DISSERTATION

MEASUREMENTS OF CURRENT-USE PESTICIDES AND OXIDATION PRODUCTS

USING CHEMICAL IONIZATION MASS SPECTROMETRY

Submitted by

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In partial fulfillment of the requirements

For the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

Spring 2018

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ABSTRACT

MEASUREMENTS OF CURRENT-USE PESTICIDES AND OXIDATION PRODUCTS

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Pesticides are both naturally occurring compounds found within a variety of plant species and also synthetic chemicals that are used to protect vulnerable organisms against disease carriers, harmful pests, and intrusive or undesirable vegetation. Pesticide use has large agricultural, economic, and health benefits which include increased staple food production, protection of susceptible ecosystems and wetlands, increased productivity of the labor force via disease control, and the creation of a booming chemical industry. In the decades following the discovery of DDT's anti-insecticidal properties, organochlorine pesticides (OCPs) were generously applied across the globe. OCPs appeared to have low toxicity to mammals, chiefly humans, but had adverse effects to non-target species like fish and predatory birds. OCPs persisted in soil, air, and water, and were transported atmospherically, as far as the Arctic. The prohibition of OCPs by most nations spurred research into less harmful and persistent pesticides. These current-use pesticides (CUPs) have mostly replaced OCPs and are applied world-wide. However, recent studies revealed the transport of CUPs to remote areas, including isolated Pacific islands, high alpine mountain lakes, and, again, the Arctic. Once in the atmosphere, these pesticides undergo physical and chemical processes that affect atmospheric lifetimes and transport, and potentially change the toxicity of the parent pesticides, which can have unforeseen impacts on sensitive ecosystems and organisms.

With pesticide use perpetually linked to negative health questions and concerns, atmospheric monitoring, understanding of chemical processes, and improving analytical methods

is necessary. Presented in this dissertation is work towards understanding pesticides and their chemistry in the atmosphere using real time mass spectrometry. A new calibration and measurement method for four CUPs, atrazine, metolachlor, permethrin, and trifluralin is shown in Chapter 2. Iodide chemical ionization mass spectrometry (CIMS) offers a real-time, sensitive measurement technique for herbicides, as well as other low volatility species. Presented in Chapter 3, ambient pesticide spray volatilization and post-application volatilization of two chlorophenoxy acid herbicides, 2,4-D and MCPA, were measured using acetate CIMS. Concentrations of 2,4-D were highest during the application period, while MCPA concentrations increased with increasing ambient temperature. Henry's Law constants and vapor pressure were found to be predictors for spray volatilization and post-application volatilization, respectively. OH radical chemistry of three aromatic herbicides are presented in Chapter 4, along with proposed oxidation mechanisms and products. Experiments were performed in an Oxidative Flow Reactor (OFR) coupled to a switching reagent ion CIMS, for a non-targeted approach for pesticide oxidation product detection. Pesticide oxidation followed typical OH oxidation mechanisms (OH abstraction with subsequent peroxide formation, OH addition to aromatic systems). MCPA and Mecoprop-p reaction rate constants with OH radical were estimated and used to calculate their atmospheric lifetimes (3 and 5 days, respectively). Newly identified products from MCPA and triclopyr oxidation are potentially harmful to the environment and to humans. Lastly, Chapter 5 covers oxidation of two nitrogen containing herbicides, trifluralin and acetochlor and mechanisms with proposed products are shown. Trifluralin photolyzed to produce NO_x, and both herbicides produced isocyanic acid (HNCO) upon OH oxidation, an atmospheric toxin.

ACKNOWLEDGEMENTS

DEDICATION

This work is dedicated to my wife, Jael, my son, Daniel, and my parents, Randy and Kathy

"An investment in knowledge pays the best interest."

-Benjamin Franklin

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LIST OF DEFINITIONS

2,4-D: 2,4-dichlorophenoxyacetic acid, "Agent Orange"
CIMS: Chemical ionization mass spectrometry
CUPs: current-use pesticides
"Dirty Dozen": Substances listed by the United Nations as Persistent Organic Pollutants (POPs) nine of which are OCPs including: DDT, Aldrin, Dieledrin, Endrin, Chlordane, Heptachlor, Hexachlorobenzene, Mirex, Toxaphene
DDT: dichlorodiphenyltrichloroethane
FIGAERO: Filter Inlet for Gas and AEROsols
HPLC: high-performance liquid chromatography
GC-ECD: Gas chromatography coupled to electron capture detection
GC-MS: Gas chromatography coupled to mass spectrometer
Henry's law constant
HR-ToF-MS: high resolution time of flight mass spectrometry
IMR: Ion Molecule Reaction chamber
LODs: Limits of Detection
MCPA: 2-methyl-4-chlorophenoxyacetic acid
NCI: Negative Chemical Ionization
NO_x: NO and NO_2 radicals
OCPs: Organochlorine Pesticides
OFR: oxidative flow reactor
Pesticide: Natural or synthetic chemical used in the control or ultimately kill an unwanted organism. Pesticides can be divided into several classes: insecticides (insects), herbicides (plants), fungicides (fungus), algicides (algae), and disinfectants (microorganisms).
ppb_v **:** parts per billion by volume
ppt_v **:** parts per trillion by volume
RH: Relative Humidity
sccm: standard cubic centimeter per minute
sLpm: standard liter per minute
SMPS: Scanning Mobility Particle Sizer
UHP: Ultra-high purity

LIST OF PESTICIDE CLASSES WITH EXAMPLES

Chloroacetanilide: alachlor, acetochlor, metolachlor, propachlor
Dinitroaniline: trifluralin, benfluralin, ethalfluralin, oryzalin, pendimethalin
Neonicotinoid: acetamiprid, clothianidin, imidacloprid, nitenpyram, thiacloprid
Organophosphate insecticides: chlorpyrifos, diazinon, dichlorvos, fenthion, malathion, parathion
Phenoxyacid: 2,4-dichlorophenoxy acetic acid, 2-methyl-4-chlorophenoxyacetic acid (MCPA), 2,4,5-trichlorophenoxy acetic acid, dichlorprop, mecoprop-p
Pyrethroid: cypermethrin, deltamethrin, permethrin, pyrethrum, transfluthrin
Triazine: atrazine, prometon, propazine, simazine, tertbutylazine

CHAPTER 1- A HISTORY OF PESTICIDES IN THE ATMOSPHERE

The development of our understanding of the environmental fate of pesticides is intrinsically linked to the history of pesticide use. The rise and fall of different classes of pesticides has followed our knowledge of the environmental and toxicological impact of different classes of these compounds. The role of the atmosphere in controlling pesticide fate has been investigated for decades, but our understanding of the atmospheric chemistry of these molecules is more recent. Here, I describe the history of pesticide use and thus our understanding of their environmental and atmospheric chemistry.
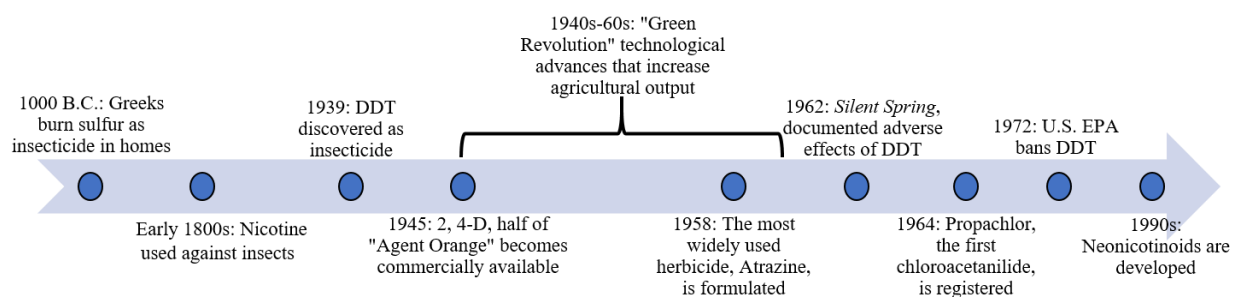
Figure 1.1. Brief timeline of the history of pesticides

1.1. Organochlorine Pesticides

Pesticide use around the world increased drastically in the 1940s, specifically due to Müller's discovery of the anti-mosquito properties of DDT (dichloro-diphenyl-trichloroethane).[1] DDT was used extensively during World War II to protect troops from malaria and typhus, leading to Muller receiving the Nobel Prize in 1948. For the next twenty years, organochlorine pesticides (OCPs), including DDT, were used to control pests, realizing huge benefits in crop protection and disease mitigation. OCPs are toxic to insects, but not to mammals or humans. Also, they did not degrade or decompose easily in the environment, which allowed for their continued effectiveness. Beginning in the 1960s with the publication of Rachel Carson's book, *Silent Spring,* in 1962,

scientists, activists, and politicians began to realize the detrimental environmental effects caused by OCPs.[2] Due to the chemical composition of OCPs, degradation in environmental media was almost non-existent, leading to accumulation in soils, plants, and in fatty tissue of wildlife. This persistence of OCPs led to detection and non-negligible concentrations in regions where no spraying occurred, even remote areas in the Arctic, suggesting substantial atmospheric transport.[3-4] OCPs evaporate from the temperate and mid latitude regions in which they are used, transport towards the poles, and condense in cold regions via "global distillation".[5] As OCPs travel north, they undergo multiple cycles of deposition and volatilization – the so-called "grasshopper effect".[6] More volatile pesticides will be transported farther than lower volatility species, essentially creating a global chromatography experiment.[7] The United States EPA banned the use of DDT in 1972 (eventually banned by most industrialized countries by the 1980s and was ratified by the United Nations Stockholm Convention in 2001). Persistence of the OCPs still impacts the globe today as it is still used in developing countries where it was deemed the benefits (i.e disease control, crop production) outweighed the potential environmental impact. Concentrations in the USA Great Lakes have decreased exponentially since the US ban, but have levelled to low, non-zero levels due to either "legacy sources", which are long-ago applied agriculture areas from which OCPs continue to volatilize, or transport from current sources in the developing world.[8] Spencer et al. measured DDT fluxes (ng m^{-3} levels) in a California field nearly 20 years post-application, while toxaphene was measured in South Carolina ten years after restriction, reinforcing the concept of a "legacy source" of OCPs.[9-10]

1.1.1. OCPs in Air and Water

OCPs remain an important environmental contaminant measured globally, in warm and cold climates, after the majority of countries ended their use. Table 1.1 illustrates a small subset

of measurements in air and water conducted since most industrialized countries banned OCPs (all but fourteen countries in the world by 2000).[11-15] Itawa et al. provided an extensive report on OCP concentrations in seawater and air samples around Asia up to the Arctic Circle and in the Atlantic on sea cruises.[14] Oehme produced back trajectories during periods of high concentrations of OCPs, demonstrating transport of re-emitted species from contaminated surfaces in Southwest Europe and the former Soviet Union to Arctic Norway.[15] Buehler et al. measured pesticides in the Great Lakes region at Integrated Atmospheric Deposition Network (IADN) stations, and found that Eagle Harbor (located in the middle of Lake Superior) had higher concentrations of OCPs than Brule River, a site closer to agriculture areas, due to re-volatilization from the lake surface water.[12] The presence of OCPs in the Arctic is unmistakable evidence these compounds are transported via the atmosphere.[3] The majority of countries still using OCPs are located in hotter climates where volatilization loss can be a significant contribution of OCPs to the atmosphere, enhancing atmospheric sources.[16]

Table 1.1. Air, water and particle concentrations (pg m^{-3}) of three OCPs (sums of isomers and metabolites) throughout the globe. Empty boxes represent missing measurements.

Location	Hexachlorocylohexane		DDT		Chlordane		Reference
	Air	**Seawater**	**Air**	**Seawater**	**Air**	**Seawater**	Itawa et al. 1993
Bering Sea	300 270-330	1700 1400-2100	3.6 1.1-5.6	1.0 0.2-2.9	16 13-19	3.9 2.9-4.6	
Gulf of Alaska	420 350-530	1900 1700-2100	3.9 1.0-7.5	1.2 0.9-1.6	22 14-34	5.3 3.8-7.5	
North Pacific	210 38-620	250 75-550	12 2.0-39	1.2 0.3-2.8	16 <1.0-49	7.6 3.8-14	
North Atlantic	260 100-430	140 80-170	8.7 4.1-17	0.8 0.7-0.9	20 <1.0-43	5.5 4.1-8.3	
Bay of Bengal and Arabian Sea	9600 690-32000	720 130-1300	30 <1.0-69	10 1.6-24	250 42-1000	9.5 3.4-17	
Ny-Alesund (Norway)	526 284-874				4.3 2.3-8.6		Oehme 1991 (Summer Data)
Karvatn (Norway)	762 337-1608				4.2 2.0-6.3		
Birkenes (Norway)	712 311-1573				4.7 2.3-11.5		
	Air	**Particle**	**Air**	**Particle**	**Air**	**Particle**	Gioia 2005
Camden, NJ, USA (urban)	254		518	3.4	133	6.4	
New Brunswick, NJ, USA (urban)	149		474	2.8	237	4.1	
Pinelands, NJ, USA (rural)	103		127	0.58	31	1.1	
Eagle Harbor, MI, USA	96±7	0.9±0.19	4.4±0.6	0.14±0.06	8.6±1.0	0.81±0.09	Buehler et al. 2001
Brule River, USA	89±7	1.2±0.4	2.9±0.3	0.44±0.08	7.8±0.7	1.3±0.2	

Enclosed bodies of water far from application regions are especially important for studying atmospheric transport, as they are solely impacted by pesticide deposition following long range transport. Further, the only way to re-enter the atmosphere is volatilization, but low temperatures increase persistence. Muir et al. measured decreasing low volatility OCPs at low (<1 ng g^{-1}) concentrations in 8 increasingly remote (increasing latitude) lakes in the Canadian Arctic, but noted that concentrations were higher than in the far less remote Great Lakes.[17] However, higher volatility OC pesticides showed no significant trend with increasing latitude. Together, these results upheld the "cold condensation" hypothesis where higher volatility compounds can be transported farther than lower volatility species that are lost much more quickly as latitude increase (i.e temperature decreases).[18] Atmospheric concentrations of some OCPs have begun to increase in recent years, potentially in response to climate change, warranting continuous monitoring of atmospheric sources, transport and sinks.[19] A warmer climate would increase volatilization from contaminated areas, and enable longer poleward transport distances.

1.1.2. Environmental and Health Effects of OCPs

The health and environmental impacts of OCPs are well studied, totaling thousands of published reports on measurements in aquatic systems, mammals, fish, birds and sediments, as well as their toxicological assessments.[20] OCPs tend to bioaccumulate in biological systems.[8] This is the process in which an organism absorbs a substance faster than it can be excreted or broken down; OCPs are particularly effective at bioaccumulation because of their relatively unreactive chemical nature. OCPs contain several features that contribute to their persistence: namely stable structures that are slow to react and degrade, thermal stability, and hydrophobicity and the presence of carbon-chlorine bonds that are resistant to hydrolysis and photolysis.

OCPs are more soluble in hydrophobic, hydrocarbon-like substances (octanol-water partition coefficient, 4-7) than in water, and are more likely to be adsorbed to surfaces like sediment and suspended particles than in the aqueous phase. As aquatic species like fish are exposed to OCPs, concentrations are stored and increase in fatty tissue. This bioconcentration enables a fish, for example, to have internal concentrations of OCPs much larger than the surrounding, aquatic concentration.[8] Biomagnification is the process in which the concentration of a chemical increases as it moves through a food chain.[8] For example, predatory birds have much higher internal OCP concentrations than the fish they eat, which have higher concentrations than the fish or plankton on which the fish feed. Bioaccumulation occurs in fish, seals, polar bears, and birds via food ingestion up the food chain, leading to chronic exposure effects including endocrine system disruption, egg shell thinning in birds, reproductive abnormalities, and immunotoxicity in mammals.

Predatory fish-eating birds were particularly affected by the use of OCPs, specifically DDT and its metabolite DDE, and provided a striking example of biomagnification. The brown pelican population in California's Channel Islands was decreased significantly between 1969-72 due to eggshell thinning, thus decreased hatchability, because of increased DDT concentrations from a Los Angeles manufacturer sewage discharge.[21] Similarly, populations of the North American bald eagle and golden eagle decreased to the brink of extinction due to DDT and other factors, leading to the 1962 Bald and Golden Eagle Protection Act, which led to the eventual banning of DDT in the United States.[22] In the Canadian, Siberian, and European Arctic, the Arctic tern was severely impacted by OCPs.[23-25] In Finland, average DDT concentrations in liver and muscles of newly hatched chicks were 10 mg kg^{-1}, but concentrations decreased as the chicks aged. Average adult male concentrations were 31 mg kg^{-1}, while females consistently had lower concentrations, likely

due to their passing of DDT to offspring.[24] Even at sub-lethal concentrations, discernable effects on birds were linked to DDT exposure. Decreased aggressiveness, attentiveness, growth, thermoregulation, and endocrine disruption were some of the reported problems discovered in avian life and attributed to DDT and its metabolites.[26-27] Since the US ban of DDT, a 90% reduction of DDT in herring gull eggs was observed.[28] Between 1971 and 2001, the mean concentrations of DDT metabolites in eggs of the Baltic guillemot decreased from 950 ppm to 0.01 ppm.[29] New reports continue to be published demonstrating the effectiveness of the OCP bans and benefit to ecosystems and avian life.

Detrimental health effects of DDT were not restricted to birds. Female seals with two to eight times higher DDT concentrations in their blubber were more likely to give birth prematurely, leading to higher rates of mortality.[30] In humans, DDT manufacturing workers were at higher risk of pancreatic cancer after spraying DDT, although the link between exposure levels and cancer remains inconclusive.[31-32] While low OCP exposure levels may not be harmful to human adults, at-risk populations, including young children and fetuses, may be more susceptible.[31, 33-34] Children come into contact with surfaces through crawling and playing, with constant hand-to-mouth actions, leading to potential ingestion of pesticides. Of concern, DDT and its metabolites are soluble in human breast milk and have been measured in several industrialized countries.[35] Concentrations were typically lowest in European measurements, followed by African nations and Mexico, and finally highest concentrations in breast milk were in China and Hong Kong, likely explained by amounts used and produced in these regions.[35] However, although OCPs are found in breast milk, the association between OCPs and breast cancer in women is murky.[36-38]

1.2. Current-Use Pesticides

As the dangers of OCPs like DDT became more widely understood and publicized, research and development shifted to the development of less toxic, less persistent and more selective pesticides. This work led to the synthesis of new "current-use pesticides", which include organophosphate insecticides, phenoxyacid herbicides, chloroacetanilide herbicides, and other classes inspired by natural products, including neonicotinoid insecticides and pyrethroid herbicides. Current-use pesticides are used globally, with annual use estimates in the USA in the billions of pounds.[39] Despite the intention of creating pesticides with less environmentally impact than OCPs, current-use pesticides are now found throughout the globe in non-agricultural, non-target ecosystems far from application sites. Several pesticides and their degradation products or metabolites have adverse effects on humans and wildlife. This is perhaps unsurprising considering the desire for potency and lack of full selectivity. Current-use pesticides have thus been the subject of numerous field measurements in air, water, and soil.[16, 40-41]

Pesticides are released into the environment by aerial (plane), tractor, and handheld applicators. During application, liquid (usually water) pesticide droplets can be carried away from the intended target (spray drift) and are subject to pesticide volatilization from the droplet. As much as 50% (aerial) and 1-30% (tractor spray) of application can be lost to drift during application. Transport of droplets is size dependent, with smaller particles travelling farther and larger drops depositing to surfaces more quickly.[42] Once a pesticide deposits on a surface (intentionally or not), its movement through the environment depends on the properties of the surfaces to which it is adsorbed. Pesticide lifetime in soil is governed by several parameters including the soil-water coefficient (k_D), soil-organic carbon coefficient (k_{OC}), soil moisture content, and whether or not the soil was incorporated, thus increasing the depth and distance

necessary for movement. Soil pesticides can be taken up by plants, thus contributing to bioaccumulation.[43] Once in soil, pesticides with higher mobility (i.e. lower soil adsorption coefficients) can move toward soil-air and/or soil-water interfaces. In both soil and water, pesticides can be broken down and degraded by microbial life or other chemical processes such as hydrolysis and surface photolysis.

Pesticides enter surface or ground waters by two pathways: leaching from soil (function of k_D, k_{OC}, and hydrophobicity), or soil runoff after rain events. Pesticides in water and soil can then volatilize back into the atmosphere days or weeks after application. Volatilization from dry soil depends on concentration at the soil surface layer and vapor pressure, while volatilization from soil moisture depends on Henry's Law constants (ratio of partial pressure in air to concentration in water). Once in the atmosphere, pesticides are subject to atmospheric processing, including photolysis, oxidation, and gas-particle partitioning. Transformations in the atmosphere impact pesticide lifetime, travel distance, vapor pressure, and water solubility. Pesticides and their transformation products can be scavenged by precipitation, condense onto particles, or directly deposit back to soil, plant, or water surfaces. Pesticides can undergo multiple transformations, depending on rates of degradation processes.

1.2.1. Current-Use Pesticides in the Atmosphere

Initial atmospheric pesticide work centered around the phenoxyacid herbicide, 2,4-dichlorophenoxy acetic acid (2,4-D), which was first detected in rainwater by Cohen and Pinkerton.[44] 2,4-D was the most widely used herbicide used in the 1960s, with as much as 40 million pounds used over 56 million acres in 1966.[45] Van Dijk et al. show 80 pesticides detected in rain and 30 pesticides detected in air.[16] A representative subset of current-use pesticides atmospheric measurements from three countries (USA, Canada, and France) is presented in Table

1.2. Typical concentrations range from tens of pg m^{-3} to low ng m^{-3} in agricultural regions during growing season. Further, concentrations can range from low pg m^{-3} in remote regions to a few µg m^{-3} near agricultural areas on the day of application. Current-use pesticides have been detected tens to hundreds of kilometers away from application areas correlating to spraying that occurred elsewhere.[16, 46-50] This has occurred in Europe, where one country has banned a specific pesticide, but the pesticide was subsequently measured in ambient air due to spraying in a neighboring country. For example, trifluralin was found in air samples collected in the Netherlands following application in Belgium.[47] In the United States, triazine herbicides were measured in air in Maryland at low concentrations (range of 0.003-0.04 ng m^{-3}) that correlated to transport north from Southeastern United States, over 1,000 kilometers away.[46] Finally, Halsall et al. measured trifluralin in Arctic air and fog, clearly thousands of kilometers from agriculture.[51]

Table 1.2. Ranges of Current-use pesticide concentrations (ng m^{-3}) from selected previous works. Work focuses on agricultural regions in the United States, Canada, and France. Empty spaces indicate pesticide was not measured or targeted.

Location	Alachlor	Atrazine	Chlorpyrifos	Diazinon	Metolachlor	Trifluralin
Centre Region, France[52]	0.12-6.03				0.12-2.49	0.12-58.79
Eastern Iowa, USA[50]	<MRL[a]-8.5	<MRL-8.5	<MRL-2.9		<MRL-27.5	<MRL-8.2
Abbotsford, Canada[53]		nd[b]-0.022	0.359-1.1	22.9-989		nd-2.22
Egbert, Canada[53]			0.019-0.246	nd-0.202	0.415-9.940	0.297-4.39
St. Anicet, Canada[54]		0-0.933	0.837-6.72		1.15-12.2	0.34-2.59
Bay St. François, Canada[54]		0.587-1.86	0.744-1.26		4.03-23.6	
Sierra Nevada, CA[49]			0.05-17.5	0.07-0.24		0.07-0.64
Mississippi River. USA[55]	nd-8.8	nd-2.8	0.12-1.6	0.04-0.36	0.45-5.6	0.23-80
Rolling Fork, MS, USA[56]			3.5[c]	8.4[c]		0.76[c]
British Columbia, Canada[57]		14.5	1.5	42.7		
Alberta, Canada[58]			nd-0.02	nd-0.12		nd-0.56
St Damase, Canada[59]		0.645–1.905	<MRL-0.233	<MRL-1.171	0.3031–19.061	0.317–1.617
Strasbourg, France[60]	0.26–2.39				0.09–0.45	0.06–0.22

[a] Method Reporting Level

[b] Not detected

[c] Maximum reported concentration

Peak pesticide concentrations occur during the spray and application season, which coincides with the warmer parts of the year (spring and summer). More volatile pesticides (~10^{-3} Pa) reach peak ambient air concentrations during or shortly after application, while lower volatility pesticides (10^{-4}-10^{-5} Pa) have lower peak concentrations, but volatilize over a longer period.[46, 61] Non-volatile pesticides and photo-labile pesticides continue to be transported 10s to 1000s of kilometers from application to areas where use may be banned or ecosystems may be particularly sensitive .

