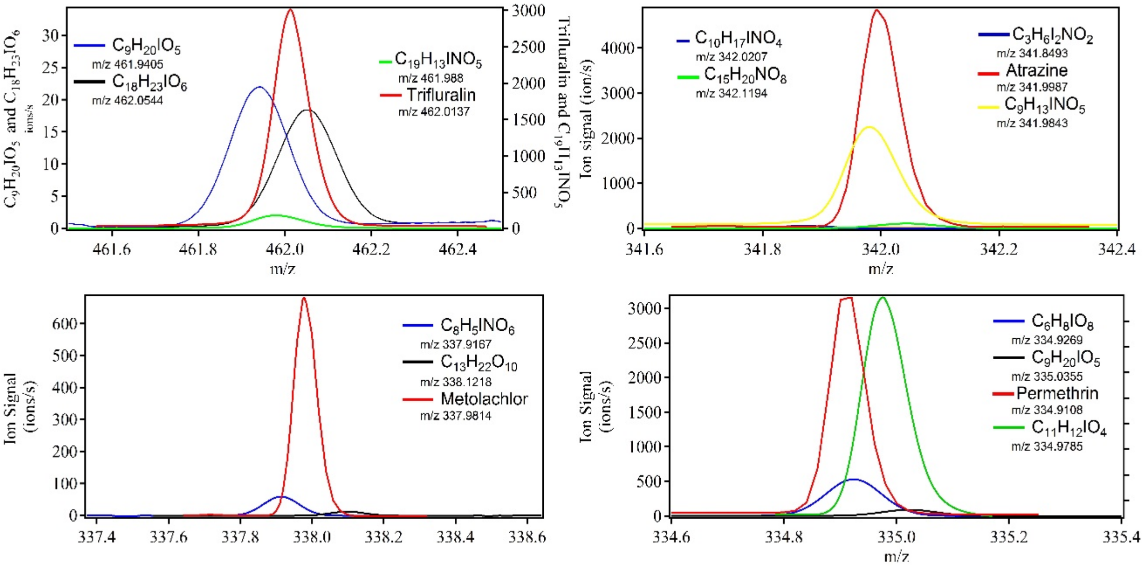

**Figure S6:** Exact locations of pesticides in the iodide ToF-CIMS mass spectra are compared with ions detected at the same nominal mass during two field campaigns, the Southern Oxidant and Aerosol Study (SOAS) and a local study in the Colorado Front Range (FRAPPE). Intensities of the pesticide peaks correspond to 1 $\mathrm{ppb_v}$ during a calibration injection. Combined with isotope signatures shown in Figure S2, this figure illustrates the power of the iodide ToF-CIMS to separate and confidently identify pesticides.

## References

Brophy, P; Farmer,D.K. A switchable reagent ion high resolution time-of-flight chemical ionization mass spectrometer for real-time measurement of gas phase oxidized species: characterization from the 2013 Southern Oxidant and Aerosol Study. *Atmos. Meas. Tech. Discuss.* **2015,** *8*, 3199-3244

Slusher, D. L.; Huey, L. G.; Tanner, D. J.; Flocke, F. M.; Roberts, J. M., A thermal dissociation–chemical ionization mass spectrometry (TD-CIMS) technique for the simultaneous measurement of peroxyacyl nitrates and dinitrogen pentoxide. *Journal of Geophysical Research: Atmospheres* **2004,** *109* (D19).

Veres, P.; Roberts, J. M.; Warneke, C.; Welsh-Bon, D.; Zahniser, M.; Herndon, S.; Fall, R.; de Gouw, J., Development of negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS) for the measurement of gas-phase organic acids in the atmosphere. *International Journal of Mass Spectrometry* **2008,** *274* (1–3), 48-55.