1.3. Processes that Control Pesticides entering the Atmosphere

Pesticides can exist in the atmosphere in either the gas or particle phase. Unlike OCPs, modern pesticides are more likely to partition into particle phase,[62-63] although temperature, humidity, existing particle concentration, seasonality, and latitude all affect pesticide partitioning between gas and particle phase.[40, 64] Pesticides, even those with significantly low vapor pressures and large water solubility, can enter the atmosphere by spray drift and volatilization.

Spray drift is the movement of a pesticide away from the intended application area during or immediately after application. Pesticide drift can affect local non-targets or, depending on meteorological conditions and application methods, ecosystems or human populations that are kilometers away. Spray drift is a well-established mechanism for pesticide transport. For example, grape farms have lost crops from application of 2,4-D on farms as far as 15 miles away.[65]

Reduction of spray drift has focused on aerial application, as ground applicators have slower application rates. During application, pesticides can immediately enter the atmosphere as liquid droplets (commonly water) that are small enough (<100 µm) to be carried long distances from the intended agricultural target. Larger droplets can also be carried off-target, but deposit more rapidly onto soil or crops. For example, droplet sizes of 400µm travel only 2.6 m compared

to 2 μm droplets that traveled 34 km.[66] Spray droplets sizes and drift are controlled by rate of application, spray nozzle size, and height of application.

Once in the atmosphere, organics in the aqueous pesticide spray may volatilize from solution. Volatilization depends on ambient temperature, Henry's law constant, vapor pressure, and the droplet concentration of the organic. For example, a pesticide in a highly concentrated solution applied through small nozzles has a greater likelihood of volatilizing than large droplets of a more dilute solution. Spray evaporation is reduced by emulsifiers, which are often as added to pesticide mixtures. Other additives, such as proprietary polymers with salts, increase surface tension and viscosity of the drops to form larger drops that deposit rapidly and reduce drift.

Direct volatilization from surfaces is the other atmospheric source of pesticides. 50-90% of the applied pesticide can be lost to volatilization.[16, 67] Volatilization depends on chemical properties of the pesticide, application method, formulation (dilute solution or pure active pesticide), and surface properties (plants vs soil vs water).

Immediately after application, volatilization is a function of vapor pressure, solubility and soil adsorption. Over time, however, pesticide residues diffuse into the soil, inhibiting volatilization. Incorporation of the pesticide to increasing depths (e.g. 5 cm or more) can decrease volatilization significantly. As pesticides at the surface evaporate, "back-diffusion" occurs as the pesticides move from depth back to the surface as a function of soil adsorption. Back diffusion can occur by diffusion or water flow. Volatilization is inhibited by soil degradation processes, including soil photolysis, thermal decomposition, microbial decomposition, and leaching into groundwater. Volatilization is enhanced by increasing soil moisture content by rainfall. The decrease in moisture results in less water adsorption to soil binding sites which then are captured

by pesticide residues drastically slowing volatilization.[68] Increased temperature can increase volatilization rates, but also dries soil, thus increasing soil adsorption and slowing evaporation.

1.4. Atmospheric Processing of Pesticides

While pesticide concentrations in the atmosphere are usually low (pg/m^3 to µg/m^3), these compounds undergo chemical transformations in the atmosphere including oxidation by OH radicals, photolysis, gas/particle partitioning, uptake into precipitation or particles, and wet or dry deposition. Rate constants for ozone + pesticides and NO$_3$ + pesticide reactions are slow (10^{-16} molecules^{-1} cm^3 s^{-1}) and thus unlikely important for atmospheric chemistry, except for species with carbon-carbon double bonds (e.g. Aldrin, 1,3-dichloropropene).[69-70] Removal by atmospheric chemistry and deposition dictates lifetimes of pesticides in the atmosphere, and thus transport distance and, to an extent, environmental impact. The atmospheric chemistry of pesticides is the least understood aspect of pesticide environmental chemistry,[71] although photolysis is relatively well studied. Pesticides typically have lifetimes against photolysis <1 hour, with the resulting decomposition or isomerization products occasionally being more toxic than the parent compound.[72-74]

1.4.1. OH Radical Chemistry

The OH radical is the dominant atmospheric oxidant, and thus expected to be the most important atmospheric degradation pathway for pesticide vapors. OH radicals are formed in the troposphere following ozone photolysis at wavelengths 220-290 nm:[69]

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \qquad\qquad R1$$

$$O(^1D) + M \rightarrow O(^3P) + M \qquad\qquad R2$$

$$O(^1D) + H_2O \rightarrow 2\ OH \qquad\qquad R3$$

OH concentrations are highest at the equator and lowest at the poles, and are typically higher in summer than winter.[75-76] Current research on OH oxidation mechanisms is focused on biogenic compounds (isoprene, monoterpenes) and ubiquitous anthropogenic pollutants such as benzene and toluene.[77-78] Pesticide oxidation in the gas phase is not well understood, with most studies focused on aqueous pesticide oxidation for water treatment applications, and rainwater pesticide transformation products.[56, 79-81]

1.4.2. Studies on Pesticide OH Radical Chemistry

OH radicals are thought to be the dominant loss pathway for pesticides,[72] but are challenging to study due to the confounding effects of photolysis and OH oxidation.[82-84] Oxidation products may be more toxic than the parent pesticide. For example, the P-S bond in organophosphate insecticides (e.g. parathion) oxidizes to form "oxons" (P=O; e.g. paraoxon), which are more toxic than the original insecticide.[85-86] Chloropicrin, a widely used insecticide, antimicrobial agent, fungicide, herbicide, and nematicide, produces phosgene (a chemical warfare agent) upon atmospheric oxidation.[87]

Recently, environmental chambers have been used to simulate atmospheric OH oxidation of pesticides. The EUPHORE chamber in Spain is a sealed, coverable (retractable housing), large volume outdoor chamber that allows solar radiation in that initiates OH radical formation. This chamber has been used in several pesticide OH oxidation studies including propachlor, chlorpyrifos, hymexazol, trifluralin, and ethalfluralin.[88-93] During a trifluralin+OH experiment, Le Person et al. detected unknown products by FTIR that corresponded to carbonyl-containing species, consistent with 'more polar compounds' detected in previous outdoor oxidation experiments.[83, 88] Chlorpyrifos, an organophosphate pesticide, was shown to form the toxic chlorpyrifos oxon as well as SO_2.[90, 94] These experiments suggested that multifunctional, highly

oxidized, polar species were formed, but their identity remains unknown. Several of the pesticides produced secondary organic aerosol, which affects global radiative balance, visibility, and human health.[88, 91-92, 94-95]

1.5. Environmental Hazards and Toxicological Impacts of Current-Use Pesticides and By-products

Current-use pesticides are synthesized to maximize target potency while minimizing persistence. However, adverse effects on environment and human health are well documented, resulting in on-going regulation.[96-98] One metric of human health is LD_{50}, which is the lethal dose of acute exposure that kills 50% of the subject population. A smaller LD_{50} represents a more toxic compound. LC_{50} is a similar metric, referring to the lethal concentration, rather than dose, and is used to determine if pesticide concentrations in water, for example, are toxic to fish.[8] Chronic exposure experiments study the impact of low dosages, typically orders of magnitude lower than the reported LD_{50}, over many months.[97] Measured effects may include a multitude of changes in the test subject including weight and growth, nervous system development, changes in behavior, physiological deficiencies, cancer, immunotoxicity, endocrine disruption, and any other possible detectable changes. Typically, test subjects for both acute and chronic exposure studies are rats or mice, and extrapolation methods are necessary to translate to humans for health impacts. Exposure studies of sub-lethal low doses have demonstrated non-lethal, yet still detrimental, effects. Two exposure topics of particular interest for current-use pesticides are pollinator and human health effects.

1.5.1. Pollinator Colony Collapse

The impact of current-use insecticides on pollinators, particularly honey bees and bumble bees, is of particularly well-publicized concern. Pollinators are worth $215 billion globally, and

affect human diets directly (honey, fruits) and indirectly (pollination of crops).[99] Decreases in honey bee colonies due to rapid loss of adult worker bees, or "Colony Collapse Disorder" (CCD) is poorly understood but dramatic, with some estimates placing annual colony losses at 30-40%.[100] CCD may be due to a number of anthropogenic factors including current-use pesticides, pathogens and parasites,[99, 101-102] although broad spectrum (non-target specific) insecticides are a leading hypothesis. Pesticides attack bees' central nervous systems leading to paralysis and eventual starvation and death.[100] Bees are typically considered immunologically deficient, and insecticides may increase the susceptibility to diseases.[103-104] Forager bees are exposed directly to insecticides through nectar or pollen, surface contact, or topical exposure by being present during application; the rest of the colony can be contaminated upon return of foragers to the hive.[105-106]

There has been a recent emphasis on pesticide-bee interactions in the scientific literature. Imidacloprid is a neonicotinoid insecticide that is toxic to honey bees, with reported LD_{50} of 3.7 and 40.9 ng/bee via oral and contact exposure, respectively. Nicodemo et al. reported lowered cellular energy production by lowering oxygen consumption by the mitochondria in honey bees after dosing of imidacloprid and fipnoril insecticides.[100] Stanley et al. exposed honey bees to recommended field doses of 15 pesticides and found 100% mortality 48 h after exposure to mustard plants treated with chlorpyrifos, dichlorvos, malathion, spinosad, and four others.[107] Akca et al. exposed the European honey bee to field recommended doses of benfurocarb, carbosulfan, and furathiocarb and found mortality rates of 70.4, 70.2, and 66.8%, respectively.[108] In real-field exposure studies, malathion, chlorpyrifos, carbaryl, acephate, imidacloprid, and cypermethrin increased the number of dead bees compared to untreated colonies.[109-112] Further, acute contact exposure to chlorpyrifos, malathion, deltamethrin, thiamethoxam, fipronil, thiodicarb, indoxacarb, acetamiprid, and clothianidin caused 100% mortality to several honey bee species in lab assays at

field recommended doses.[107, 113-114] A pesticide is considered highly toxic if the LD_{50} is <2µg/bee and moderately toxic between 2—11 µg/bee.[115] In some cases however, chronic exposure of pesticide concentrations much lower than acute LD_{50} can be just as important, especially for developing larvae.[109]

1.5.2. Sub-lethal Effects

"Sub-lethal" effects of current-use pesticides to pollinators include changes in behavior, memory recall issues, reduced lifespan, reproduction and development problems, loss of navigation ability, and problems with foraging bees communicating with the hive.[107] For example, Morandin et al. showed that exposure to realistic concentrations of the insecticide Spinosad in treated pollen during development impaired foraging and produced a trembling effect in bees attempting to land on flowers.[116] Chlorpyrifos affects honeybees at pg concentrations, orders of magnitude lower than reported LD_{50}. Chlorpyrifos, aldicarb, and coumaphos are pesticides that inhibit neurotransmission at the synapses and result in hyperstimulation of muscles. The oxidation products of chlorpyrifos and coumaphos, chlorpyrifos-oxon and coumaphos-oxon, showed greater acetocholinesterase inhibition than the parent insecticide.[117] Exposing honey bees to these pesticides caused bees to take longer to correct themselves after falling over. Impacts on the olfactory system of honey bees from sub-lethal chlorpyrifos exposure inhibited foraging ability, as bees returning to the colony were unable to communicate the rewarding food source.[118]

1.5.3. Pesticide Effects on Human Health

Humans are exposed to pesticides by drinking contaminated water, eating contaminated produce and meat, inhalation, contact exposure during and after application, breast-feeding of children, and accidental skin exposure when handling chemicals. It is difficult to assess pesticide effects on human health from animal studies, and several studies have emphasized results from

case studies of poisoning, voluntary exposure, and occupational exposure. Agricultural workers see the largest concentrations, although workers' families and children also have elevated risk due to living proximity to application and possible contact exposure. Different routes of exposure impact human health differently for each pesticide.[119] Below we present health concerns from two prominent current-use pesticides.

2,4-D is one of the top herbicides used in the country. Grover et al. reported a median cumulative (inhalation, dermal, and hands) exposure of 40 µg per kg body weight per kg of acid to workers who applied 2,4-D.[120] Urine samples from farmers and their families in South Carolina and Minnesota found median 2,4-D concentrations in urine of 71.9 µg L^{-1} (applicators), 1.7 µg L^{-1} (spouse), 6.5 µg L^{-1} (children 4-11 years old), and 1.9 L^{-1} (children >12 years old).[121] Unlike OCPs, 2,4-D is water soluble, does not bioaccumulate, and can be distributed throughout the body in the ionized form and excreted via urine. In rats, 2,4-D has been found in the liver, kidneys, brain, and uterus, but is quickly removed by urination. Unless concentrations are acutely severe, there is no observable effect on reproductive and nervous systems in mice, rats, and dogs, and no carcinogenicity.[122-123] However, correlations of sarcoma and non-Hodgkin's lymphoma in workers exposed to 2,4-D were found in one study, although critical evaluation of the employed methodologies and other possible contributing factors were unable to validate the association.[124]

Malathion is a broad-spectrum organophosphorus insecticide used in crop, food storage, and human protection. Malathion has low toxicity and causes insignificant adverse health effects even at unrealistically high concentrations.[125] However, impurities in malathion formulations, including isomalathion and malathion's degradation product malaoxon, are more toxic than malathion by a factor of 3 to 22 times depending on impurity concentrations.[125-126] Other pesticide classes, including chloroacetanilides, pyrethroids, and triazines, are of low toxicity to humans, but

little is known about their degradation products. Degradation products formed in the atmosphere are expected to be more polar, water soluble, and likely to condense onto atmospheric particles, but the health and environmental effects of pesticide chemistry are relatively unknown and a necessary area of research.

1.6. Overview of Thesis

This thesis focuses on investigating the atmospheric chemistry of current-use pesticides. The structure is:

Chapter 2: Describes a new calibration and measurement method for real-time gas-phase detection of four current-use pesticides, atrazine, metolachlor, permethrin, and trifluralin

Chapter 3: Describes field measurements of two chlorophenoxyacid herbicides, MCPA and 2,4-D, in the atmosphere during and after application using the new CIMS techniques

Chapter 4: Presents OH radical chemistry of three aromatic herbicides, along with proposed oxidation mechanisms and products.

Chapter 5: Presents oxidation experiments of two nitrogen containing herbicides, trifluralin and acetochlor, including proposed oxidation mechanisms and an investigation of the fate of the nitrogen

Chapter 6: Brief conclusion.

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CHAPTER 2- DEVELOPMENT OF A REAL-TIME MEASUREMENT FOR GAS PHASE PESTICIDES USING IODIDE CHEMICAL IONIZATION TIME OF FLIGHT MASS SPECTROMETRY[†]

2.1. Introduction

The widespread use of agricultural pesticides has resulted in the observation of many such compounds in soil and water samples. While the ecological implications of these observations have been the focus of much research, little work has focused on their atmospheric chemistry, despite the fact that many of these pesticides are transported through the atmosphere.[1-9] The chemical fate of compounds in the atmosphere- including oxidation, gas-particle partitioning, and surface deposition- ultimately controls their chemical identities and concentrations, and thus their impact on ecosystems and human health. Global atmospheric concentrations of pesticides are typically considered to be small, yet the local concentrations near point sources can be large enough to result in pesticide drift to neighboring farms, negative impacts on pollinator populations, and substantial occupational exposure of agricultural workers.[10-11]

Trifluralin, atrazine, permethrin, and metolachlor are among the top twenty most frequently used pesticides in the last decade. [1212] These compounds are thought to be much less toxic, less carcinogenic, and less likely to bio-accumulate than the organochlorine pesticides deemed persistent organic pollutants (POPs).[13-17] However, the environmental and health impacts of current-use pesticides and chemical parameters controlling their atmospheric fate are not well understood. These pesticides have been studied with regard to deposition and volatilization, but the investigation of surface-atmosphere fluxes is limited by currently available instrumentation.[6,]

[†] Murschell, T.; Fulgham, S. R.; Farmer, D. K., Gas-phase pesticide measurement using iodide ionization time-of-flight mass spectrometry. *Atmos. Meas. Tech.* **2017,** *10* (6), 2117-2127.

[18] In order to fully understand transport, concentrations, and chemical behavior in the atmosphere, *in situ* measurements of these pesticides need to be fast (<1 hour), sensitive and selective in both the gas and particle phases.[19]

Volatilization of these current-use pesticides from agricultural soils to the atmosphere removes up to 27% of the applied pesticide (26.5%, 12.4%, and 7.5% for trifluralin, metolachlor and atrazine, respectively).[6] The resulting atmospheric concentrations vary, and these current-use pesticides have been detected hundreds of meters to kilometers away from application sites in both gas and particle phases.[2-3, 20] Atrazine, trifluralin and metolachlor have been observed near application areas in concentrations ranging from <1 ng m^{-3} to as high as 61 µg m^{-3}, and in urban and remote locations that are far from sources with concentrations <2 ng m^{-3}.[1, 4-5, 20-21]

For detection of pesticides in the atmosphere, air samples are typically collected on solid phase micro-extraction (SPME) fibers or other adsorbent materials with sampling times of 2 h – 1 week.[1, 3-5, 18] These solid adsorbents are analyzed by offline techniques, typically gas chromatography coupled to mass spectrometry (GC-MS) or electron capture detection (GC-ECD).[1, 3-6, 18, 20-21] These measurement approaches are adequate for offline quantitation of airborne pesticides with detection limits for trifluralin ranging from 1.3 pg/m^3 (GC-MS) to 0.4 µg/m^3 (GC-ECD) with sample collection times of 24 hours and 2 hours, respectively.[1, 5] These techniques have proven successful in quantifying atmospheric pesticide concentrations, although offline analysis introduces steps that can alter a compound's structure and reduce sampling efficiency, and are inadequate for rapid ambient measurement.[3, 5-6, 20] Rapid measurements are necessary for (1) observing pesticide drift in real-time to understand meteorological effects; (2) directly measuring volatilization and surface-atmosphere fluxes by eddy covariance or other micrometeorological approaches; (3) determining whether agricultural workers are exposed to low concentrations over a long period of time, or high

concentrations over a short period of time, and thus for identifying activities that can be targeted to reduce exposure; and (4) laboratory smog chamber or flow reactor measurements in which oxidation chemistry is typically observed on timescales of minutes. Studies of oxidation chemistry require such rapid measurement as atmospheric lifetimes of pesticides can be short due to reaction with OH radicals. Atkinson et al. reported rapid trifluralin reaction with the OH radical (>1 x 10^{-10} cm^3 molecules^{-1} s^{-1}) and photolysis rates on the order of minutes, while the half-life for atrazine plus OH is 2.6 hours for a global average radical concentration of 1 x 10^6 molecules cm^{-3}.[22] As an example of the need for rapid detection for indoor exposure estimates, Vesin et al. showed that pesticides must be measured rapidly (<1 h) due to high emission variation from electronic vaporizers.[23] Here, we investigate the use of chemical ionization mass spectrometry for real-time *in situ* atmospheric pesticide measurement.

Chemical ionization mass spectrometry (CIMS) has been previously explored for pesticide detection. Dougherty et al. detected aromatic chlorinated pesticides, including DDT and DDE, using isobutane reagent ions in positive and negative mode.[24] Tannenbaum employed chloride as a reagent ion to detect the chlorinated pesticide Aldrin.[25] More recently, Vesin et al. showed that high-sensitivity proton transfer reaction mass spectrometers can be calibrated to measure indoor concentrations in the 0.5-600 ppb$_v$ range of four pyrethroid pesticides with limits of detection (LODs) of 50 ppt$_v$ with 1 s time resolution.[23] However, these studies are limited by the use of a quadrupole mass spectrometer, which only has unit mass resolution ($m/\Delta m \sim 1000$), and thus limits the selectivity of the measurement. As pesticides are typically quite large with molecular weights of 200-500 Da, a separation step before analysis of ambient air is often required to eliminate other isobaric molecules that may act as interferences. CIMS is increasingly used to measure trace gas species in the atmosphere because of high sensitivities, resolution, and selectivities of the different

reagent ions employed.[26-32] Chemical ionization can be achieved by positive or negative ions, including hydronium, acetate, iodide, and nitrate. CIMS coupled with high resolution time-of-flight mass spectrometry (ToF-MS) is a viable detection technique for atmospheric pesticides because of its fast time resolution (1-10 Hz), field portable design, high mass resolution ($m/\Delta m$ 4000-6000), and mass accuracy (<20ppm). These features result in measurements of numerous compounds in a complex atmospheric matrix with no need for pre-separation. The elemental composition of analyte ions can be determined for a broad range of m/z ratios (typically 0-1000).[28, 31, 33] Iodide is an obvious target reagent ion for pesticide CIMS, as iodide has been used to measure oxidized nitrogen and halogenated species- including N_2O_5, $ClNO_2$, and $ClNO_3$- and more recently semi-volatile organic compounds, particularly organic acids.[28, 34-35] Pesticides often contain one or multiple of these previously detected functional groups, suggesting that iodide is an appropriate reagent ion for their detection.

In this paper, we explore the potential of iodide ToF-CIMS to detect and quantify four current-use, semi-volatile pesticides: atrazine, metolachlor, permethrin, and trifluralin. We present calibrations using heated injections into an iodide CIMS, and demonstrate that these compounds can be detected at atmospheric and laboratory relevant concentrations with fast (seconds – minutes) time resolution.

2.2. Experimental Method

2.2.1. Chemicals

Standard solutions of trifluralin in acetonitrile (98 ng/µL ± 5%; Sigma Aldrich) and metolachlor in acetonitrile (103 ng/µL ± 5%; Sigma Aldrich), atrazine in methyl tert-butyl ether (MTBE) (1032 µg/mL ± 12; SupelCo, Bellefonte, PA), and permethrin in acetone (999 ± 26

µg/mL; SPEX CertiPrep, Metuchen, NJ) were used in the present study. Solvent choice was dictated by commercial availability of standards.

2.2.2. High Resolution Time-of-Flight Chemical Ionization Mass Spectrometer (TOF-CIMS)

The TOF-CIMS (Tofwerk AG, Switzerland and Aerodyne Research, Inc., Billerica, MA) and iodide (I⁻) ionization scheme used herein are described elsewhere.[28, 31] Briefly, our Iodide TOF-CIMS has five primary components: the ion molecule reactor (IMR), two RF-only quadrupoles, an ion lens focusing region, and a time-of-flight mass analyzer ($m/\Delta m$ ~4000) with a pair of microchannel plate detectors. Sample air is continuously drawn into the IMR at 1.9 sLpm (standard Liter per minute) where the sample interacts with iodide reagent ions. I⁻ is generated by flowing ultra-high purity (UHP) N_2 (99.999%, AirGas) over a CH_3I permeation device; the N_2 carries gaseous CH_3I into a ^{210}Po source to produce I⁻ reagent ions.[36] Iodide is typically thought to ionize neutral species (M) through a ligand exchange reaction with an iodide-water adduct (R1).[36]

$$[I \cdot H_2O]^- + M \rightarrow [I \cdot M]^- + H_2O \qquad (R1)$$
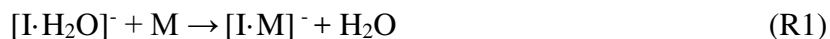
However, deprotonated species have also been observed in ambient measurements, though it remains unclear whether these species are deprotonated in the initial ionization step or declustered during transmission to the TOF detector. [31]

2.2.3. Heated Pesticide Injections and Calibrations

As most pesticide compounds are commercially available as liquids or solids, calibration of these compounds in the Iodide TOF-CIMS necessitates quantitative conversion of solutions to the gas phase. We developed a heated injection system (Figure A1.1) based on work by Lee et al.[28] We placed a new 2 µm pore Teflon Filter (Pall Life Sciences) for each experiment onto an in-line filter holder (Advantec MFS, Dublin, CA) connected by 13 cm of unreactive ¼" (OD) PEEK tubing to the IMR. Pesticide solutions were then injected as liquid samples onto the filter. The

filter holder was connected to a four-way stainless steel union tee (Swagelok). A septum was placed in the second port directly opposite the filter, and a third port, upstream of the filter holder, was connected to a dry UHP zero air flow controlled by two 2000 sccm (standard cubic centimeter per minute) mass flow controllers (MKS, Andover, MA). The air flow was directed through a ½ in. stainless-steel tube packed with cleaned steel wool, and heated to 200°C by a resistive heating wire on the outside of the tube with a PID temperature controller (Omega, Stamford, CT) attached to a thermocouple located between the wire and tube near the exit of the tube. The heated zero air passed over the filter to volatilize the liquid sample to the gas phase before entering the Iodide TOF-CIMS. The fourth port was open to the room to allow the zero air to overflow the system, exhausting to ambient pressure. The zero-air flow was always greater than the inflow of the Iodide TOF-CIMS in order to maintain constant pressure in the IMR and a known flow rate over the pesticide-containing filter.

For each set of experiments, we injected known volumes (1-6 µL) of solvents (blanks) and commercial standard solutions through the septum onto the filter with a 10 µL syringe (Hamilton, Reno, NV). Following each injection, mass spectra time series (Figure 2.1) were allowed to return to the same signals as zero air before the next injection was made as can be seen in Figure 2.1b. Following an injection, pesticide-related peaks rapidly increased, and then decayed in 30-120 minutes. Iodide TOF-CIMS data were collected at 1 Hz.

2.2.4. Data Analysis

In order to identify peaks in the mass spectrum that changed from blank injections during the pesticide injection experiments, we calculated the signal-to-noise ratio (S/N) for every nominal *m/z* peak in the mass spectrum. Nominal masses with S/N > 3 during the injection period were identified as potential signals from the pesticide samples, and the high resolution mass spectra

were fit at those *m/z* ratios to identify the elemental composition of each ion contributing to the signal (Tofware 2.4.3, Figure A1.2).[31] The mass spectral peaks identified during the injections corresponded to iodide-molecule adducts ([I·M]$^-$, trifluralin and atrazine) or iodide-molecular fragment adducts ([I·F]$^-$, permethrin and metolachlor). The isotopic patterns for each peak were used to verify our identification of elemental compositions based on the natural abundance of isotopes.

We normalize the signal of each pesticide ion by a ratio of the reagent (defined as the sum of the signals of I$^-$ plus its water adduct [I·H$_2$O]$^-$) ion signal during the background signal to the reagent signal at each second of the pesticide injection. This normalization accounts for changes in the reagent ion concentration, and thus ion-molecule collision rates and overall ionization rates, and allows for comparisons across different CIMS instruments with different reagent ion count rates and standardization within a single instrument as the ion source ages. The normalization assumes that variations in the ionization efficiency from temperature or pressure changes are adequately captured by the normalization of the summed reagent ions, although the humidity-dependence suggests that mechanisms may not be simple, and the assumption should be tested for field conditions.

The start of the injection/desorption period is obvious in the data (Figure 2.1) with a sharp initial increase in signal above the background (zero-air signal) count rate; we define the end of the injection/desorption period as the time at which the mass spectral pesticide signal has returned
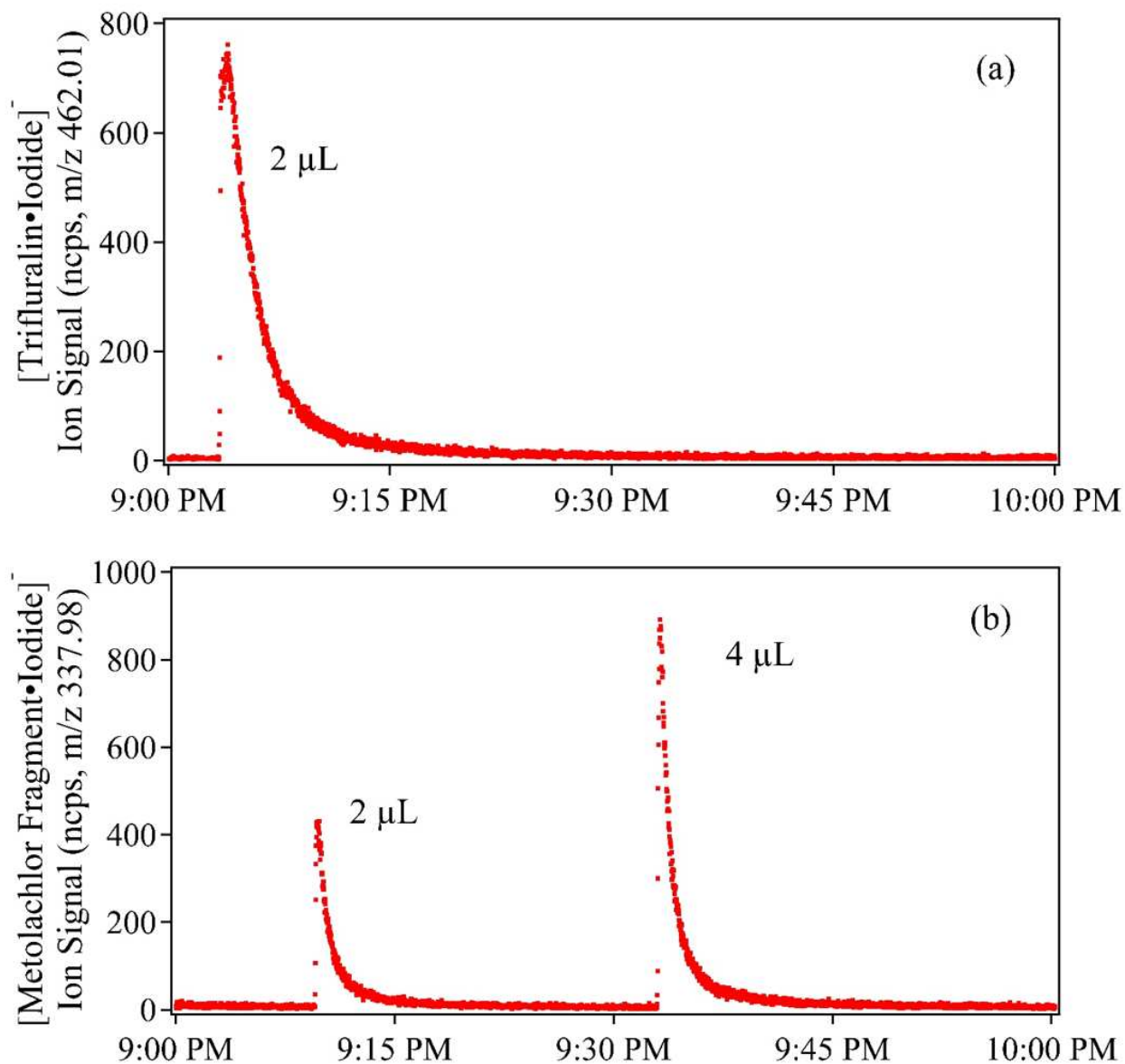
Figure 2.2. Sample data of injections of trifluralin (a, 1 µL) and sequential metolachlor (b, 2 and 4 µL). The observed mass spectrometer signals are shown as 1s data time series. Trifluralin is observed at m/z 462.01 indicative of clustering between the iodide reagent ion, while metolachlor is detected at m/z 337.98, a cluster of a molecular fragment and iodide.

to within 5% of the background count rate. Typical desorption periods for injections were 10 min – 1 h for the range of trifluralin and metolachlor injections and 1-3 h for the range of atrazine and permethrin injections. Extended tailing (0.5-2 h) indicates slow volatilization of the liquid sample to the gas phase. The background count rate is determined from a 20-40 minute average and standard deviation (σ) of signals detected from UHP zero air, and it is subtracted from the pesticide mass spectral signals described in the subsequent analysis. We use the time series of each pesticide-relevant mass spectrometric peak to develop a calibration curve by assuming that the total integrated signal at a given *m/z* ratio observed during the injection and subsequent desorption is directly proportional to the known mass of pesticide injected on, and assumed to be completely volatilized from, the filter. Thus, the signal collected at each 1 Hz data point is taken to represent the fractional mass of the pesticide standard injection. That is, if 5% of a single injection's background-subtracted mass spectral signal is observed in one second, that signal corresponds to 5% of the calibrant mass injected on the filter. As the flow rate is constant, this fractional mass can be converted into a mixing ratio (parts per billion by volume, ppb$_v$, liters of pesticide per 10^9 liters of air), and each 1 Hz data point provides an observed signal for a given mixing ratio. Each injection peak can thus be used to construct a calibration curve and derive the instrument's sensitivity to the analyte of interest at a given high resolution *m/z* ratio. Multiple injections allow for the calculation of an average sensitivity for each analyte, and were used to determine average limits of detection (LODs, S/N = 3) from the standard deviation of the average background count rate of the blanks. This calibration approach assumes that all of the standard solution deposited on the filter is volatilized and that the instrument response is linear over the concentration range of each injection/desorption period.

We note that this calculation differs from the calibration approach described in Lee et al., in which the total summed signal for an injection is divided by the number of molecules injected, and then converted to a mixing ratio using the instrument flow rate at one second.[28] While that calculation is specific for calibrating collected aerosol samples that are subsequently desorbed from a filter surface, as described by Lee et al. for the Filter Inlet for Gas and AEROsols (FIGAERO), it does not capture the variation in concentration that occurs on the fast (seconds) timescale of gas-phase variation and measurement, and it would result in an increasing sensitivity with decreased mass spectral averaging times.[29] The calibration approach described herein is thus specific for *gas-phase* calibrations using an injection/desorption technique.

2.2.5. Calibration Technique Comparison

To validate this approach of gas phase calibrations by solution injection and thermal desorption, we compared well-characterized HR-TOF-CIMS calibrations of formic acid from a home-built permeation tube with injections of a formic acid standard solution (2-4 µL of 10 ng µL^{-1} of formic acid in acetone) on the injection/desorption calibration setup described herein. However, as the high-performance liquid chromatography (HPLC)-grade solvents contain trace quantities of formic acid, identical volume injections of acetone solvent were necessary to identify and subtract formic signal of the solvent blank from each standard solution injection/desorption period.

2.2.6. Relative Humidity Tests

Due to the ligand-switch mechanism described above, analyte detection by iodide TOF-CIMS is expected to vary with ambient relative humidity (RH).[28, 35] As field measurements are a desired outcome in the development of a real-time pesticide detector, we investigated the sensitivity of trifluralin and metolachlor with replicate injections of trifluralin (2.4 µL of 98 ng µL^{-}

^{1} solution) and metolachlor (3 µL of 103 ng µL^{-1} solution) over an RH range of 0-80 % (Figure A1.5). The RH of zero air was controlled by bubbling zero air (0-2000 sccm) through water (HPLC grade, Sigma Aldrich) and diluting with dry zero air (2000-0 sccm) prior to entering the heated tube and injection region of the calibration apparatus described above. The RH of zero air entering the heated tube was detected by a RH probe/transmitter (Omega HX71, Stamford, CT).

2.3. Results and Discussion

2.3.1. Comparison of Calibration Techniques

The results of the formic acid permeation tube and injection calibrations are presented in Figure 2.2. The injection method produces an average sensitivity to formic acid of 3.8 ± 0.4 normalized counts s^{-1} ppt$_v$$^{-1}$, while the permeation tube calibration produces a sensitivity of 3.8 ± 0.2 normalized counts s^{-1} ppt$_v$$^{-1}$. The injection method signal is more variable than the permeation tube, likely due to the large formic acid background in acetone; uncertainties in the syringe volume; and larger, more variable background formic acid in the zero-air due to thermal decomposition of species to formic acid in the heated stainless-steel tube. Error in the concentration of formic acid from the permeation tube arise from uncertainties in the mass loss rate in the home-built permeation oven. The formic acid injections are much shorter (<1 min) than the pesticide injections, indicative of its higher vapor pressure than the pesticides, but the data analysis is identical. The injection calibration method for CIMS does prove to be sufficient for calibration of lower-volatility compounds and can be used for the pesticides presented herein, for which calibration by permeation tubes is impossible.

2.3.2. Pesticide calibrations

The calibration technique described herein is a dynamic gas phase calibration approach for low volatility compounds that are otherwise challenging to quantitatively convert to the gas phase.

While target analytes must be soluble in non-reactive solvents that do not substantially interfere with instrument background or reagent ion concentrations, this versatile technique is a viable alternative to permeation tubes, which require 5-15 mL of pure liquid analyte and can take weeks to months for equilibration and mass loss analysis. Thus, this approach enables calibration of semi-volatile and intermediate-volatility compounds that diffuse through typical Teflon permeation tubes too slowly, or not at all, for detectable mixing ratios and for measurable mass loss (an essential component in determining permeation rates).
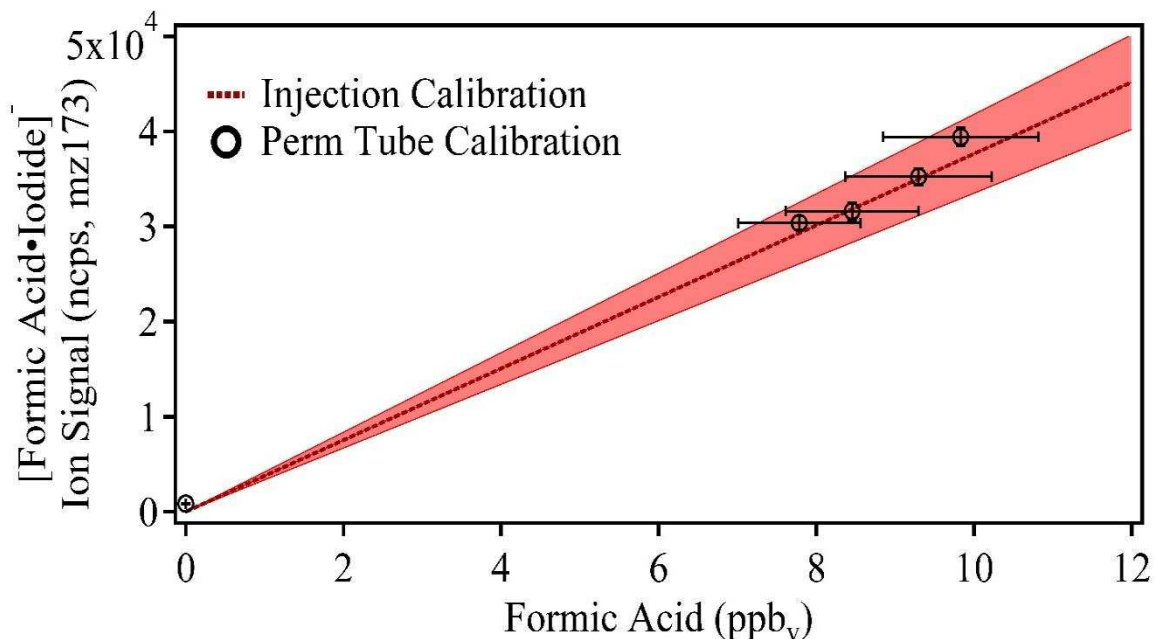
Figure 3.2. Calibration comparison between the conventional formic acid permeation tube calibration method (black open circles) and formic acid injections using the method described herein. Error in the formic acid concentration is represented by the horizontal bars, while error in the y axis is the standard deviation of the signal. The average calibration from the injection method is presented as the dashed red line, and the shaded red area region is the standard deviation of the injection sensitivities.

The iodide TOF-CIMS detected the four pesticides in the gas phase with sufficient sensitivity for laboratory experiments and certain field settings (Table 2.1, Figure 2.3). Figure 2.3 shows the calibration curves (red) generated by the single injections per the calculations described above, with the average calibration curve (black) of the four pesticides studied. In the UHP zero-air carrier gas, the average background count rates for the analytes in synthetic air are very low, between 1-7 ncps for the four *m/z* ratios. LODs for gas phase atrazine, trifluralin, metolachlor, and permethrin are 120±20, 50±30, 110±20, and 150±80 ppt$_v$, which correspond to concentrations of 0.56, 0.37, 0.67, 1.1 µg/m^3, respectively and are reported in Table 2.1. These concentrations are potentially useful for particle phase measurements by the iodide TOF-CIMS, where gases are captured on a thermal denuder and particles are subsequently volatilized either using a heated inlet or filter system.[37] Trifluralin has been detected in a number of field studies with average ambient gas phase concentrations ranging from 0.228-1.93 ng m^{-3} and detected concentrations as low as 0.0013 ng m^{-3} [5, 20]. Trifluralin volatilization measured the day of application was as high as 61 µg m^{-3}, decreasing by an order of magnitude the next day.[1]

Metolachlor average gas-phase concentrations are 0.37-12.74 ng m^{-3} with the lowest reported concentration of 0.0059 ng m^{-3}.[5, 38] Similarly, atrazine average gas- phase concentrations covered a similar order of magnitudes (0.0018-8 ng m^{-3}).[5, 39] The LODs of the iodide TOF- CIMS suggest that this instrument is appropriate for real-time ambient measurements made near agricultural targets several days after application, but not in remote locations.

Table 2.1. Characteristics of the pesticides studied and figures of merit using the Iodide TOF-CIMS

	Trifluralin	Atrazine	Metolachlor	Permethrin
Pesticide Class	Dinitroaniline	Triazine	Chloroacetanilide	Pyrethroid
Use	Herbicide	Herbicide	Herbicide	Herbicide & Insecticide
Vapor Pressure (bar)	6×10^{-8}	4×10^{-10}	2×10^{-8}	2×10^{-11}
Chemical Formula	$C_{13}H_{16}F_3N_3O_4$	$C_8H_{14}ClN_5$	$C_{15}H_{22}ClNO_2$	$C_{21}H_{20}Cl_2O_3$
Ion Detected	$I \cdot C_{13}H_{16}F_3N_3O_4$	$I \cdot C_8H_{14}ClN_5$	$I \cdot C_{11}H_{14}ClNO$ (Fragment)	$I^- \cdot C_8H_{10}Cl_2O_2$ (Fragment)
m/z of Ion Detected	462.01	341.99	337.98	334.91
Standard Concentration	98 ± 4.9 ng/µL	1032 ng/µL ± 12	103 ± 5.2 ng/µL	999 ± 26 ng/µL
Solvent	Acetonitrile	Methyl tert-butyl ether	Acetonitrile	Acetone
Boiling Point in solution[a] (°C)	87	53	81	55
Injection Volumes for calibration (µL)	1,2,3,4	1.4, 2.8, 4.5, 6	1,2,4,6	0.9,1.8, 4
Sensitivity (ncps ppb$_v^{-1}$)	180 ± 40[b]	80 ± 20	38 ± 6	100 ± 40
LOD (ppt$_v$)[c]	50 ± 30	120 ± 20	110 ± 20	150 ± 80

[a]From manufacturer's data

[b]Error reported as standard error of the average sensitivities

[c]ppt$_v$ = parts per trillion by volume
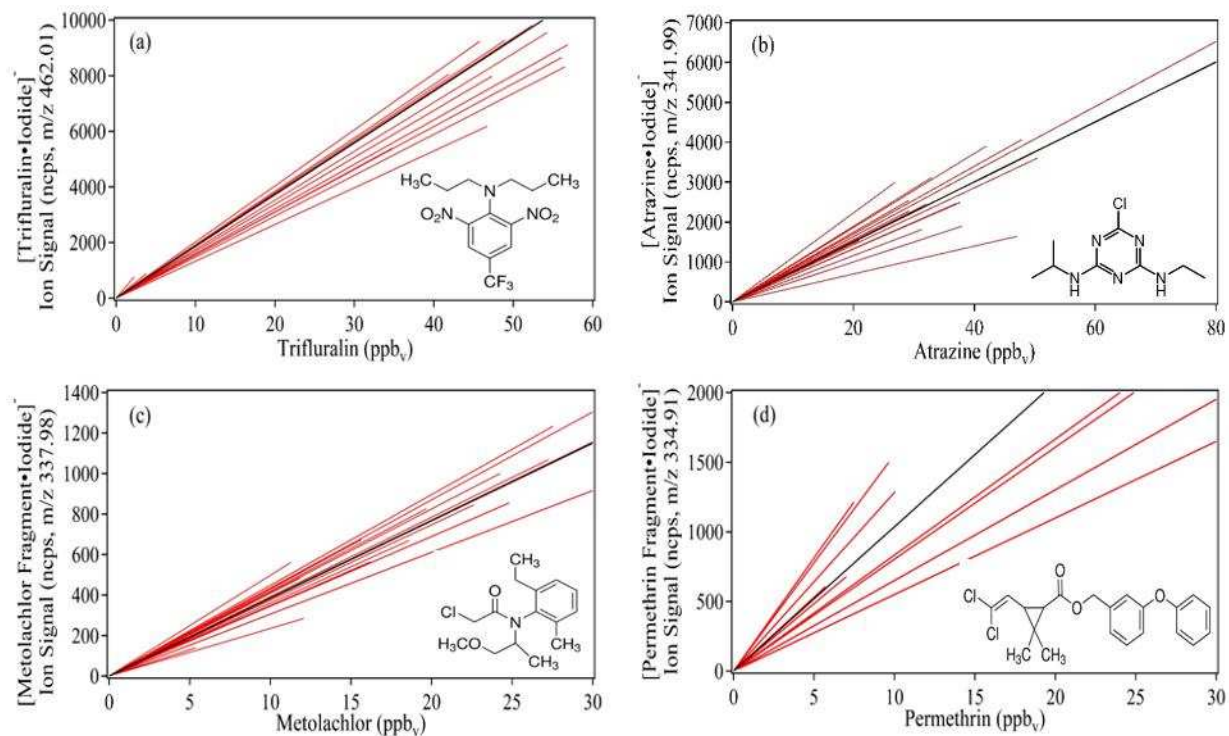
Figure 2.4. Calibration curves of pesticide solutions on the iodide ToF-CIMS, metolachlor (a), trifluralin (b), atrazine (c), and permethrin (d). Red lines represent the signals from single injections as a function of the calculated gas-phase mixing ratio. The average sensitivity (black line) is derived from each set of calibration curves. The error in sensitivity is calculated as the standard error of the average sensitivity for each pesticide.

While the resolution for the TOF-CIMS might be limited at larger *m/z* ratios during ambient measurements, these pesticides provide one particular advantage for detection by mass spectrometry: the presence of halogen and other heteroatoms such as nitrogen, sulfur and phosphorus results in detected ions that have distinct isotopic signatures. The fitting procedures used in the Tofware software package allow for confirmation of peak identity not only by the exact mass of the peak fit, but also by the fit of isotope-containing peaks. Such fitting has allowed for measurement of trace compounds in complex environmental and laboratory samples.[28-29, 37, 40] For example, Figure A1.6 shows potential interferences at the expected *m/z* ratios of the four target pesticides based on previous field campaigns relative to the signal for 1 ppb$_v$ of each pesticide. Potential interferences for metolachlor are minor; potential interferences for trifluralin, atrazine and permethrin are more substantial, but as none of the interfering peaks hold identical halogens, the pesticide isotopes at higher masses can be used to validate the observation (e.g. Figure A1.2). However, we do acknowledge that mass resolution will be a limiting factor for field measurements of these three pesticides that are far from agrochemical sources.

CIMS has been used in atmospheric chamber experiments to explore oxidation reactions and mechanisms with starting precursor concentrations between 1-100 ppb$_v$.[40-42] The iodide ToF-CIMS is thus more than suitable for chamber and laboratory experiments of pesticide oxidation chemistry and kinetics. Due to known relative humidity effects on iodide CIMS sensitivities, trifluralin and metolachlor were measured at multiple relative humidities (Figure A1.5). The observed pesticide sensitivities decreased by 70% and 59% between 0 and 80% RH for trifluralin and metolachlor, respectively. Only small changes (8%) were observed in the background signal and noise (5-30%) between 0 and 80% RH. These changes in sensitivity caused the LOD to increase from 108 (50) ppt$_v$ at 0% RH to 421 (110) ppt$_v$ at 80% RH for metolachlor (trifluralin).

The decrease in instrument sensitivity with increased relative humidity suggests ionization occurs through a clustering reaction with bare iodide reagent ions, rather than a ligand exchange reaction. Therefore, relative humidity effects on iodide CIMS sensitivity necessitates inclusion of RH measurements with ambient field measurements of pesticides.

Table 2.2 compares the iodide TOF-CIMS to previous measurement techniques of the four pesticides. Our work, to the best of our knowledge, is the first online detection and quantification of atrazine, trifluralin, metolachlor, and permethrin. Unlike previous work shown in Table 2.2, the iodide TOF-CIMS detected the pesticides *in situ* with no collection, extraction, and separation on a gas or liquid chromatograph, enabling rapid (1 Hz) detection. The LODs we report are comparable to those reported by Vesin et al. for on-line, *in situ* measurement of transfluthrin, a pyrethroid compound that is structurally similar to permethrin.[43] However, LODs calculated in this work are larger than other techniques and could be improved by longer averaging of sampling time (1-5 min). No significant relationship between decay time of the injection and vapor pressure was found. While iodide TOF-CIMS has been typically used for the measurement and quantification of semi-volatile $C_xH_yO_z$ or small oxidized halogen compounds (Cl_2, BrO), atrazine ($C_8H_{14}ClN_5$) is a triazine derived compound with multiple amine groups and a chloride. [34, 44] This suggests that iodide TOF-CIMS might be appropriate for detecting other triazine or organic halide compounds.[44]

2.3.3. Fragmented Pesticides

While trifluralin and atrazine were detected as quasi-molecular ions with the parent molecule clustered with iodide reagent ions, metolachlor and permethrin were detected as iodide adducts of molecular fragments. Fragmentation is a well-known phenomenon in CIMS but is not

Table 2.2. Comparison of LODs[a] *(µg/m³)* between iodide TOF-CIMS and previous pesticide measurements

Reference	Instrument	Approach	Phase	Atrazine	Trifluralin	Metolachlor	Permethrin	Collection Time
Lenoir et al. 1999	GC-CIMS[b]	Off-line	Gas	n/a[c]	1.6×10^{-6}	n/a	n/a	>8 h
Foreman et al. 2000	GC/MS-SIM	Off-line	Gas and Particle	6×10^{-6}	1×10^{-6}	1.2×10^{-5}	2.9×10^{-5}	4 h 5 min/h
Peck et al. 2005	GC/MS-SIM	Off-line	Gas	9.8×10^{-6} µg/m³	1.3×10^{-6}	5.9×10^{-6}	n/a	24 h
Bedos et al. 2006	GC/MS-SIM GC/ECD	Off-line	Gas	n/a	0.004 0.4	n/a	n/a	2-10 h
This work	Iodide ToF-CIMS	in situ	Gas	0.56	0.37	0.67	1.1	(No collection) 1 s sampling

[a] Each work reported different method of calculation for LOD.

[b] Methane chemical ionization mass spectrometry

[c] Pesticide was not studied.

typically thought to dominate mass spectra in atmospheric measurements.[28] However, the intact permethrin-iodide adduct was not detected (*m/z* 518.19). Instead, the dichloro-allyl-cyclopropyl acid fragment is detected clustered with iodide ([I·$C_8H_{10}ClO_2$]⁻, *m/z* 334.91) following fragmentation at the ester bond. This is consistent with previous experiments of pyrethroid compounds similar to permethrin using electron impact ionization showed fragmentation at the ester bond, the same bond at which the fragmentation occurs in this study.[43] Similarly, the intact metolachlor molecule was not detected as a quasi-molecular ion ([I·M]⁻, i.e. as an iodide cluster with the parent molecule at *m/z* 410.79) during either room temperature or heated injections, but instead as a fragment clustered to iodide ([I·$C_{11}H_{14}ClNO$]⁻, at *m/z* 337.98). The observation is consistent with fragmentation at the bond between nitrogen and the second carbon of the methoxypropane group, although we did not observe the corresponding smaller fragment (C_4H_8O) as either a bare ion or iodide adduct. We note that none of the four pesticides' fragments or molecular ions were observed unbound to iodide reagent ions, as is occasionally observed for some oxidized organic compounds in other iodide TOF-CIMS instruments.[28, 31]

2.3.4. Assumptions for Injection Calibrations

The injection calibration approach makes four assumptions: (1) volatilization of the pesticide solutions does not cause thermal dissociation or other chemistry of the analyte prior to ionization; (2) the sensitivity of the instrument to the detected pesticide ions is linear across the mixing ratio range created during each injection, (3) complete volatilization of the pesticide after injection on the filter occurs within the integration time, and (4) negligible analyte loss to connection between the filter and the CIMS. We tested the first assumption of negligible thermal chemistry during the volatilization step by varying the temperature of the heated air and testing nitrogen as a carrier gas for the calibrations. We injected the permethrin solutions at two different

temperatures, 23°C (unheated) and 200°C (heated) and metolachlor solution at three different temperatures, 23, 100, and 200°C. The mass spectra were identical in the unheated and heated injections, albeit over substantially longer timeframes, with permethrin requiring 6-9 hours to return to baseline in the unheated experiment versus 150 minutes or less for the heated system. Metolachlor sensitivity decreased substantially during the injections at 23°C and 100°C, due to the inability of the pesticide to volatilize. Permethrin sensitivity decreased 70% during the room temperature injection, therefore injections at 200°C were pursued. The iodide-molecule fragment adduct was the sole ion observed by the mass spectrometer at both temperatures for permethrin and metolachlor, while the iodide-molecule adduct was not observed. Thus, there is no evidence that the permethrin and metolachlor fragments are produced during the volatilization step; they are thus likely generated in the ion-molecule reaction chamber during ionization. Oxidation of the pesticide standards by O_2 in zero air could occur to suppress observed concentrations and thus sensitivity; we note that the sensitivity of iodide TOF-CIMS to trifluralin increased 38% when UHP nitrogen was used as the carrier gas and no ambient O_2 was present in the calibration system or mass spectrometer. However, we also note that ion-molecule reactions are altered in the absence of ambient O_2, and thus use UHP-zero air for all calibrations described herein.[45]

We test the second assumption, linearity in instrument response, by examining the sensitivities for different volumes and concentrations for each pesticide standard. These different volumes and concentrations reach different mixing ratio ranges: a non-linear detection response would result in a systematic shift in observed sensitivities as the mixing ratios reached larger ranges. However, the sensitivities of trifluralin, metolachlor and atrazine are normally distributed around the mean with no observable systematic bias given the concentration ranges (Figure A2.3). Thus, the assumption of linear instrument response is justified for these three pesticides in the

concentration range used. For example, trifluralin injection volumes of 2 µL (mixing ratio range of 0-10 ppb$_v$) provided the same mean sensitivity (180 ± 20 ncps/ppb$_v$) as larger injection volumes (e.g. 4 µL injection, mixing ratio ranged from 0-60 ppb$_v$ gave a mean sensitivity of 160 ± 30 ncps/ppb$_v$) within the error. This observation is consistent with calibrations of small acids, including formic acid, acetic, propionic, and nitric acids, which have previously shown linear calibrations using identical Iodide TOF-CIMS.[28, 35, 37] Permethrin standards are less clear, but do not show a consistent trend between sensitivity and injection volume (Figures A2.3, A2.4). To test the third assumption of complete volatilization, we first note that the baseline signal of the detected *m/z* returned to within 5% of the pre-injection value within 30-120 minutes, suggesting that volatilization was complete before subsequent injections. Further, replicate injections at multiple volumes are normally distributed for atrazine, metolachlor, and trifluralin, suggesting that uncertainties are random, while incomplete and inconsistent volatilization would likely produce unpredictable error, and thus non-Gaussian distributions (Figure A1.3). Permethrin has a lower sensitivity for the 4 µL injections than for the 0.8 or 2 µL injections, consistent with incomplete volatilization at the higher (>15 ppb$_v$) concentration. Finally, to mitigate potential loss of analyte between the filter and instrument, we use the shortest possible piece of unreactive PEEK tube (13 cm) to connect the filter to the iodide TOF-CIMS entrance.

2.4. Conclusions

This work demonstrates a calibration technique for semi-volatile compounds newly adapted for TOF-CIMS; while applied here to pesticide measurement with iodide TOF-CIMS, this approach may be used in future studies for quantification of other low-, intermediate- and semi-volatile compounds of atmospheric interest using an array of real-time instruments. These calibrations demonstrate that iodide TOF-CIMS is sensitive, selective, and fast enough for on-line

measurements of trifluralin, metolachlor, permethrin, and atrazine in the laboratory in the gas phase. Application to field measurements is more challenging than controlled laboratory conditions for several reasons: (1) LODs can be higher than needed for ambient pesticide concentrations, (2) changes in relative humidity must be considered for quantitative *in situ* measurements, and (3) the large number of potentially interfering peaks in the mass spectrum can make peak identification ambiguous. Coupling to an aerosol inlet, including a heated tube or filter system, will enable particle-phase measurements in the laboratory and potentially in the field.[29, 37] Such real-time measurements are essential for laboratory kinetic and oxidation product studies to understand the atmospheric fate of pesticides, including oxidation chemistry and secondary organic aerosol (SOA) production, and to better understand regional and global impacts of these widely-used compounds.

CHAPTER 2 REFERENCES

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CHAPTER 3- INVESTIGATING ATMOSPHERIC SOURCE MECHANISMS OF
HERBICIDES WITH REAL-TIME FIELD MEASUREMENTS OF 2,4-D AND MCPA[†]

3.1. Introduction

Herbicides are widely used throughout the United States, with up to 2.5 billion pounds of total herbicide applied annually.[1] Off-target effects from aquatic transport and soil run-off of pesticides are the typical focus of environmental studies, but the atmospheric source and fate of pesticides also impact ecosystems and human health. Atmospheric concentrations cause unintentional exposure to agricultural workers and pollinator populations.[2-6] Atmospheric transport enables deposition to off-target areas (e.g. neighboring agricultural sites via short-range transport and more distant areas via long-range transport),[7-14] and is controlled by atmospheric chemistry, including gas/particle partitioning, oxidation chemistry, and removal by wet or dry deposition.

The relative importance of different atmospheric sources of herbicides likely depends on their chemical properties. Application spray releases aqueous droplets that are large enough to rapidly deposit, and thus are thought to contribute to off-target effects over short distances only through spray drift. However, while spray droplets are in the atmosphere, organic compounds can volatilize directly from spray droplets, forming a spray volatilization source mechanism of gas-phase pesticides to the atmosphere during the application process. Herbicide volatilization from soil or water surfaces to the atmosphere is better studied.[15-16] Short-term volatilization directly from ground and plant surfaces is considered well-described by vapor pressure.[4] Once pesticides have penetrated soil, volatilization is slower (long-term volatilization), and is typically described

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[†] The writing for this chapter has been prepared for publication by Trey Murschell, but has not yet been submitted for publication.

by a combination of vapor pressure, Henry's Law constant, soil adsorption and water solubility. Compounds with lower Henry's Law constants are more mobile in soil, and can thus accumulate at soil surfaces and volatilize.[17-19] However, recent studies suggest that vapor pressure is the main predictor of volatilization, while other physio-chemical properties change the effective vapor pressure.[20-21] However, these models focus on long-term volatilization over tens of days, rather than short-term volatilization immediately after application. Time-resolved atmospheric herbicide measurements are necessary to constrain short-term volatilization in the hours after application. Most atmospheric pesticide measurement techniques cannot distinguish between spray drift volatilization and post-application volatilization because sample collection times range from hours to days.[15, 22] However, recent developments in field-portable mass spectrometry enable much faster measurements.[23-24]

Phenoxy acids are a class of herbicides that include 2,4-dichlorophenoxyacetic acid (2,4-D). Popularly known as "Agent Orange", 2,4-D was widely used as a defoliating agent by the US military in the Vietnam war, and is still widely used in agriculture. 2,4-D is toxic to humans, and is linked to cancer and reproductive issues.[25-27] 2,4-D is often paired with other herbicides in commercial mixtures, including 2-methyl-4-chlorophenoxyacetic acid (MCPA) and other chlorinated aromatic alkyl acids. Few atmospheric measurements of these 2,4-D-type compounds exist. A four-year study of phenoxy acid herbicides in Canada showed gas-phase atmospheric 2,4-D and MCPA concentrations on the order of pg/m^3,[28] although higher concentrations have been observed in the agricultural prairie regions (0.11-2.73 ng/m^3 [0.014-0.355 ppt_v, STP] for 2,4-D and 0.17-1.88 ng/m^3 [0.017-0.190 ppt_v] for MCPA).[29]

2,4-D and MCPA are currently used in both agriculture and commercial applications. Like many university campuses, Colorado State University sprays herbicides annually to maintain

campus grounds and protect from broadleaf weeds. This annual spraying provided an opportunity to test, to the best of our knowledge, the first measurements of herbicides in the atmosphere during and after application, and to gain insight into the atmospheric source mechanisms of 2,4-D and MCPA.

3.2. Experimental Section

Commercially-available herbicide mixtures were applied between 6:42-7:08am (local time, MST) on 3 September 2017 to a 2000 m^2 plot of grass adjacent to the Chemistry building on the main campus of Colorado State University (Fort Collins, CO). The active ingredients in the mixture included 2,4-D, the dimethylamine salt of MCPA, the triethylamine salt of triclopyr (3,5,6-trichloro-2-pyridinyloxyacetic acid), and the methylheptyl ester of fluroxypyr (4-amino-3,5-dichloro-6-fluoro-2-pyridyloxy-acetic acid, 1-methylheptyl ester) (Table A2.1). The herbicide spray solution was prepared in a 1136 L drum according to the manufacturer's specifications: 9.4 L of commercial 2,4-D (19.6 % by weight) and 11 L of a commercial mixture of MCPA, triclopyr, and fluroxypyr (30.9, 3.09, 2.92 % of the original commercial mixture, respectively) were added to the drum; water was added to fill the remaining volume.

A 4 m boom sprayer pulled by a small tractor applied the herbicide mixture. The applicator sprayed ~64 L of the herbicide solution 0.3 m from the ground. The application covered a circular pattern, in which each successive loop was smaller, ~4-5 m closer towards the center of the plot. Gas-phase mixing ratios were measured by a time-of-flight chemical ionization mass spectrometer with acetate reagent ions (hereafter referred to as acetate-CIMS). The acetate-CIMS was located on a paved footpath in the middle of the application area. At its innermost loop, the booms passed ~1 m from the instrument inlet. No further herbicide application was conducted in the vicinity of the measurement area after 7:08 am to avoid confusing drift with volatilization.

3.2.1. Acetate-CIMS

The acetate-CIMS (Tofwerk AG and Aerodyne Research, Inc) is a method for softly ionizing trace gas-phase inorganic and organic acids in the atmosphere and is described elsewhere.[30-31] The inlet was oriented vertically, sampling 1.3 m above ground level. Unlike previous measurements with this particular acetate CIMS,[30] there was no glass inlet attachment for particle skimming, but contribution from aerosol to herbicide signal is expected to be minor. Ambient air was pulled into the instrument at 1.9 standard L min^{-1} into an ion-molecule reaction chamber (IMR, 100 mbar, 40ºC), where molecules in the air were ionized by acetate reagent ions. Acetate ions were generated by passing acetic anhydride carried by nitrogen through a ^{210}Po ionizer. The mixture of air and reagent ions was directed through two segmented quadrupole regions as the pressure in the mass spectrometer dropped to 10^{-6} mbar. Ions were pulsed orthogonally into a time-of-flight mass spectrometer. The acetate-CIMS was tuned in negative ion mode, with a range of m/z 4-500, mass accuracy <20 ppm, mass resolution ($m/\Delta m$) > 4000, and time resolution of 1 s. The high mass resolution of the TOF enabled ion elemental composition analysis. The acetate-CIMS was portable (300 kg; 0.6m x 1.1m x 1.3m; on wheels; power requirements <2 kW), thus enabling field measurements.[30, 32-34]

Acetate ionization occurs by either deprotonation,[31] or by a clustering reaction in the IMR that can be coupled to a declustering reaction in the segmented quadrupoles. As the gas-phase basicity of acetic acid is so high, acetate-CIMS is extremely sensitive to organic acids and nitrophenols, and is well-suited for the phenoxy acid herbicides.[30, 34-35] We calibrated the acetate-CIMS using heated solution injections, as reported in Murschell et al., of 2,4-D and MCPA standards (US EPA Pesticide Repository, 99%) diluted in methanol (HPLC grade, Sigma Millipore).[23] Briefly, Ultra High Purity (UHP) zero air (AirGas Inc, total hydrocarbon content

<0.01 ppm) zero air is heated to 200°C and directed through a filter into the CIMS. Herbicide standards were injected through a septum onto the filter, and the corresponding signal was converted to a concentration, thus creating a calibration curve (Figure A2.1). 2,4-D is observed at the molecular ion ($C_8H_6Cl_2O_3^-$, *m/z* 218.96), with minor contribution (relative ion signal is 2:1) from a fragment ion ($C_6H_4Cl_2O^-$, *m/z* 160.95). The sensitivity of the acetate-CIMS is 1.3 ± 0.4 and 1.5 ± 0.4 normalized counts ppt_v^{-1} (parts per trillion by volume) for 2,4-D and MCPA, corresponding to detection limits (3σ/sensitivity) of 3.1 ppt_v and 12 ppt_v in 1 s averaging, respectively. We overflowed the inlet with UHP zero air each hour for 2-5 minutes to quantify the instrument background. Data collection began at 06:30 am, and continued until 11:30 am, when ambient temperatures reached 32°C and the ToF temperature reached 40°C, as the instrument was not in an enclosed or air-conditioned structure.

3.2.2. Data analysis

We analyzed data using Tofware (v2.5.6, Tofwerk AG) and Igor Pro (v6.37, Wavemetrics). We fit mass spectral peaks that corresponded to the applied herbicides (targeted analysis). We also fit all mass spectral peaks that met an enhancement criterion – i.e. the ratio of any signal during the closest pass of the herbicide applicator to the pre-spray period ≥3 (non-targeted analysis). The targeted analysis identified peaks corresponding to 2,4-D and MCPA, but not triclopyr or fluroxypyr. The non-targeted analysis additionally identified a peak at *m/z* 160.95, corresponding to dichlorophenol (DCP). Multiple lines of evidence validated the assignment of mass spectral peaks to 2,4-D, MCPA and DCP (Figure A2.3). Each identified ion has multiple isotopes, and signals for those isotopes were proportional to expected natural abundances. NO_2^- and NO_3^- are strong tracers of diesel exhaust,[36] and displayed little correlation with the pesticide signals ($r^2 \approx$ 0.1), confirming that the signals attributed to herbicides were not from the tractor exhaust. Finally,

four zero air overflow experiments throughout the field experiment demonstrated that ambient signals were substantially higher than background signals, confirming that the herbicide signal was truly ambient, and neither variable instrument background nor inlet artifact.

3.3. Results and Discussion

Acetate-CIMS was adequately sensitive to observe gas-phase phenoxy herbicides. Herbicide application caused clear increases in both 2,4-D and MCPA mixing ratios above background (Figures 3.1, 3.2, A2.2). No herbicide-related peaks were observed before application. Once spraying commenced, peaks associated with 2,4-D were immediately apparent, reaching a maximum of 13 ppt$_v$ during the closest pass of the spray boom, with an average of 4 ±3 ppt$_v$ (1σ) during the application period. MCPA mixing ratios were also enhanced above background during the application period (average 4 ppt$_v$), but reached their maxima several hours after application (70 ppt$_v$ at 10:15 am). Neither triclopyr nor fluroxypyr were observed in the atmosphere, likely due to their low concentrations in the application mixture. Non-targeted analysis of the mass spectra showed gas-phase dichlorophenol in the atmosphere during and after application. Dichlorophenol is a starting material for 2,4-D synthesis, and may have been an unintended impurity in the commercial mixture, which was not analyzed. Chlorophenol contaminants and/or co-formulants have been detected previously during phenoxy acid measurements.[37] While acetate-CIMS cannot identify structural isomers, 2,4-dichlorophenol (2,4-DCP) is a likely culprit based on (1) *a priori* knowledge of 2,4-D structure, (2) isotopic signature of two chlorines in the mass spectrum, and (3) authentic standard calibrations. The 2,4-DCP signal was not merely a fragment of 2,4-D in the mass spectrometer: calibration of authentic 2,4-D standards produced a fragment at *m/z* 160.95 (i.e. the 2,4-DCP molecular ion) that is 1.3 ± 0.3% of the molecular ion signal (*m/z* 218.96), while the application and post-application field observations had signal at the 2,4-DCP

ion that is 50% of the 2,4-D ion. Due to the structural similarity between 2,4-DCP and 2,4-D, we applied the sensitivity of 2,4-D to the background-subtracted 2,4-DCP signal, deriving an estimated average mixing ratio of 130 ± 60 ppt$_v$ during the spray period, with a maximum of 477 ppt$_v$. The signals decreased after application, but remained apparent (average 70 ± 40 ppt$_v$), reaching peak post-application mixing ratios of 200-300 ppt$_v$.
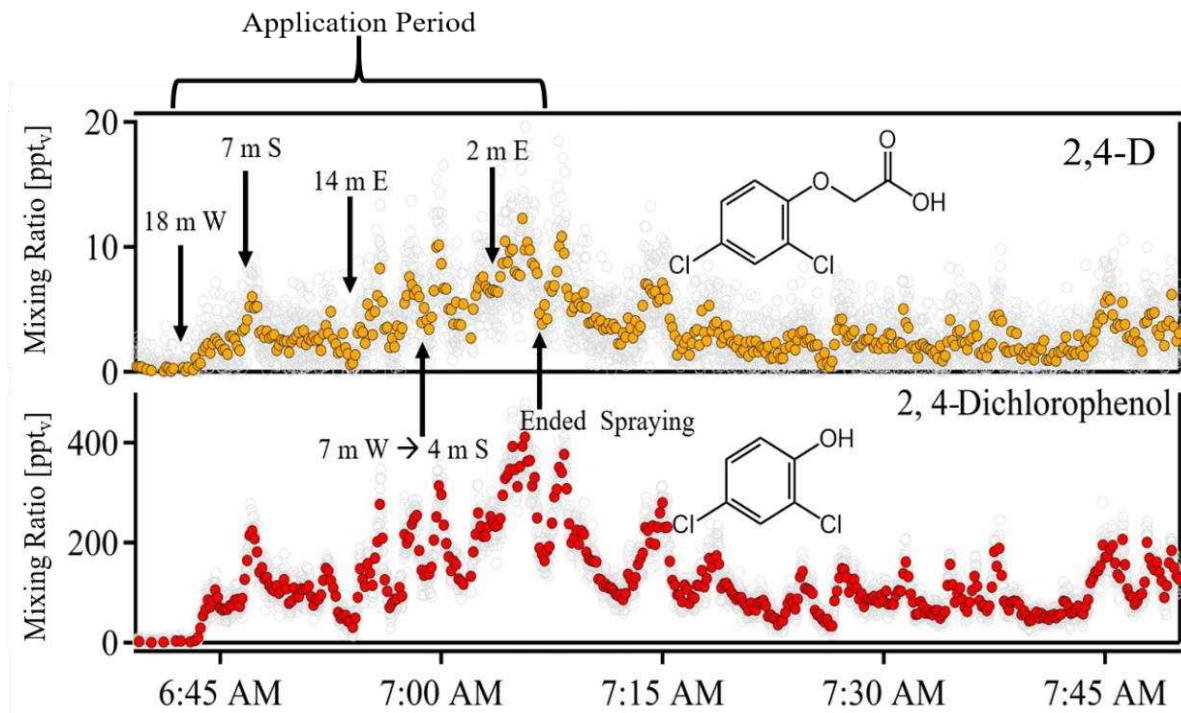
Figure 3.5. Time series of 2,4-D (upper panel, detected as a deprotonated molecular ion m/z 218.96) and 2,4-dichlorophenol (lower panel, detected as a deprotonated molecular ion m/z 160.95) mixing ratios before, during, and immediately after the application period. Grey circles represent the 1 s data points, while colored circles are the 10 s averages. Application began at 6:42 am local time and ended at 7:08 am; each applicator pass is annotated on the time series of 2,4-D with the distance of the tractor (e.g. 18 m), and the direction of closest point of the applicator (East, West, South of the acetate-CIMS). Decreases in signal during the application period correspond to time periods when the spray boom was briefly turned off.

Application of phenoxy herbicides caused elevated mixing ratios of three confirmed compounds during and after application. The magnitude and timing of the atmospheric enhancement varied by compound. Two atmospheric source mechanisms of herbicides were possible during these experiments: (1) spray volatilization from herbicides in spray droplets partitioning to the gas-phase and (2) short-term volatilization from direct partitioning of the applied mixture on soil and grass surfaces to the atmosphere. Herbicides that have permeated into soil require longer (days to weeks) timescales for volatilization because these compounds bind with soils, dissolve in soil moisture, and require time to transport back to the soil surface for subsequent volatilization. Such long-term volatilization was thus unlikely to contribute to gas-phase pesticides observed during this field experiment. Mixing ratios of 2,4-D and 2,4-DCP were highest during the application process, indicating that spray volatilization was the dominant atmospheric source mechanism of both compounds. A spray volatilization source of MCPA was also apparent: gas-phase mixing ratios were slightly elevated above background during the application process but did not share the same periodic spraying (peaks and valleys) trends as 2,4-D and 2,4-DCP. However, spray volatilization was not the dominant atmospheric source mechanism of MCPA in that mixing ratios maximized after application ceased. The concentrations of the three species during and directly after application are consistent with the extent of spray volatilization being described by the Henry's Law constant, which describes the ratio of gas-phase to aqueous concentration at equilibrium. That is, a higher Henry's Law constant would indicate a greater propensity for a compound to partition into the gas phase from water droplets (i.e. in this study, 2,4-D and 2,4-DCP), while species with lower Henry's Law constants (MCPA) would be more likely to be retained by the water and deposit on applied surfaces. To the best of our knowledge, these are the first field measurements to suggest that spray volatilization could be a substantial

source mechanism of gas phase pesticides to the atmosphere. Further investigations with herbicides of varying Henry's Law constants are necessary for confirmation, as evidence herein is limited.

Post-application volatilization was apparent for 2,4-D, MCPA and 2,4-DCP, but dominated the atmospheric source mechanism of MCPA (Figure 3.2, A2.2). Post-application MCPA mixing ratios were well-correlated to calculated vapor pressure (r=0.75). Post-application 2,4-D and 2,4-DCP are less correlated with temperature (r=0.6 for 2,4-D, r=-0.3 for 2,4-DCP). 2,4-DCP has a much higher vapor pressure and Henry's Law constant than the herbicides (Table A2.1), consistent with both spray volatilization and direct volatilization from applied surfaces being atmospheric source mechanisms of this compound.

3.4. Implications

Gas-phase pesticides have three potential environmental impacts: (1) direct inhalation and exposure to people and off-target ecosystems in the local area, (2) oxidation or other chemistry to form secondary air pollutants, and (3) atmospheric transport to off-target and remote areas. There is no evidence that short-term exposure to herbicides at the mixing ratios observed is dangerous. Concentrations of the two herbicides are well below reported LD_{50} levels for acute exposure via inhalation are far beyond concentrations measured here (1.79 and 6.3 mg/L ,~100 and 700 ppm$_v$ for 2,4-D and MCPA in rats, respectively), although sub-lethal health effects are possible and correlations between phenoxy acid herbicide exposure and Non-Hodgkin's lymphoma have been observed in agricultural workers.[38-39] Our observations imply that applicators should continue to wear personal protective equipment when working in an affected area for several hours after application. Of course, phenoxy herbicides are not the only pesticides subject to spray droplet volatilization and direct volatilization: other compounds with comparable Henry's Law constants

and vapor pressures may also have substantial atmospheric concentrations during and after application. Several pesticides, including chlorpyrifos, acephate, and diazinon, have lethal and sub-lethal effects on bees; the chemical properties of those molecules (Henry's Law Constants of 4.16 x 10^{-6}, 5.2 x 10^{-13}, 0.112 x 10^{-6} atm m^3 $mole^{-1}$ and vapor pressures of 2.2, 0.17, and 9.01 x 10^{-5} mmHg, respectively) suggest that atmospheric sources could contribute to pollinator exposure.[40-42] Anthropogenic organic compounds, including the phenoxy herbicides described here, can be oxidized by OH radicals and other oxidants in the atmosphere. Oxidation products can have lower vapor pressures than parent compounds and thus contribute to secondary organic aerosol.
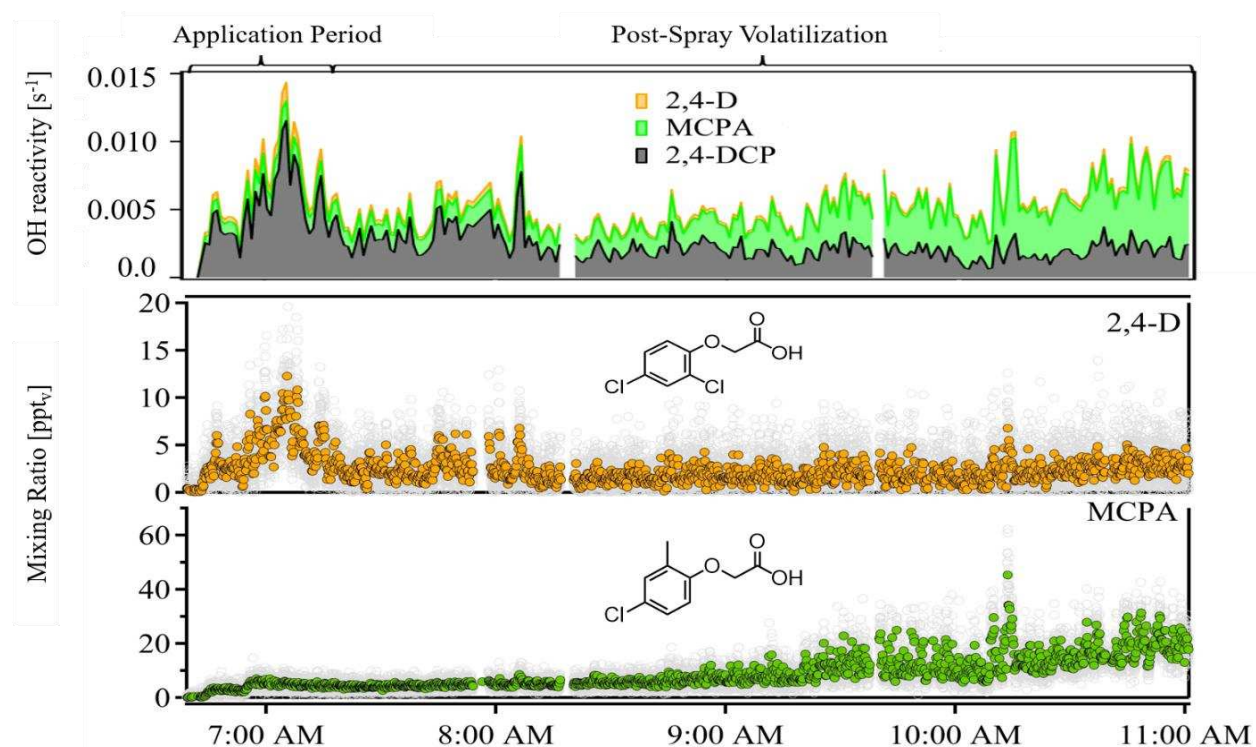

Figure 3.6. Calculated OH radical reactivity (top panel) from 2,4-D (black), MCPA (green), and 2,4-DCP (red) during application and volatilization periods. Compounds with higher Henry's Law constants dominate reactivity during the application spray period, while compounds with higher vapor pressures are important during short term volatilization. Time series of 2,4-D (middle panel) and MCPA (lower panel) during the entire measurement period. Ambient temperature rose from 15ºC to 35ºC at the conclusion of the measurement period.

Atmospheric oxidation of organic compounds by OH in the presence of NO and NO_2 also contributes to ozone.[43] OH reactivity is a useful metric for the chain initiation step of ozone production. To investigate this effect, we calculate the OH reactivity from the two herbicides and 2,4-DCP (Figure 3.2) using estimated reaction rate constants (k_{OH}) multiplied by the concentrations reported herein.[44-46] The reactivity from these compounds was small (0.01 s^{-1} maximum) relative to the OH reactivity in the Front Range (typically 1-3 s^{-1}),[47] but we note that the CSU spray solution was formulated and diluted to minimize volatilization, while larger agriculture operations typically spray more concentrated solutions less judiciously. Further conclusions are not made as to whether herbicides react with OH due to insufficient evidence in this study, but reaction with OH could be a major loss process. While the atmospheric sources had a minor effect on ozone production in the local area for the CSU study, volatilization from larger-scale applications could impact local air quality and thus warrants future measurements with CIMS.

Spray volatilization and post-application direct volatilization are thus relevant mechanisms for phenoxy herbicides to enter the atmosphere. Herbicides can enter the atmosphere through partitioning from spray droplets during the application process (spray volatilization), volatilization from the applied herbicide mixtures from soil and plant surfaces (short-term volatilization), and volatilization from the applied herbicides following ground-penetration (long-term volatilization). Both MCPA and 2,4-D can be transported to off-target areas. The transport distance depends on wet and dry deposition rates, oxidation chemistry and gas-particle partitioning. In the absence of precipitation events, a dry deposition velocity of 1.0 cm/s corresponds to a lifetime of ~29 hours (assuming a typical boundary layer height of 1000 m), while using k_{OH} estimates for the three compounds corresponds to a lifetime of 16 h (MCPA), 28 h (2,4-D), and 7 days (2,4-DCP),

assuming average OH of 1.5 x 10^6 molecules cm^{-3}. Partitioning to the aerosol phase only removes herbicides from the gas-phase – and potentially extends their atmospheric lifetime, as sub-micron particles are typically thought to have atmospheric lifetimes on the order of 7 days. Thus, while the gas-phase herbicide concentrations observed are not acutely toxic, volatilization sources warrant further consideration.

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CHAPTER 4- ATMOSPHERIC OH OXIDATION OF THREE CHLORINATED AROMATIC HERBICIDES[†]

4.1. Introduction

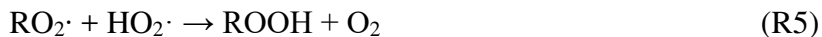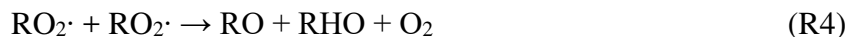Over 2.5 billion pounds of herbicides are used in residential, commercial and agricultural applications in the United States, accounting for a $20 billion industry; despite extensive use, the environmental chemistry and fate of these compounds is poorly understood.[1] Environmental herbicide research has focused on soil and water degradation reactions, and few studies have investigated their atmospheric chemistry.[2-5] Herbicides enter the atmosphere during spray application, following wind erosion from soil, and/or through volatilization from surfaces. Airborne pesticides can be transported regionally and globally, though the distance potentially traveled depends on their atmospheric lifetime.[6-10] Atmospheric lifetimes for any given molecule are a function of chemical and physical loss rates. Chemical losses include photolysis, reactivity with atmospheric oxidants (OH, O_3, NO_3), partitioning to particles, and aqueous oxidation in aerosol particles. Physical losses include wet and dry deposition. The dominant atmospheric oxidant for pesticides is the OH radical, while direct photolysis can also be an important degradation process for some species, including trifluralin and ethalfluralin.[11-15] OH oxidation of organic compounds can potentially produce more persistent or more toxic by-products,[16-17] form lower volatility compounds that produce secondary organic aerosol,[13, 18] and contribute to ozone (O_3) production.[19] Thus an improved understanding of oxidation rates and products is essential to predicting the environmental transport and fate of herbicides – and the health and ecosystem effects of their wide-spread use.

[†] The manuscript writing for this chapter has been submitted to ES&T for publication by Trey Murschell.

2,4-Dichlorophenoxyacetic acid (2,4-D) and its analogs (the chlorinated phenoxy acids, including mecoprop-p and 2-methyl-4-chlorophenoxyacetic acid [MCPA]) are a particularly widely-used class of herbicides, with millions of pounds applied annually.[20] Aqueous degradation mechanisms of 2,4-D and mecoprop-p are well-studied,[21-24] as are the aqueous degradation reactions of MCPA in the presence of TiO_2 and ozone, H_2O_2, and UV light.[25-26] However, the atmospheric OH degradation chemistry of these chlorinated phenoxy acids is under-researched. Due to the relatively low volatility (0.12-1.2 x 10^{-5} mmHg) and high Henry's Law constants (0.48-1.6 x 10^{-10} atm m^3 $mole^{-1}$), the atmosphere is not expected to be the dominant fate of applied chlorinated phenoxy acids, and concentrations are likely low.[27-28] However, spray drift from these herbicides has been reported,[29-30] and even a small amount of toxics in the atmosphere can have health and ecosystem consequences. Triclopyr is a chlorinated pyridinyl acid herbicide, and is often formulated with 2,4-D and its analogs in commercial mixtures. To the best of our knowledge, there are no published studies of the atmospheric chemistry of these chlorinated aromatic herbicides. This knowledge gap is likely due to the combined challenge of running OH oxidation experiments, which typically require sophisticated smog chamber setups, and detecting not only the parent pesticide, but also the vast array of daughter oxidation products. However, the recent combined rise of oxidation flow reactors and chemical ionization time-of-flight mass spectrometry enables low-NO_x photooxidation experiments to be conducted more easily than previous experimental designs. [31-33]

Gas-phase photooxidation studies of other organic molecules provide insight on the potential reactions of phenoxy herbicides in the atmosphere. OH radicals typically either abstract H atoms to form H_2O and an organic radical (R1a), or add to an aromatic or double bond to form an alcohol-containing organic radical (R1b). In both cases, O_2 adds rapidly at the radical site to

form peroxy (RO_2) radicals (R2). In the presence of NO_x (=$NO+NO_2$), RO_2 radicals react with NO to either form alkoxy (RO) and NO_2 radicals, or an organic nitrate ($RONO_2$) (R3a, b). The alkoxy radicals can rearrange to form an array of oxidized organic products. In the absence of NO_x, RO_2 radicals can either react with other RO_2 or HO_2 radicals to form carbonyls or peroxides (R4, R5). In addition, some RO_2 radicals are thought to undergo autoxidation, or decompose to form carbonyl and alcohol containing organic products.[34]

$$RH + \cdot OH \rightarrow R\cdot + H_2O \qquad \text{(R1a)}$$

$$Alkene + \cdot OH \rightarrow HOCR\cdot \qquad \text{(R1b)}$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \qquad \text{(R2)}$$

$$RO_2\cdot + NO\cdot \rightarrow RO\cdot + NO_2\cdot \qquad \text{(R3a)}$$

$$RO_2\cdot + NO\cdot \rightarrow RONO_2 \qquad \text{(R3b)}$$

$$RO_2\cdot + RO_2\cdot \rightarrow RO + RHO + O_2 \qquad \text{(R4)}$$

$$RO_2\cdot + HO_2\cdot \rightarrow ROOH + O_2 \qquad \text{(R5)}$$

Of course, the consequent oxidized organic molecules are subject to further atmospheric processing and OH oxidation, leading to an array of multigenerational, and often multifunctional, oxidation products. The toxicity of these products can be different from parent compounds. For example, oxidation of the pesticides malathion and chlorpyrifos forms the more toxic products malaoxon and chloropyrifos oxon, respectively.[35-36] When these products have adequately low vapor pressures, they can partition to the particle phase. The resulting secondary organic aerosol can affect human health[37] and alter the radiative balance of the planet.[38] Aerosols have different atmospheric lifetimes from gases, and can thus be transported over different distances from gas-phase pesticides or pesticide oxidation products. The oxidation chemistry can also form tropospheric O_3, which detrimentally impacts human health, ecosystems and crop yields.

Here we present oxidation flow reactor experiments coupled to high resolution chemical ionization mass spectrometry to investigate gas-phase OH oxidation mechanisms under low-NO_x conditions of three current-use pesticides: two chlorinated phenoxy acid herbicides (MCPA and mecoprop-p) and one chlorinated pyridinyl acid (triclopyr). These herbicides are often sold together as multicomponent solutions. We also present the yields of smaller, yet atmospherically-relevant species, such as formic acid. We discuss the implications of these mechanisms and products on the atmospheric chemistry of herbicides.

4.2. Experimental Section

We introduce gas-phase pesticides into an oxidation flow reactor (OFR) using pesticide solutions that are injected into a heated airstream. Parent pesticides and a subset of organic products are detected by chemical ionization time-of-flight mass spectrometry. Using both iodide and acetate reagent ions enables rapid, non-targeted analysis of a broad suite of organic and inorganic products. The experimental setup and detection are described in detail below.

4.2.1. Solution Injections

To quantitatively introduce pesticides into a flow reactor, we use a home-built solution injection system.[39] We use a dynamic syringe pump (KD Scientific) to continuously inject pesticide standard solutions onto a filter in a closed (i.e. gas-tight) gas manifold. Heated (200ºC) ultra-high purity (UHP) zero air (99.999%, AirGas) continuously flows through the filter, volatilizing the pesticide solution into the airstream. Pesticide solutions of 9-10 mg/mL are injected at a rate of 7-17 µL/h onto the filter and volatilize into 2 sLpm of heated zero air, resulting in gas-phase pesticide concentrations of ~ 55-180 ppb. This airstream is further diluted with UHP zero air to generate concentrations of ~18-60 ppb that are directly and continuously introduced into the flow reactor. These concentrations may be higher than much of the atmosphere, but are the typical

precursor mixing ratios used in OFR experiments[31, 40] The 50 µL glass, gas-tight syringe (Hamilton, Reno, NV) enables an ~5 h experiment. Pesticide standards (neat, US EPA Pesticide Repository) were dissolved in methanol (Sigma Aldrich, HPLC grade).

4.2.2. Oxidative Flow Reactor

The Oxidative Flow Reactor (OFR) is a 13.1 L aluminum, continuous flow cylinder with UV lamps that have quartz filters, which allow 254 nm light into the reactor.[31, 40] UHP zero air containing O_3 (600 ppb) and H_2O (10% RH) continuously flows through the system. The 254 nm light photolyzes O_3 to form $O(^1D)$, which reacts with H_2O to form OH radicals. Adjusting the intensities of the UV lamps and the airflow rate through the system (and thus residence time) controls OH exposure. The OH exposure for a given light setting/O_3/RH/flow rate was determined by measuring loss rates of $SO_{2(g)}$ at increasing UV lamp intensity in a separate experiment. [31] The total airflow is held constant at 6.6 sLpm across all experiments described herein, corresponding to an OFR residence time of 2 minutes. For each pesticide, we conduct three separate experiments in the OFR: (1) pesticide injection (injected pesticide + solvent + OH); (2) solvent-only injection (injected solvent + OH, no pesticide); and (3) OFR background (OH and zero air only, no pesticide/solvent injection). Each experiment began with the UV lamps off, before ramping UV lamps up in ~15 minute increments. Lamps are not turned on or increased until we observe a stable signal of formic acid, the solvent, and (if applicable) the herbicide. OH exposure ranges from 7.52 - 247 x 10^6 molecules-h cm^{-3}, equivalent to 0.3 - 8 days of OH aging at an average ambient OH concentration of 1.5 x 10^6 molecules cm^{-3}. After each experiment, the OFR, CIMS, and filter holder line are flushed with zero air for 24 hours before the next experiment. The OFR is cleaned with acetone, methanol, and water between each experiment.

4.2.3. Chemical Ionization Mass Spectrometer

Exhaust from the OFR is directed through 10 cm of PFA tubing (1/4" o.d.) into a chemical ionization time-of-flight mass spectrometer (CIMS; Tofwerk AG and Aerodyne Research, Inc.) for gas-phase measurements of pesticide and oxidation products. The CIMS is described in detail elsewhere.[33, 41-42] Briefly, 1.9 sLpm of air is sampled through a critical orifice into the Ion Molecule Reaction chamber (IMR; held at 100 mbar, 40ºC). In the IMR, the sample flow is mixed with reagent ions, which ionize analyte molecules through reagent-specific reactions. Air is pulled through a second critical orifice and through a series of segmented quadrupoles before orthogonal extraction into a time-of-flight mass spectrometer (TOF). The TOF was tuned in a negative ion mode for a mass to charge (m/z) range of 4-779, with 1 s time resolution, mass resolution ($m/\Delta m$) >5000, and mass accuracy < 20 ppm.

We alternate between two reagent ions: iodide and acetate. Iodide reagent ions form adducts with analyte molecules, $[I \cdot M]^-$, by either direct formation, or through a ligand switch reaction with iodide-water adducts, $[I \cdot H_2O]^-$. Iodide CIMS is sensitive to organic acids, peroxides, epoxides, and inorganic halogenated species.[41] We recently demonstrated the use of this reagent ion for pesticide detection, including measurements of trifluralin, acetochlor, permethrin and atrazine.[39] While acetate reagent ions have been traditionally thought to ionize through a proton transfer reaction with molecules that have more negative gas-phase basicity, recent evidence suggests that in the Aerodyne/Tofwerk CIMS, acetate ions more likely form adducts with analytes.[43] These adducts can be separated in the segmented quadrupoles, and, given the appropriate instrument tuning, can be detected as deprotonated ions. Acetate ionization is particularly sensitive for organic acids, and is thus an obvious reagent ion choice for studying

chlorinated phenoxy and pyridinyl acids. Mecoprop-p oxidation experiments were only conducted with Iodide CIMS.

To form acetate ions, UHP N_2 is flowed at 10 sccm into the headspace of a quartz glass reservoir containing 50 ml of acetic anhydride (Sigma Aldrich, >99%). The resulting air is further diluted by UHP N_2 and sent through a sealed [210]Po radioactive source. The resulting acetate ($H_3C_2O_2^-$) ions enter the IMR for reaction with sample air. Iodide ions are generated similarly by flowing N_2 into a homebuilt 40ºC oven holding a CH_3I permeation tube, and then into a [210]Po source.[40] We operate Iodide CIMS in a 'clustering regime' to favor detection of adducts, but operate Acetate CIMS in a 'declustering regime' to break apart any acetate-analyte clusters.[33] Voltage settings were optimized for instrument sensitivity and resolution with Thuner software (Tofwerk, Switzerland).
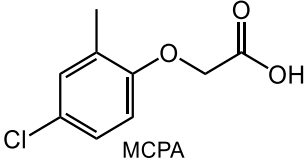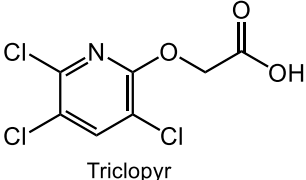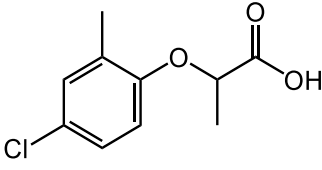
MCPA, triclopyr, and mecoprop-p are all detected by Acetate CIMS as deprotonated carboxylates ([M-H]$^-$) and by Iodide CIMS as iodide adducts ([M·I]$^-$). Instrument sensitivities for the herbicides and organic acids are determined by heated injection calibrations and permeation tunes.[39] A typical pesticide OFR experiment produces CIMS mass spectra with over 900 peaks. While the mass resolution and accuracy of the CIMS enables the user to determine the elemental composition of most peaks, we focus our mechanistic analysis by identifying peaks at unit mass resolution that meet a signal-to-noise threshold. We apply high-resolution peak fitting analyses only at m/z ratios for which the signal changed by at least 3x the standard deviation of the background (background is the signal during the solvent + OH experiment). We assign elemental composition to peaks from the observed exact mass derived from the peak fits and by following rules of covalent bonding, making selections based on OH chemistry of similar functional groups in the Master Chemical Mechanism (Version 3.3.1, Leeds, UK), and constraining isotope

signatures. We then identify pesticide oxidation products with S/N ratios >3 at each OH exposure (where noise is defined as the standard deviation of 'lights off' pesticide experiments and signal is the average signal at each 'lights on' step). We remove peaks that are indistinguishable from the zero air + OH or solvent + OH experiments at identical OH exposures.

4.3. Results and Discussion

Observed products are summarized in Table 4.1. Below we discuss each of the three herbicides, using the observed products to propose OH oxidation mechanisms. We note that large signal intensity does not necessarily indicate greater production than a compound of smaller signal intensity: the sensitivity of CIMS can vary greatly by chemical structure. Thus, without calibration standards for the oxidation products, we cannot determine branching ratios for observed species.

Table 4.1. Oxidation products of MCPA, triclopyr and mecoprop-p. All products detected by Iodide CIMS are iodide adducts, except where noted. Products detected by Acetate CIMS are considered deprotonated due to the declustering voltage settings of the CIMS.

Pesticide	Oxidation products (Iodide CIMS)	Detected m/z [I·M]⁻	Oxidation products (Acetate CIMS)	Detected m/z, [M-H]⁻
MCPA **$C_9H_9ClO_3$** **2-methyl-4-chlorophenoxyacetic acid**	$C_9H_9ClO_4$ $C_9H_9ClO_6$ C_7H_7ClO $C_7H_7ClO_2$ $C_7H_7ClO_4$ $C_7H_7ClO_5$ $C_7H_5ClO_5$ $C_3H_4O_3$ CH_2O_2	342.92 374.91 266.91 284.92 316.91 332.90 330.88 214.92 172.91	$C_7H_5ClO_2$ $C_7H_5ClO_3$ $C_4H_3ClO_3$ $C_6H_5ClO_4$ $C_5H_6O_2^*$ $C_7H_6O_4^*$ $C_3H_4O_3^*$ $C_2H_4O_3^*$ CH_2O_2	154.98 170.98 134.99 174.98 97.03 153.02 87.00 75.00 44.99
Triclopyr **$C_7H_4Cl_3NO_3$** **3,5,6-Trichloro-2-pyridinyloxyacetic acid**	$C_7H_4Cl_3NO_4$ $C_7H_4Cl_3NO_5$ $C_5H_2Cl_3NO_2$ $C_3H_6O_2^\dagger$ $C_3H_4O_3$ CH_2O_2	397.83 413.82 339.82 200.94 214.92 172.91	$C_5H_2Cl_3NO$ $C_7H_3Cl_2NO_3$ $C_5H_3Cl_2NO$ $C_4H_2ClNO_2^*$ $C_3H_4O_3$	195.91 217.94 161.95 129.97 87.00
Mecoprop-p **$C_{10}H_{11}ClO_3$** **Methylchloro-phenoxypropionic acid**	$C_{10}H_{11}ClO_4$ $C_{10}H_{11}ClO_6$ $C_5H_5ClO_2^*$ $C_3H_6O_4^{**}$ $C_3H_4O_3$ $C_2H_4O_2$ $C_2H_4O_3$ $CH_2O_2^\dagger$	356.94 398.92 258.90 105.02 214.92 186.93 202.93 172.91	N/A	N/A

*Multiple isomeric structures possible
** Detected as deprotonated in Iodide CIMS
† Only observed at highest OH exposure

4.3.1. MCPA

Figure 4.1 shows a typical time series and high-resolution mass spectra from the MCPA oxidation experiment for Iodide CIMS. In this experiment, zero air is initially exposed to maximum OH (2.47×10^8 molecules-h cm^{-3}) before the MCPA (green trace) is injected. OH in the OFR is stepped from high to low exposure (8 days to 7 hours) before the lights are turned off (i.e. zero OH). MCPA is highest at the final step (i.e. lowest OH concentration), while oxidation products (black traces) decrease with OH exposure. From these products, we hypothesize a photooxidation reaction mechanism for MCPA (Scheme 4.1). However, as CIMS is unable to distinguish structural isomers, we show only one possible structure in the reaction schemes; other possible structures are presented in Appendix 2.

One initial step of MCPA photooxidation is OH addition to the aromatic ring. Two products are formed that necessitate that initial OH attack. $C_9H_9ClO_4$ is detected as an iodide adduct (m/z 342.92); parallel to established OH chemistry with toluene, we propose an OH attack to any of the three available carbons of the aromatic ring, followed by reaction with O_2 and subsequent loss of HO_2. We also observe $C_9H_9ClO_6$ (m/z 374.91, Iodide CIMS), which corresponds to a second generation (i.e. two OH reaction steps) product via the addition of a peroxide group to the first generation $C_9H_9ClO_4$. This peroxide group is the result of OH radical hydrogen abstraction from either the methyl group or carbon of the ether bond.

Simultaneous to OH addition, OH can attack the aromatic carbon of the hydroxyacetic acid group, with the eventual elimination of hydroxyacetic acid (m/z 75.00 in acetate, m/z 202.92 in iodide). From the intermediate C_7H_7ClO species, there are two possible OH reactions: addition of OH to the aromatic ether bond, or abstraction of a hydrogen from the methyl group. The first possible reaction (OH addition) forms a dihydroxy compound, $C_7H_7ClO_2$ (m/z 284.92, detected by

Iodide CIMS), which shows increasing signal with OH exposure. The second possible reaction (H abstraction) leads to a peroxide, $C_7H_7ClO_3$, and subsequent OH reaction with the peroxide produces a carbonyl.[44-45]

The largest oxidation product peak in the acetate mass spectra from MCPA+OH is $C_7H_5ClO_2$ (*m/z* 154.98). This peak is consistent with chlorosalicylaldehyde, or a structural isomer thereof. We hypothesize that this chlorosalicylaldehyde ($C_7H_5ClO_2$) is produced following (i) H abstraction from MCPA to form the chloroalkyl phenol (C_7H_7ClO, observed), followed by (ii) OH addition and subsequent formation of a peroxide to form $C_7H_5ClO_3$ (not observed), and (iii) OH addition and loss of water and OH to form chlorosalicylaldehyde. Specifically, we propose the isomer is 5-chlorosalicylaldehyde, based on the starting MCPA structure. ($C_7H_5ClO_2$, observed). This chlorosalicylaldehyde has at least two fates: reaction with OH to form a chlorosalicylic acid (*m/z* 170.98, detected by Acetate CIMS), or photolysis. Similar to benzaldehyde, photolysis of chlorosalicylaldehyde ($\lambda < 350$ nm) could form a benzyl peroxy radical.[45] This peroxy radical can form a dihydroxyperoxide, $C_6H_5ClO_4$, following reaction with HO_2. Alternately, the $C_6H_5ClO_4$ dihydroxyperoxide could also be formed from the $C_7H_7ClO_4$ compound detected by Iodide CIMS. The production of chlorosalicylaldehyde and chlorosalicylic acid (Figure A3.1) from MCPA oxidation is intriguing: 5-chlorosalicylaldehyde is a known skin and respiratory irritant in gas and liquid phase.[46] It is also toxic to aquatic life, specifically a reported LC_{50} (lethal concentration required to kill 50% of the population) for minnows, 0.71 - 0.83 mg/L.[47] 5-chlorosalicylic acid is harmful to humans if ingested, ulcerogenic to mice with a reported 261 mg kg^{-1} LD_{50} (lethal dose at which 50% population is killed) in fasted rats.[48-50]

We observe $C_7H_7ClO_4$ (*m/z* 316.91, detected by Iodide CIMS), which is likely a dihydroxyperoxide. This product has two plausible pathways to formation, both of which suggest

this is a third-generation oxidation product: (1) OH addition to the aromatic ring of $C_9H_9ClO_6$ and subsequent cleavage of the C-O bond, eliminating hydroxyacetic acid, or (2) Hydrogen abstraction from the methyl group of $C_7H_7ClO_2$, followed by the reaction with HO_2 to form the peroxide. From the dihydroxyperoxide, another OH addition to the aromatic ring will form $C_7H_7ClO_5$ (*m/z* 332.9, Iodide CIMS), which appears later in the experiment and at low signal intensity, consistent with a fourth-generation production.

Finally, there is some evidence that OH oxidation of MCPA can also follow an aromatic ring opening pathway. We observe $C_4H_3ClO_3$ (*m/z* 134.99, Acetate CIMS; not shown), but only at the highest OH exposures. Products from ring opening of toluene have been reported, including -oxobut-2-enoic acid,[51-52] and we hypothesize that the observed $C_4H_3ClO_3$ is 3-chloro-4-oxobut-2-enoic acid and the result of a parallel ring-opening reaction of MCPA.

4.3.1.1. Chlorosalicylic compounds.

To further investigate the chlorosalicylic compounds, we quantify the signal response for Acetate CIMS to 5-chlorosalicylaldehyde and 5-chlorosalicylic acid by solution injections following our previous work.[39] We confirm that 5-chlorosalicylaldehyde and 5-chlorosalicylic acid are observed as a deprotonated molecular ions by Acetate CIMS at *m/z* 154.98 and 170.98, respectively. We note that while the aldehyde compound does not contain a carboxylic acid group, it is detected as a deprotonated ion by Acetate CIMS. This parallels the detection of nitrophenols,[53] in which electron-withdrawing groups (in this case, chlorine) coupled to the aromaticity and resonance with the aldehyde, allows gas-phase deprotonation of the alcohol functional group in 5-chlorosalicylaldehyde, as well as the presumed chloro-diphenol peroxide $C_6H_5ClO_4$. Assuming no other isomer contributes to the observed signal, we quantify the yields of these species from MCPA (Figure A3.1) We follow previous works that used the OFR to calculate reaction rate coefficients

to calculate a coefficient for 5-chlorosalicylaldehyde +OH. By plotting the emission factor of 5-chlorosalicylic acid over MCPA (mg kg^{-1}) as a function of OH exposure time (Figure A3.2), we fit the data to an exponential to derive rate constant for 5-chlorosalicylaldehyde +OH. We assume pseudo-first order kinetics and derive a rate constant of 3.7 (± 0.7) x 10^{-12} cm^3 molecules^{-1} s^{-1} for 5-chlorosalicylaldehyde + OH for the laboratory setup (temperature in OFR = 300-310K). We note that there are two OH reactions that occur between the two salicylic compounds; the k_{OH} thus represents the slower, rate limiting step (not determined here). This k_{OH} value is much slower than for analogous reactions that occur from benzaldehyde to benzoic acid (k_{OH}=1.1 x 10^{-11}),[54] although the additional chlorine and hydroxyl groups on the chlorosalicylic compounds are likely to affect the kinetics.
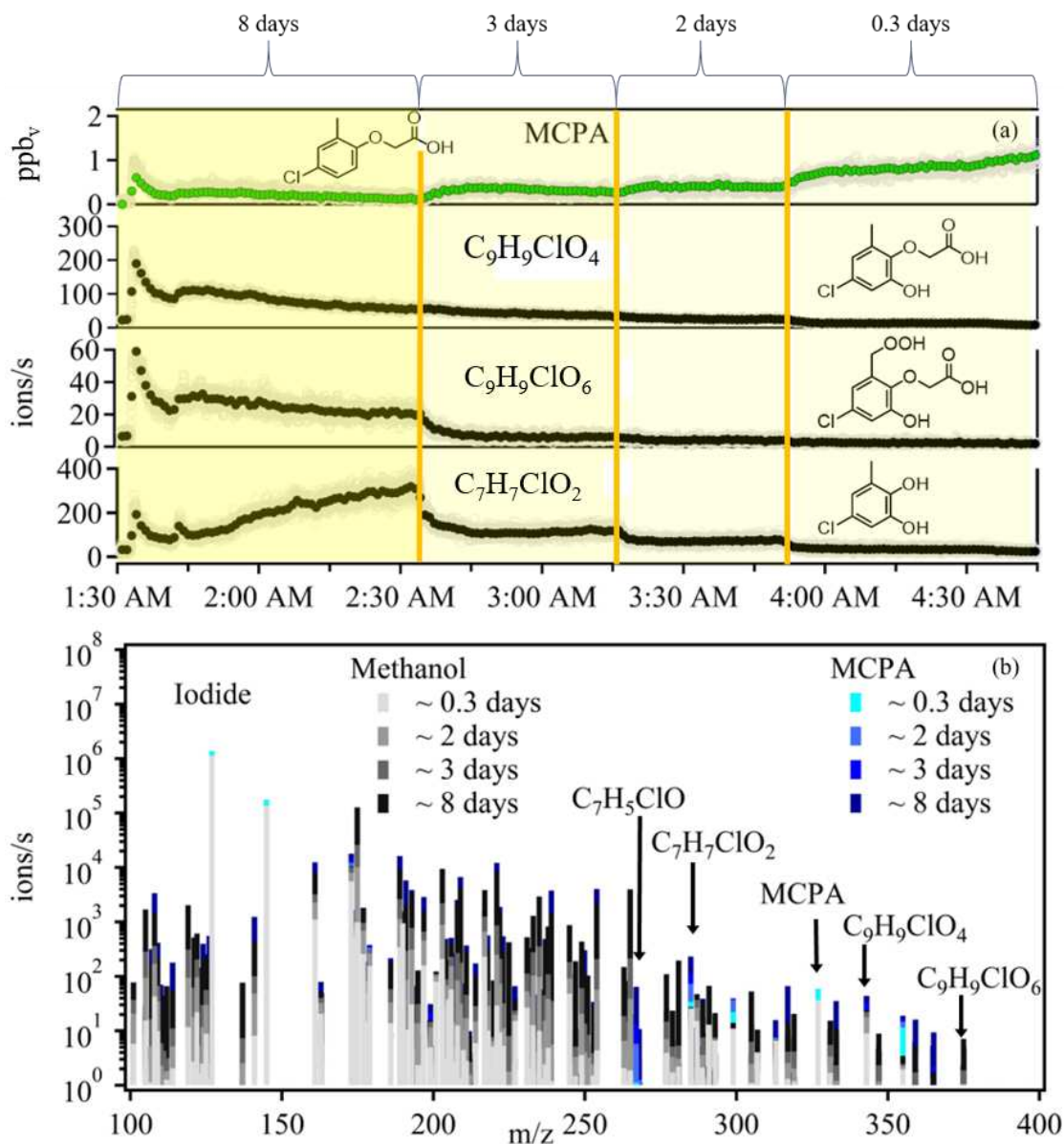
Figure 4.1. The upper panel (a) shows time series (1s data in gray open circles, 1-min averages in solid circles) of MCPA (green) and three oxidation products (black) from a single OFR experiment coupled to Iodide CIMS. All species are detected as clusters with iodide (*m/z* 126.91). OH decreases sequentially from 8 to 0.3 equivalent days of aging ([OH] = 1.5 x 10^6 molecules cm^{-3}). MCPA signal increases as OH decreases, while three major oxidation products, $C_9H_9ClO_4$ (likely the first-generation hydroxyl MCPA product), $C_9H_9ClO_6$ (likely the second-generation hydroxyl-peroxide MCPA product), and $C_7H_7ClO_2$ decreases. The bottom panel (b) shows averaged high-resolution iodide mass spectra (*m/z* range of 100-400) of identified ions that changed during each oxidation step in the OFR. The gray scale mass spectra are taken from the methanol oxidation background, and blue-scale mass spectra are from the MCPA in methanol oxidation. Several proposed products are indicated at the *m/z* of molecules clustered with iodide.
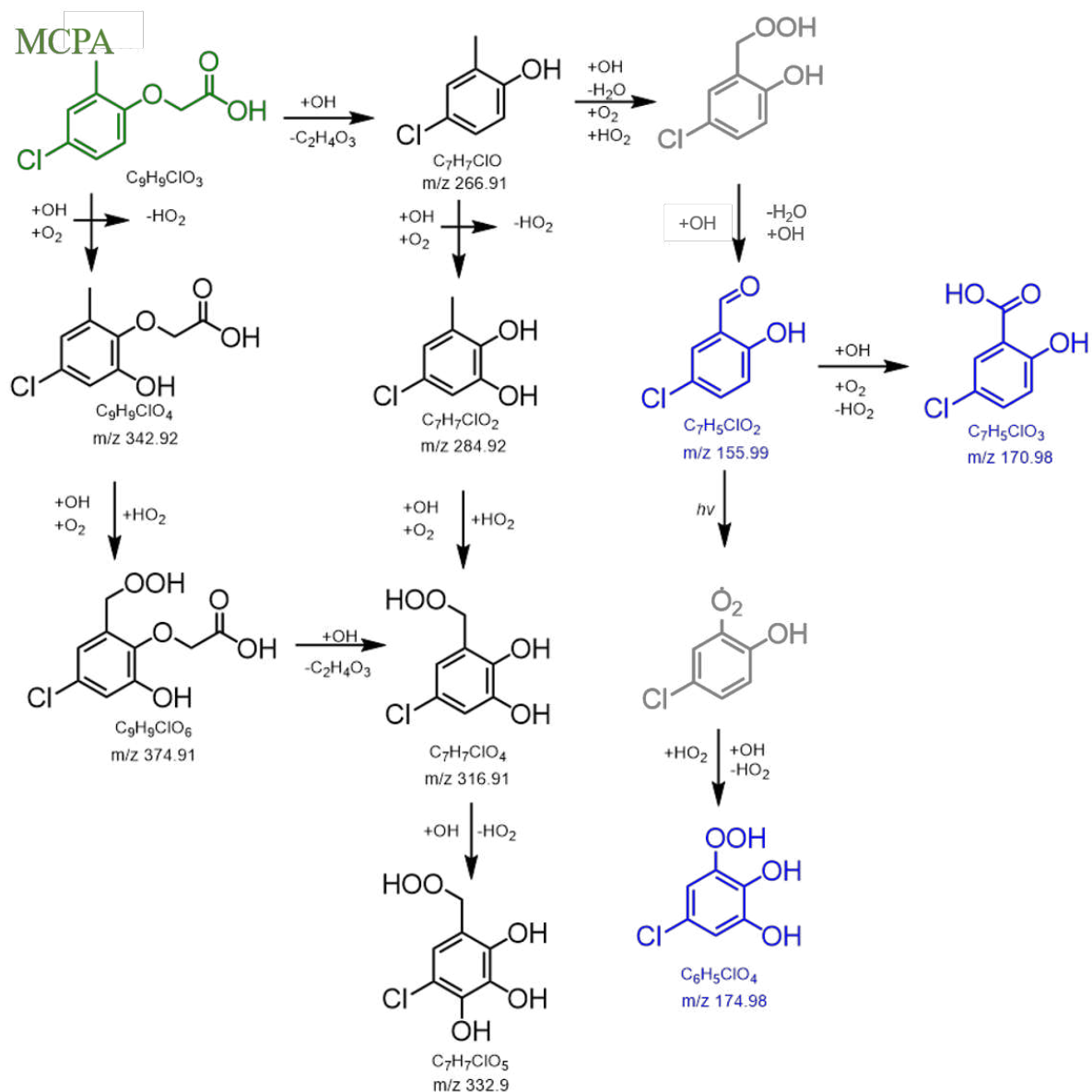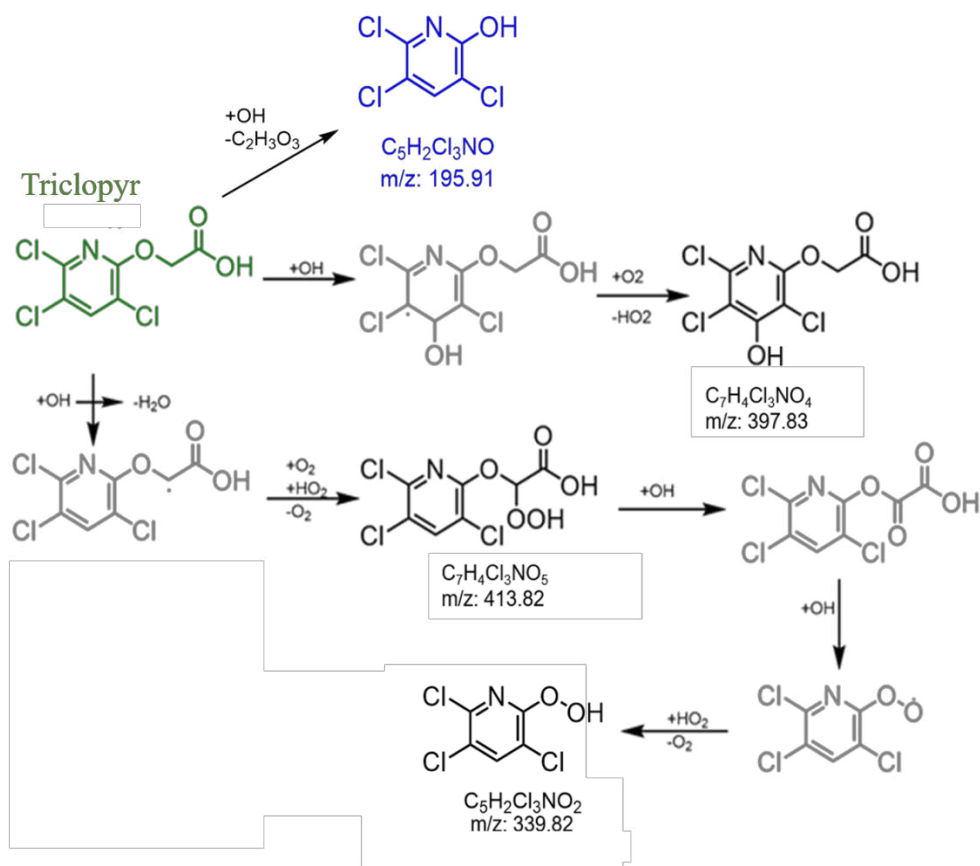
Scheme 4.1. Proposed MCPA (green, measured by both reagent ions) oxidation mechanism from compounds that are measured using Iodide CIMS (in black) and Acetate CIMS (blue); the intermediate compounds in grey are unmeasured. The proposed mechanism is similar to previously reported reactions of toluene, ether, and alkane compounds. The mechanism shows only one set of possible isomers formed that are consistent with the elemental composition of ions detected by mass spectrometry.

4.3.2. Triclopyr

Triclopyr oxidation products provide evidence for OH addition to the aromatic ring, H abstraction on the hydroxyacid chain, and photolysis reaction mechanisms. We observe no evidence for ring-opening products from triclopyr+OH. There is only one carbon available for OH addition to the heterocyclic aromatic ring. OH addition at this carbon produces $C_7H_4Cl_3NO_4$, which is the largest product ion detected by Iodide CIMS, and is observed as an iodide cluster (Scheme 4.2).

In contrast to MCPA, there is evidence of hydrogen abstraction and peroxide formation on the methylene bridge of the hydrooxyacetic acid group. Specifically, we observe $C_7H_4Cl_3NO_5$ clustered to iodide (*m/z* 413.82, Iodide CIMS). The simplest explanation for this product is the H-abstraction reaction shown in Scheme 4.2 that adds a peroxide to the hydroxyacetic acid. Next, the $C_7H_4Cl_3NO_5$ peroxide can react with OH, photolyze or decompose to produce the $C_5H_2Cl_3NO_2$ product observed by both Acetate and Iodide CIMS. Similar peroxide-producing reactions have been proposed for simple ethers and esters like dimethyl ether, methyl t-butyl ether and methyl acetate.[44, 55-56] Deprotonated $C_5H_2Cl_3NO$ is the largest product ion detected by Acetate CIMS during triclopyr oxidation experiments. This formula, and its detection by Acetate CIMS, is consistent with a pyridine substituted with three chlorine atoms and an alcohol group. One plausible formation pathway for this compound is the addition of OH to the carbon of the aromatic to the carbon-oxygen bond, followed by the elimination of hydroxyacetic acid. Alternatively, the peroxide group on $C_5H_2Cl_3NO_2$ could react with OH to form an RO_2 radical, which can react with other RO_2 or HO_2 species to form an alcohol.

Scheme 4.2. Proposed OH oxidation of triclopyr using both Iodide (black) and Acetate (blue) CIMS. Compounds in green are measured by both reagent ions. Compounds in gray are unmeasured, proposed intermediates.

Photolysis is a known photodegradation process of chlorinated aromatics at the wavelengths between 185-254 nm.[57] Two products observed by Acetate CIMS are consistent with photolysis of a C-Cl bond adjacent to the hydroxyacetic acid group: $C_7H_3Cl_2NO_3$ and $C_5H_3Cl_2NO_2$. However, exact mechanisms for formation of these species are speculative at best (Scheme A2.1). The phenoxy radical produced after photolysis at the C-Cl bond could either (i) form a bicyclic pyridinyl acid after H abstraction by OH ($C_7H_3Cl_2NO_3$), or (ii) form a peroxide ($C_5H_3Cl_2NO_2$) via an intra-molecular hydrogen abstraction, O_2 reaction, and a second reaction with OH.

4.3.3. Mecoprop-p

OH oxidation of mecoprop-p produces two clear products in Iodide CIMS, $C_{10}H_{11}ClO_4$, and $C_{10}H_{11}ClO_4$ (Figure A3.3). These products indicate that, similar to MCPA and triclopyr, the initial step of OH oxidation of mecoprop-p is attack at any of the three available carbons on the aromatic ring to produce $C_{10}H_{11}ClO_4$ (Scheme 4.3).

$C_{10}H_{11}ClO_6$ is a second-generation product that appears in the mass spectrum as OH exposure increases. The net addition of two oxygen atoms to the first-generation product suggests that $C_{10}H_{11}ClO_6$ contains peroxide groups. Hydrogen abstraction could take place on the aromatic methyl group, or on the methylene or methyl groups of the hydroxy propanoic acid chain. Reaction with O_2 and subsequent reaction with HO_2 produces nine potential isomers. Fragmentation of the aromatic carbon to oxygen bond may also occur during the OH oxidation of mecoprop-p: we observe $C_3H_6O_4$ deprotonated (m/z 105.02, Iodide CIMS), which is likely an oxidation product of the hydroxy propanoic acid group.
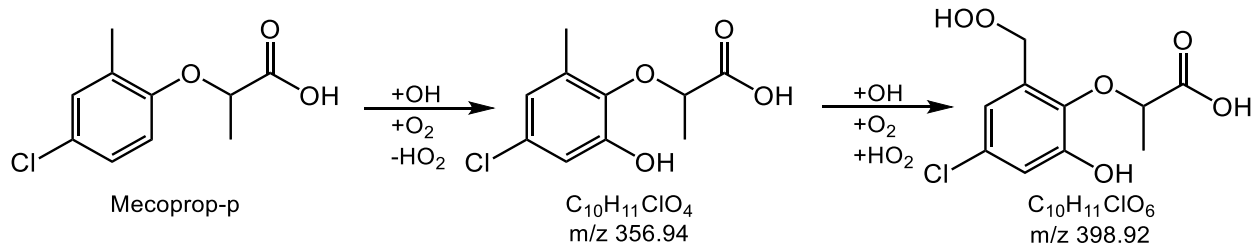
Scheme 4.3. Mecoprop-p OH oxidation as observed using Iodide CIMS. The two products shown represent only one of the potential isomers at each step.

4.3.4. Organic acid yields

Oxidation of anthropogenic and biogenic hydrocarbons are thought to be substantial sources of atmospheric carboxylic acids.[58-59] Consistent with this hypothesis, OH oxidation of the chlorinated phenoxy herbicides produces an array of carboxylic acids, including formic acid, pyruvic acid, acetic acid, and glycolic acid (Table A3.1). Formic acid is a clear oxidation product of all three herbicides. Formic acid yields ($ppb_{formic\ acid}/ppb_{herbicide}$) are 0.6-43% (0.3-8 days) for MCPA and 1.4-3.8% for triclopyr. The enhancement is only observed at the highest OH exposure for mecoprop-p (5.5% yield), indicating indicating multiple oxidation steps are necessary for formic acid production. Despite the presence of oxyacetic acid on both MCPA and triclopyr, acetic acid is not observed as a clear oxidation product for either herbicide, but is produced from mecoprop-p (11% yield for 8 days of aging).

4.4. Atmospheric Implications

The atmospheric lifetime of the chlorinated aromatic herbicides – and thus their potential for transport and production of oxidation products – is determined by their removal processes. Atmospheric removal of reactive trace gases includes wet deposition, dry deposition, and reaction with oxidants. Reaction with the OH radical is thought to dominate the chemical removal of these species, which lack the alkene or alkyne functionality typically required for rapid reaction with

other key atmospheric oxidants (O₃ or NO₃).[11] Experimentally measured rate constants with OH are not available for these three species, but estimates based on structures are reported for MCPA (1.3 x 10^{-11} cm³ molecules^{-1} s^{-1}) and mecoprop-p (1.7 x 10^{-11} cm³ molecules^{-1} s^{-1}).[60] To constrain the chemical lifetimes of MCPA, triclopyr and mecoprop-p, we assume first order kinetics to approximate the rate constant with OH (k_{OH}, cm³ molecules^{-1} s^{-1}):

$$k_{OH+pesticide} = \frac{-ln\frac{[X]_f}{[X]_i}}{[OH]t} \qquad \text{(Eq. 1)}$$

$[X]_f$ is the concentration of the pesticide at a given OH exposure in the OFR, $[X]_i$ is the intial pesticide concentration introduced into the OFR, and $[OH]t$ is the OH exposure in molecules cm^{-3} s^{-1}. We calculate k_{OH} values from concentration differences at each OH exposure for the experimental conditions (atmospheric pressure = 850 mbar in Fort Collins, CO; temperature of OFR = 300-310 K). The k_{OH} for MCPA is 1.5 ($\pm$ 0.7) x 10^{-12} cm³ molecules^{-1} s^{-1} and for mecoprop-p is 2.6 ($\pm$ 0.3) x 10^{-12} cm³ molecules^{-1} s^{-1}. The k_{OH} for triclopyr is not quantified due to challenges in maintaining consistent OH exposures during those experiments, coupled to potential wall loss of the parent compound in the OFR. These rate constants are comparable to reported rate constants (in cm³ molecules^{-1} s^{-1}) for OH with toluene (5.3$\pm$ 0.2 x 10^{-12}), ethyl benzene (7 x 10^{-12}), and benzene (1.2 $\pm$ 0.2 x 10^{-12}).[61-62] This observation is consistent with OH addition to the aromatic ring dominating the OH+herbicide reaction, as opposed to reaction with the oxyorganic acid groups. The chlorine substitution on the herbicides may contribute to the slower reaction rates for the two herbicides over their non-halogenated, substituted analogs. The lifetimes of MCPA and mecoprop-p to a daily average OH radical concentration of 1.5 x 10^6 molecules cm^{-3} are ~5 and 3 days, respectively.[63] These lifetimes are long enough for substantial OH oxidation chemistry to occur (experimental OH conditions in these experiments ranged from 7 to 192 hours of daytime

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average OH). While previous studies have suggested that wet deposition will be rapid due to the high solubility of these phenoxy acids, this loss process requires precipitation. The vapor pressure of these species suggests that partitioning to the particle phase may be an efficient atmospheric sink; however, particles have typical atmospheric lifetimes of ~7 days. Overall, these calculations suggest that the chlorinated phenoxy acid herbicides described herein may remain in the atmosphere long enough for multiple generations of OH oxidation to occur – but that oxidation remains slow enough for these species to be transported away from initial application areas following volatilization and deposit on off-target areas.

The chlorinated aromatic acids undergo multigenerational chemistry to produce an array of peroxide- and alcohol-containing products and carboxylic acids. These molecules may impact atmospheric chemistry by contributing to O_3 production or partitioning to secondary organic aerosol, or may be deposited downwind of the application region. Addition of OH radicals to the aromatic rings occurs consistently across the three herbicides, although the MCPA experiments demonstrate that OH can also add directly to the hydroxyacetic acid group, fragmenting the ether bond and producing potentially environmentally harmful chlorinated toluic compounds. Specifically, the chlorosalicylic compounds observed during MCPA oxidation (5-chlorosalicylaldehyde and 5-chlorosalicylic acid) have established toxicity to both mammals and aquatic life.[47-50] Predicting the impact of these compounds on human and ecosystem health requires chemical transport and ecotoxicology models, which is beyond the scope of this work. However, while volatilization is expected to be a minor fate of applied herbicides, the atmospheric chemistry of chlorinated phenoxy acid and pyridinyl acid herbicides is relevant for understanding the environmental impact of these species on both local and regional scales.

CHAPTER 4 REFERENCES

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CHAPTER 5- ATMOSPHERIC OH OXIDATION CHEMISTRY OF TRIFLURALIN AND ACETOCHLOR[†]

5.1. Introduction

Pesticides are substances that kill or control unwanted organisms, and are ubiquitous in the environment. The detection of organochlorine pesticides in the Arctic first demonstrated that pesticides can be transported through the atmosphere to non-target ecosystems far from application areas.[1-4] Pesticides enter the atmosphere through spray drift during application, volatilization from ecosystem surfaces following application, or wind erosion of soil.[1, 4-5] Once in the atmosphere, pesticides have several fates, including physical transformations between gas and particle phase, chemical transformations to an array of oxidation and photolysis products, or wet and dry deposition to soil, plant or water systems. The potential impact of transported pesticides thus depends on their physical and chemical properties: pesticides with longer lifetimes can transport in their native state further from source regions. Depending on the relative impact of pesticides versus their atmospheric products, atmospheric chemistry can either diminish or enhance the consequences of pesticides to the environment. However, understanding these consequences, and the potential transport and lifetime of pesticides in the atmosphere, requires a detailed understanding of their chemical sinks.

OH radicals are a key oxidant, controlling the fate and lifetime of most organic species in the atmosphere. Typically, the OH radical initiates oxidation through either (i) hydrogen abstraction from a C-H bond (R1a), or (ii) addition to a C-C double bond (R1b).[6-7] Both pathways result in an alkyl radical that is readily captured by O_2 to form a peroxy radical (RO_2; R2). In the

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[†] The manuscript writing for this chapter has been submitted to Elementa for publication by Trey Murschell.

presence of NO_x (i.e. urban and sub-urban regions), the RO_2 can react with NO to form an alkyl nitrate (R3b, a reservoir for NOx) or an alkoxy radical (R3a). In the absence of NO_x (i.e. in rural and remote regions), the RO_2 can react with another peroxy (R4) or hydroperoxy (HO_2; R5) radical.

$$RH + OH\cdot \rightarrow R\cdot + H_2O \tag{R1a}$$

$$Alkene + OH\cdot \rightarrow HOCR\cdot \tag{R1b}$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \tag{R2}$$

$$RO_2\cdot + NO\cdot \rightarrow RO\cdot + NO_2\cdot \tag{R3a}$$

$$RO_2\cdot + NO\cdot \rightarrow RONO_2 \tag{R3b}$$

$$RO_2\cdot + RO_2\cdot \rightarrow RO\cdot + RHO + O_2 \tag{R4}$$

$$RO_2\cdot + HO_2\cdot \rightarrow ROOH + O_2 \tag{R5}$$
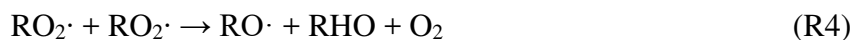
Pesticide oxidation chemistry has potential negative consequences for air quality and human health. Agrochemicals can impact local air pollution through the production of ozone: R3a represents the chain propagation step of tropospheric ozone production, while R3b, R4 and R5 are chain termination steps. The functionalized organic products from OH oxidation can have sufficiently low volatility to partition into the aerosol phase. Finally, pesticide oxidation products may be air pollutants. For example, organophosphate insecticides, including widely used malathion and chlorpyrifos produce more toxic "oxons" upon oxidation.[8]

Trifluralin ($C_{13}H_{16}F_3N_3O_4$) is one of the most widely used herbicides in the United States. Gas or particle phase trifluralin enters the atmosphere through volatilization or wind erosion, and has been shown to transport from agricultural application areas to non-target remote regions including the Arctic.[9-11] The atmospheric lifetime and degradation of trifluralin has thus been the focus of several studies.[9, 12-16] Trifluralin has a lifetime against photolysis of 15 min (real sunlight

conditions) and a lifetime against OH of 8.5 hours[15], although the observation of this pesticide in remote regions suggests that trifluralin can persist in the atmosphere for longer timeframes. Soderquist et al used a glass photoreactor to expose trifluralin to artificial sunlight and identified several particle phase photolysis products, including 2,6-dinitro-N-n-propyl-α,α,α-trifluoro-p-toluidine and 2,6-dinitro-α,α,α-trifluoro-p-toluidine from trifluralin dealkylation and benzimidazoles from cyclization.[12] That study noted numerous additional "polar products" that could not be identified. However, the photoreactor method was both time and labor intensive: photolysis took 12 days, and the reactor then needed to be rinsed to collect analyte, followed by extensive sample preparation for GC-MS analysis. Environmental chamber experiments of trifluralin + OH observed similar products by FT-IR, including several carbonyl-containing species.[15]

Acetochlor ($C_{14}H_{20}ClNO_2$) is an herbicide from the chloroacetanilides family (e.g. alachlor, metolachlor, propachlor). This herbicide is typically sprayed on corn and soybean, and is widely used in the United States (>18 million kg applied in the US in 2015).[17] Like trifluralin, acetochlor has been observed in the atmosphere. For example, in the Mississippi River Valley, acetochlor was detected in gas phase air samples near agricultural areas, and in the particle phase at sites >100 km away ([acetochlor] >12 pg m^{-3}).[9] Atmospheric concentrations reached 158 and 23 pg m^{-3} in gas and particle phases, respectively, in the Czech Republic during the growing season.[18] While other chloroacetanilide herbicides from have been studied in laboratory oxidation chambers (e.g. Munoz et al's studies on propachlor[19]), acetochlor oxidation remains unexplored – work typically focuses on its contamination and fate in water.[20-22]

Here, we investigate the atmospheric OH oxidation mechanisms, organic nitrogen fate and SOA formation of trifluralin and acetochlor using an oxidative flow reactor coupled to a high-

resolution time-of-flight chemical ionization mass spectrometer (CIMS). We detect trifluralin oxidation gas phase products previously identified, reinforcing our method, while measuring the proposed unknown compounds from both works.[12, 15] We identify acetochlor OH oxidation products and begin to construct a previously unknown mechanism scheme.

5.2. Method

5.2.1. Solution Injections and Oxidative Flow Reactor

The Oxidative Flow Reactor (OFR) is a 13.1 L aluminum, continuous flow cylinder with UV lamps that have quartz filter sleeves, which allow 254 nm light into the reactor.[23-24] Ultra-high purity (UHP) zero air (99.999 %, AirGas) containing O_3 (145 ppb_v) and H_2O (10% RH) continuously flows through the system. The 254 nm light photolyzes O_3 to $O(^1D)$, which reacts with H_2O to form two OH radicals. OH exposure is determined by intensity of the UV lamps, flow rates (i.e. residence time in OFR), relative humidity and ozone concentration; we quantify OH exposure for combinations of these parameters by measuring loss rates of $SO_{2(g)}$.[23] In the experiments described herein, total airflow is held at 6.6 sLpm, corresponding to residence time in the OFR of ~2 minutes.

Trifluralin and acetochlor standards (99% EPA Pesticide Repository) were dissolved in high performance liquid chromatography (HPLC) grade methanol (Sigma Millipore) to form 9-10 mg/mL solutions. We use a dynamic syringe pump (KD Scientific) coupled to a 50 µL glass, gas-tight syringe (Hamilton, Reno, NV) to continuously inject the pesticide solutions into a closed, gas-tight manifold. Heated (200 ºC) UHP zero air continuously flows through the manifold, volatilizing the pesticide solution into the airstream. Pesticide solutions are injected at 7 µL/h and volatilize into 2 sLpm of heated zero air. This airstream is further diluted with UHP zero air to generate concentrations of ~20 ppb that are continuously introduced into the OFR. These

concentrations may be higher than those measured in the atmosphere but are typical of precursor mixing ratios used in OFR experiments. [9-10] These mixing ratios are much lower than previous pesticide oxidation experiments.[15, 19, 23-27]

For each pesticide, we conduct three separate experiments in the OFR: (1) pesticide injection (injected pesticide + solvent + OH); (2) solvent-only injection (injected solvent + OH, no pesticide); and (3) OFR background (OH and zero air only, no pesticide/solvent injection). UV lamps are initially off and then power to the lamps are increased in ~20 minute increments; lamp intensities are not altered until we observe a stable signal of formic acid, solvent, and herbicide. OH exposure ranges from 2.7- 88.9 x 10^{10} molecules s cm^{-3}, equivalent to 0.3 - 8 days of OH aging (OH days) at an average ambient OH concentration of 1.5 x 10^6 molecules cm^{-3}. Given the current OFR setup (flow rates and humidity), along with slow rate constant for trifluralin with ozone (<1 x 10^{-17} cm^3 $molecules^{-1}$ s^{-1}), we assume ozonolysis is negligible.[15, 24] After each experiment, the OFR and quartz sleeves are rinsed with acetone, methanol, and water. The entire system (OFR, CIMS detector, and tubing) is closed and continuously flushed with zero air for a week before the next experiment.

5.2.2. Iodide CIMS

We detect herbicides and their oxidation products with a high resolution time-of-flight chemical ionization mass spectrometer (CIMS; Tofwerk AG, Switzerland and Aerodyne Research, Inc., Billerica, MA) coupled to iodide (I^-) reagent ions (hereafter referred to as I-CIMS).[28-29] The I-CIMS has five primary components: the ion molecule reactor (IMR), two RF-only quadrupoles, an ion lens focusing region, and a time-of-flight (ToF) mass analyzer (m/Δm ~4000) with a pair of microchannel plate detectors. Sample air is continuously drawn at 1.9 sLpm into the IMR, where the sample interacts with I^- reagent ions. I^- is generated by flowing ultra-high purity N_2 over a CH_3I

permeation device and into a ^{210}Po source.[30] Iodide is typically thought to ionize neutral species (M) through a ligand exchange reaction with an iodide-water adduct (R1).[30]

$$[I \cdot H_2O]^- + M \rightarrow [I \cdot M]^- + H_2O \quad\quad\quad (R1)$$

Deprotonated species have also been observed in ambient measurements,[29] though it remains unclear whether these species are deprotonated in the initial ionization step, declustered during transmission to the ToF detector, or decomposition of peroxyacids.[31]

Trifluralin is detected as the Iodide-molecule adduct at m/z 462.01. Acetochlor is detected at the m/z of the Iodide-molecule adduct (m/z 396.02) and a $C_{11}H_{14}ClNO$ fragment-Iodide adduct (m/z 337.98). The pesticide injection began with lights in the OFR off until a stable pesticide signal was achieved. There were five OH exposure steps in the oxidation experiments (0.3, 2, 3, 5, 8 OH days). There is evidence of acetochlor and trifluralin loss in the OFR and IMR (as much as 35 and 97%, respectively, Figure A4.1), likely due to uptake to the walls in the experimental system. Increases and instability of the pesticide concentrations are induced by volatilization from increases in UV lamp intensity, which increases temperature in the OFR. Generally, a decreasing stepwise pesticide signal is expected corresponding to a stepwise increase in OH exposure (light intensity) and oxidation products. From a single oxidation experiment, the I-CIMS detects almost one thousand peaks, which may or may not be relevant to the oxidation experiment. Thus, a cutoff is applied to m/z signals (nominal mass) during the pesticide + OH experiments to focus only on peaks that increase by at least 3x the standard deviation of the background (i.e. OH + solvent experiment). Only m/z signals above that threshold are subject to high-resolution analyses and elemental composition identification. Products are conceived following strict bonding rules, previous mechanistic work on OH reactions with hydrocarbons and structurally similar pesticides (e.g. determining likely reaction sites), and using only precursor chemical elements. Proposed

product generational order is determined by comparing ion growth and decay over different oxidation steps.

A second CIMS equipped with acetate reagent ions detects isocyanic acid (HNCO) as the deprotonated NCO⁻ ion (m/z 41.99). We use the previously reported[32] ratio of isocyanic acid sensitivity to formic acid sensitivity for the specific CIMS multiplied by the current instrument formic acid sensitivity to determine the acetate CIMS sensitivity for these experiments (6.39 normalized counts s^{-1} (ncps) ppt^{-1}).

5.2.3. Additional instrumentation

Particle size distributions are measured by an SMPS (Scanning Mobility Particle Sizer, TSI, USA; 3081 DMA coupled to a 3070 CPC; 1 sLpm sample flow with a 10 sLpm sheath flow for 7-254 nm diameter range). NO_x ($NO+NO_2$) is measured by a commercial chemiluminescence detector with a MoO catalytic converter (ThermoScientific, Model 42-iTL), although we note the NO_2 measurements are subject to interferences from peroxyacyl nitrates and organic nitrates.[33]

5.3. Results and Discussion

5.3.1. Trifluralin + OH mechanism

We use identified ions that changed over the methanol background in high resolution mass spectra during OFR experiments to investigate potential oxidation mechanisms for trifluralin + OH, following product identification and proposed mechanisms from previous works (Scheme 5.1).[8, 12, 15] Trifluralin can undergo three initial chemical transformations: (i) *H abstraction* by OH from the two alkyl chains, (ii) *OH addition* to the aromatic ring, and (iii) *dealkylation*, potentially due to photolysis. We note that I-CIMS cannot identify structural isomers; while only one possible structure for each ion is presented in Scheme 5.1.

Trifluralin is photolabile (measured absorption cross section at 300 nm is ~10^{-17} cm^2 molecule^{-1})[34] and the C-N bonds can be broken at 254 nm. We observe previously reported photolysis products (Scheme 5.1, Dealkylation Path). We measure 2,6-dinitro-N-n-propyl-α,α,α-trifluoro-*p*-toluidine (**T.2**), the known first generation photolysis product. From the first generation C$_{10}$ product, **T.2** can undergo further photolysis/dealkylation to form 2,6-dinitro-N-α,α,α-trifluoro-*p*-toluidine (**T.3**; $C_7H_4F_3N_3O_4$; previously reported by Soderquist et al.), or react with OH, O$_2$, and HO$_2$ to form a peroxide, **T.4** ($C_{10}H_{10}F_3N_3O_6$).

Following the H abstraction pathway (Scheme 5.1), OH can abstract H from one of the six carbons on either alkyl chain. The resulting alkyl radical will rapidly react with O$_2$ and HO$_2$ to form a peroxide, **T.5** ($C_{13}H_{16}F_3N_3O_6$; *m/z* 494.00). **T.5** can react with OH (i) on the peroxy group to form a carbonyl group (**T.6**) ($C_{13}H_{14}F_3N_3O_5$; *m/z* 475.99), or (ii) on the aromatic ring via OH addition to form **T.8** ($C_{13}H_{16}F_3N_3O_7$; *m/z* 509.99). **T.5** may also photolyze to produce **T.4** in the dealkylation path. **T.8** ($C_{13}H_{16}F_3N_3O_7$) could also be formed in the "OH addition Path." This third path is initiated by an OH addition to the aromatic ring of trifluralin, forming **T.7** ($C_{13}H_{16}F_3N_3O_5$; *m/z* 478.00), which can be followed by H abstraction to form **T.8** ($C_{13}H_{16}F_3N_3O_7$; *m/z* 509.99).

The most prominent product detected in the I-CIMS during the trifluralin oxidation experiment was **T.9** ($C_{11}H_{10}F_3N_3O_5$, *m/z* 447.96), likely an amide produced by OH oxidation coupled to fragmentation and/or photolysis. **T.5** is a likely precursor for this C$_{11}$ carbonyl product **T.9**, although we did not detect likely intermediates. In an analogous reaction, OH oxidation of 2-aminoethanol (monoethanolamine, C_2H_7NO) undergoes H abstraction at the carbon adjacent to the amine before reacting with O$_2$ to produce an amide.[35] We note that the prominent signal intensity from the trifluralin C$_{11}$ amide does not necessarily mean that this species is the highest in concentration, as the I-CIMS sensitivity varies by ion.
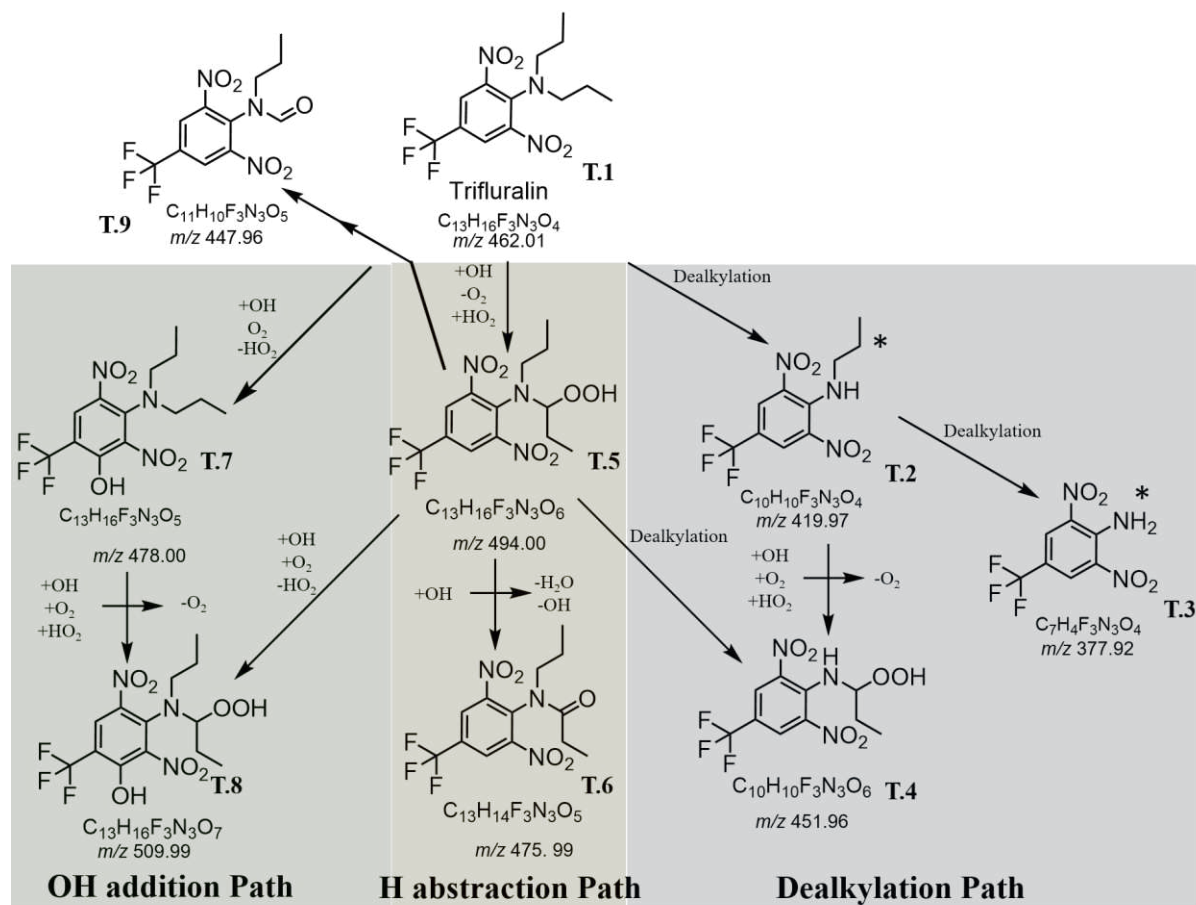
Scheme 5.2. Proposed OH oxidation mechanism of trifluralin based on high resolution I-CIMS data. Only one set of isomers are shown. Asterisks indicate previously reported photolysis products.

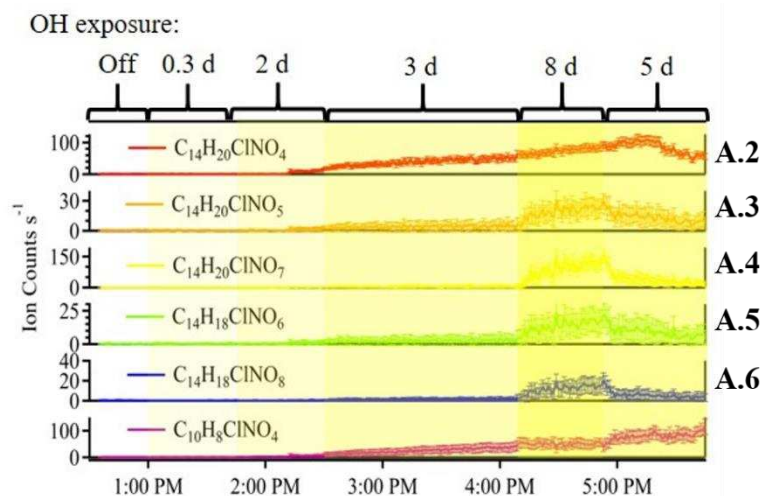## 5.3.2. Acetochlor + OH Mechanism

Figure 5.1. Time series (ion counts, 1 min averages) of six products detected and identified during the oxidation of acetochlor with changes in UV light intensity. Shading corresponds to equivalent OH exposure time (days).

Based on the immediate appearance in the mass spectra of $C_{14}H_{20}ClNO_4$ (**A.2**) at the first OH exposure step (Figure 5.1), we propose the primary reaction between acetochlor and OH is a hydrogen abstraction at one of the seven carbons to form the peroxide (**A.2**; *m/z* 428.01). However, **A.2** could also be formed from two OH additions to the aromatic ring, with two subsequent losses of HO_2. $C_{14}H_{20}ClNO_5$ (**A.3**), observed at *m/z* 444.00, is the proposed second-generation product in the mechanism, formed by the addition of OH to the aromatic ring of **A.2**. $C_{14}H_{20}ClNO_7$ (**A.4**; *m/z* 475.99) does not appear until 8 OH exposure days (Figure 5.1), indicating multiple oxidation steps characteristic of a later generation product. **A.4** may be a di-peroxide phenolic acetochlor product (Scheme 5.2). Further reaction with OH at either of the peroxides on **A.4** would produce an aldehyde, consistent with the observed product, $C_{14}H_{18}ClNO_6$ (**A.5**; *m/z* 457.99). The aldehydic hydrogen of **A.5** is susceptible to OH abstraction, reaction with O_2, and reaction with HO_2, forming a peroxy acid ($C_{14}H_{18}ClNO_8$, **A.6**; *m/z* 489.97). We again note that these are proposed, potential structures without authentic standards, and further work is needed to isolate specific isomeric information. $C_{10}H_8ClNO_4$ is the second largest product ion signal detected in the mass spectrum

(Figure 5.1), but we cannot identify a likely production pathway. The presence of this ion is consistent with fragmentation of the ethoxymethyl carbon to the nitrogen (which occurs to form the acetochlor fragment), followed by the loss of another carbon, either the methyl group or a carbon from the ethyl group on the aromatic.
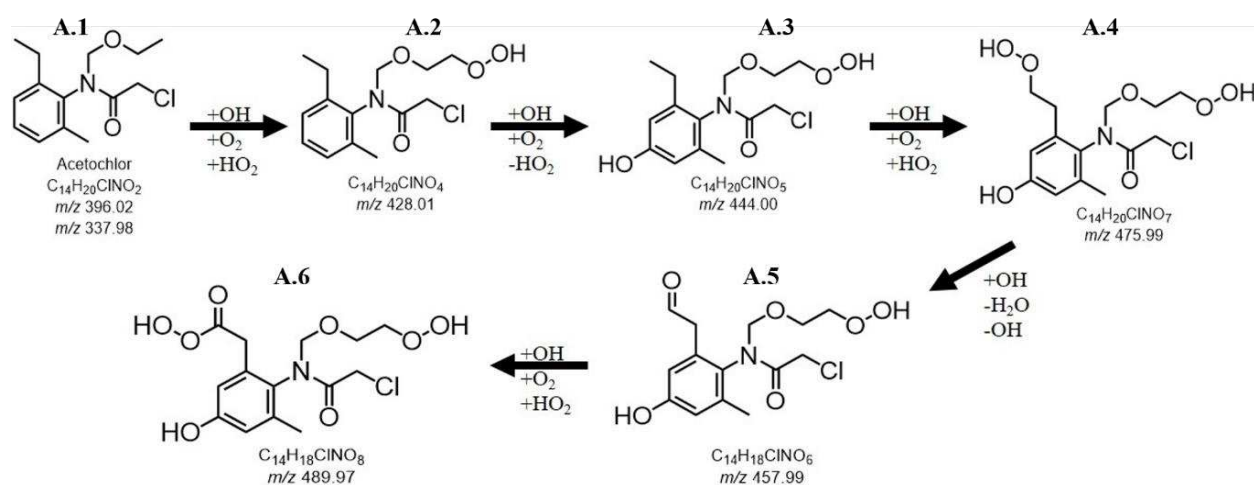
Scheme 5.3. Proposed OH oxidation products detected during acetochlor oxidation in the OFR. Only one of the potential structural isomers are shown for each detected ion.

5.3.3. Fate of Nitrogen

Both trifluralin and acetochlor contain reduced nitrogen atoms; trifluralin also contains two nitro ($-NO_2$) groups. These experiments thus provide a useful case study to investigate the oxidative fate of organic nitrogen, which is thought to depend on the oxidation state of nitrogen.[35-38] Trifluralin and acetochlor produce NO_2 radicals and isocyanic acid (HNCO) (Figure A4.2). HNCO and NO_2 concentrations from the herbicides were calculated by subtracting the average signal during each OH exposure time step during the methanol background from the corresponding oxidation step in the herbicide experiment.

The fate of organic nitrogen in the atmosphere is poorly understood. HNCO is one oxidation product of particularly interest due its association with a number of negative health effects, even at exposure mixing ratios as low as 1 ppb$_v$ (based on *in vivo* studies).[39-40] Amines

react with OH radicals at the carbon adjacent to the nitrogen to form an amide, which is further oxidized to form an isocyanate.[37] OH reaction with the N atom is slow, energetically unfavorable, and with a branching ratio <0.1.[38, 41] Via OH oxidation, small amines and the resultant amides can produce isocyanic acid (HNCO).[36, 38] Borduas et al. showed computational mechanisms and kinetic studies to validate their observations of HNCO formed in the oxidation of five different amides, attaining 17-19% yields.

HNCO was detected during the oxidation of both herbicides. HNCO is most likely from the tertiary amine of acetochlor and trifluralin. The nitro groups on trifluralin would require complete fragmentation of the aromatic system followed by the loss of the two O atoms and the reduction of the N atom. While fragmentation of aromatic rings have been observed during OH oxidation of toluene and benzene,[42] this seems an improbable pathway for HNCO formation. To calculate HNCO yields from trifluralin, we compare the observed HNCO (14 ± 5 and 120 ± 30 ppt$_v$ at 3 and 8 OH equivalent days) to the predicted measured initial input concentration of trifluralin (0.53 ppb$_v$) minus trifluralin remaining following reaction with OH based on known first order kinetic rate constants[15]. We calculate an HNCO yield (moles HNCO formed : moles trifluralin reacted) of 3% (3 days) and 20% (8 days). We note that trifluralin that had been deposited to the OFR walls re-volatilizes at the higher temperatures associated with higher UV intensities. This re-volatilized trifluralin can react with OH and contribute to the observed HNCO, and these yields should thus be considered upper bounds. Acetochlor is even more susceptible to wall loss coupled to re-volatilization (Figure A4.1a). HNCO was only observed at the detection limit at 8 OH equivalent days of oxidation. We thus consider an upper bound for HNCO yields to be 0.2%, calculated from the difference in HNCO and acetochlor detected at 8 days (90 ± 30 ppt$_v$ HNCO, 55 ppb$_v$ acetochlor) versus 3 days (<LOD HNCO, 111 ppb$_v$ acetochlor) of oxidation.

During both herbicide oxidation experiments, NO_2 increased with OH exposure. Detected NO_2 concentration were much higher for trifluralin than acetochlor (13 ppb$_v$ NO_2 from 0.6 ppb$_v$ trifluralin versus 1.5 ppb$_v$ NO_2 from >56 ppb$_v$ acetochlor after 8 d of OH exposure). Three possible sources of this detected NO_2 include: photolysis of nitro groups ($R-NO_2$) of trifluralin; surface photochemistry from trifluralin or acetochlor deposited on walls of the OFR; interference from nitrogen-containing oxidized organics. Amines are not thought to be NO_x sources, except through combustion processes. Light at 254 nm can cleave the C-N bond in nitrobenzene, which is analogous to trifluralin, to release NO_2 and NO at ratios >3:1.[43] When excited, nitrobenzene isomerizes to form phenyl nitrite, which produces NO.[43-44] Heterogeneous and multiphase photochemistry is a known source of NO_x and could contribute to concentrations observed in the OFR from herbicides that deposited to the walls during the experiments.[45-47] For example, photodegradation of nitro-PAHs on surfaces produces NO_x.[46-47] The MoO converter that is coupled to the NO_x analyzer suffers from known interferences by gas phase nitric acid, organic nitrates, and peroxyacyl nitrates.[33] While no NO_x was observed under 'lights off' conditions from the parent herbicides, the oxidized organics may be contributing to the detected NO_2. We note that only NO_2 was observed by the NO_x detector; any NO formed by the photolysis of the nitro groups would react with ozone in the OFR ($k_{O3+NO} = 1.9 \times 10^{-14}$ cm^3 molecules^{-1} s^{-1}) to form NO_2.[48] The detection of NO_2 during oxidation of trifluralin and acetochlor thus warrants further investigation as a potential fate of organic nitrogen, whether from photolysis of nitro groups or production of more oxidized organic nitrogen.
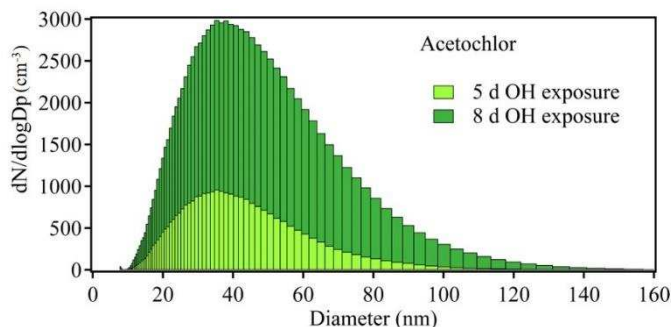
Figure 5.2. Average size distributions from the SMPS during the acetochlor OH oxidation in the OFR at 5 days (light green) and 8 days (dark green).

5.3.4. Particle Formation

Aerosol was observed during oxidation of acetochlor, but not trifluralin, and only at the two highest levels of OH exposure and acetochlor concentration: we observe 3 ± 2 µg m^{-3} (5 d) and 12 ± 3 µg m^{-3} (8 d) of submicron aerosol (Figure 5.2). Using the changes in acetochlor relative to the 3 d exposure experiment, we estimate upper bound SOA yields of $5\pm3\%$ (5 d) and $2\pm1\%$ (8 d), respectively. We hypothesize that the lower yield at 8 d is due to temperature increases in the OFR (Figure A4.3), which shift more volatile organic products from the particle to gas phase, outcompeting SOA formation from oxidation chemistry. We note that aerosol production only occurred at the artificially high acetochlor concentrations (via re-volatilization from OFR walls, >100 ppb$_v$) and highest OH exposure time (5 and 8 d). As these two conditions are unlikely to be found simultaneously in the ambient atmosphere, these two herbicides appear to be negligible SOA sources. This conclusion contrasts with previous work. Le Person et al observed SOA formation from trifluralin, but at much higher precursor concentrations (33 - 69 ppb$_v$ versus ~1 ppb$_v$ in this experiment).[15]

5.4. Conclusions

Using an OFR and I-CIMS enables us to investigate multigenerational oxidation chemistry of herbicides. Trifluralin has three initial pathways of degradation: OH addition to aromatic ring,

H abstraction, and photolysis. Acetochlor undergoes H abstraction and peroxide formation, with little evidence for OH addition to the aromatic ring. Isocyanic acid is a potentially toxic oxidation product of both herbicides, although the yields are sufficiently low that the source is unlikely of environmental or health concern in most ambient settings. However, the work does show that tertiary amines can be a secondary source of isocyanic acid. Similarly, SOA formation from these herbicides was minor. Thus, while the atmospheric degradation of these two nitrogen-containing herbicides produces an array of oxidation products, but in and of themselves may not have a substantial impact on secondary air pollution in agricultural regions, unless application loadings are particularly high.

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CHAPTER 6 - SUMMARY AND CONCLUSIONS

Pesticides are anthropogenic contributors to atmospheric chemistry and can impact environmental and human health at ppt_v-ppb_v concentrations.[1-11] Fast and sensitive measurements are necessary to understand their transport and chemical processes in the atmosphere. Chemical ionization mass spectrometry (CIMS) is a potentially valuable tool for studying the atmospheric fate and oxidation of pesticides. CIMS enables online pesticide measurements in the laboratory or field. In this dissertation I presented:

- A technique to quantitatively volatilize standard solutions for pesticide calibrations for ToF-CIMS.

  - Atrazine, metolachlor, trifluralin, and permethrin sensitivities were reported for 1 second measurements, the highest time resolved measurements described in the literature to date.

  - LODs were adequate for laboratory experiments and ambient measurements during and directly after (<1 day) application (low ppt_v)

- During a small field study at Colorado State University, I used Acetate CIMS to measure short term gas-phase herbicide source mechanisms: spray volatilization and post-application surface volatilization

  - 2,4-D volatilized instantaneously from droplets during spray periods, a process consistent with Henry's Law Constants.

  - MCPA volatilized from the applied surface post-spray as the ambient temperature increased, a process consistent with vapor pressure.

- Local ambient concentrations were too low to be concerning for workers' health, but high enough to suggest that in heavy pesticide-use areas, oxidation by OH radical could occur and may have impacts on local ozone especially.

- I presented novel OH radical oxidation mechanisms using an oxidative flow reactor coupled to acetate and/or iodide CIMS for five herbicides: three chlorinated aromatic acids and two nitrogen-containing species,
  - Several identified oxidation products measured by this method have established toxicity and sub-lethal health effects to mammals and aquatic life including: 5-chlorosalicylaldehyde, 5-chlorosalicylic acid, and 3,5, 6-trichloropyridinol.[12-18]
  - Approximate reaction rate constants with OH radical for mecoprop-p (2.6 ± 0.3 x 10^{-12} cm^3 $molecules^{-1}$ s^{-1}) and MCPA (1.5 ± 0.7 x 10^{-12} cm^3 $molecules^{-1}$ s^{-1}) correspond to atmospheric lifetimes with respect to OH of ~3 and 5 days, respectively (for a daily average for OH radical concentration of 1.5 x 10^6 molecules cm^{-3}).
  - Trifluralin and acetochlor produced isocyanic acid from tertiary amine functional groups, while nitro groups photolyzed from trifluralin's aromatic ring to produce NO_x.
  - OH oxidation of acetochlor produced aerosol, but at herbicide concentrations above that typically expected in the ambient atmosphere.

Pesticide use is ongoing and represents billions of dollars for globally in terms of research and development, human health, and agricultural production. The atmosphere serves as an important reservoir for pesticides, affecting the entire globe. Atmospheric monitoring for

pesticides will remain necessary, particularly as transformation and degradation processes can lead to more environmentally harmful yet unknown compounds.

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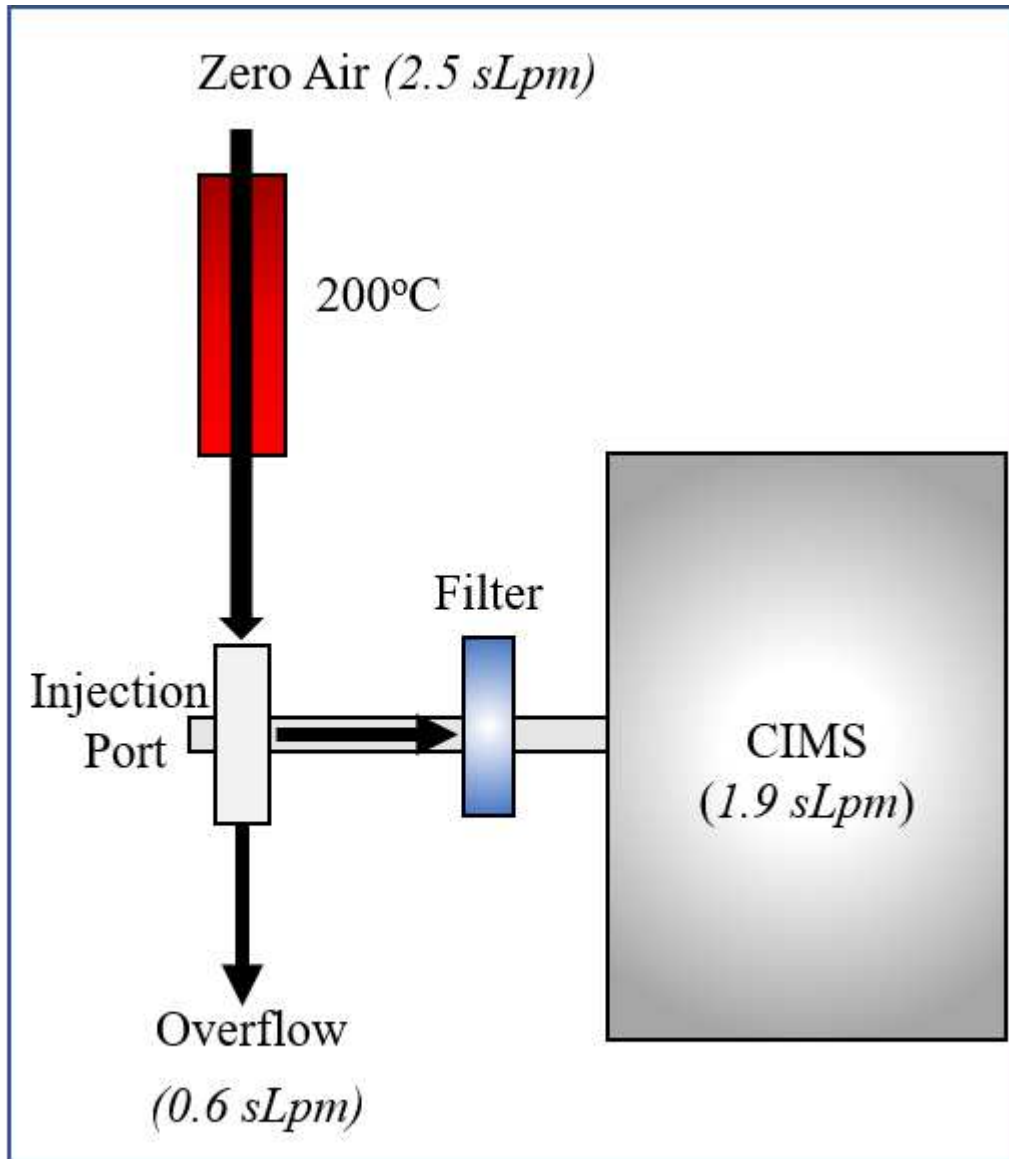
Figure A1.1. Ultra high purity zero air is flowed at 2.5 standard liters per minute (sLpm) through a heated tube filled with stainless steel wool in order to produce uniformly heated air. The air is pulled into the CIMS (1.9 sLpm) over a filter and overflow is sent out of the exhaust. The injection port is a septum placed in a Swagelok ¼" end nut.
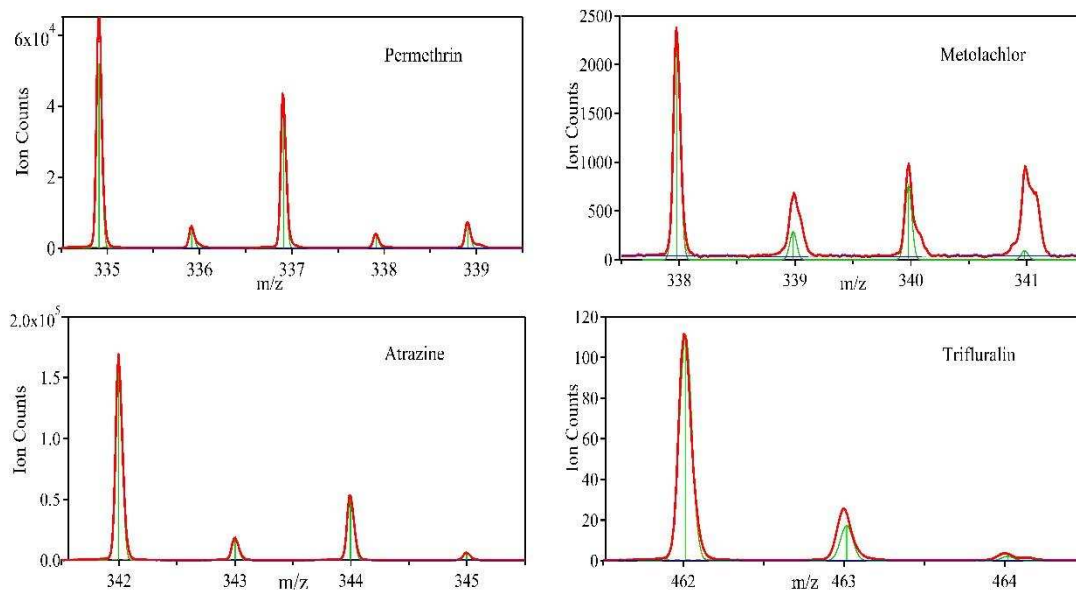
Figure A1.2. High resolution peak fits (green) of the raw signal (red) at the mass-to-charge ratios where the pesticides are detected, as well as their isotope patterns. During zero air backgrounds and solvent blanks, no other ions are present at the relevant mass-to-charge ratios which provides further confidence in identifying the pesticides and lower limits of detection. Each mass spectrum was taken during 1 s at the peak of the injection period.
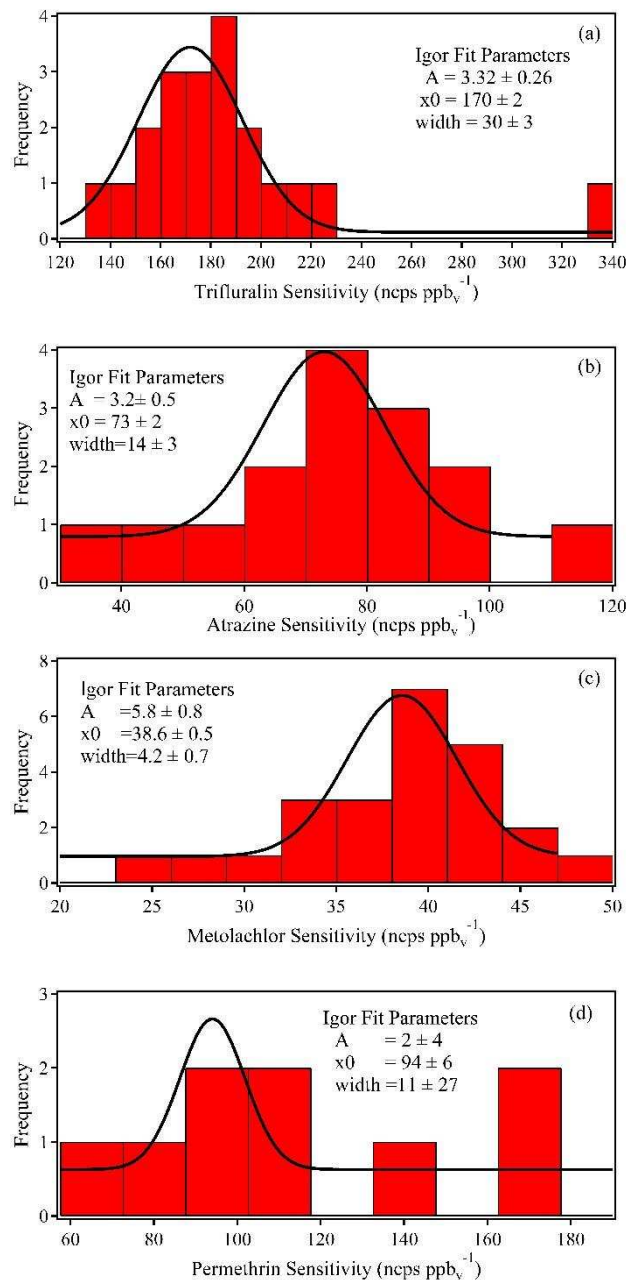
Figure A1.3. Histograms of the sensitivities (normalized counts per second per ppb$_v$) of the injections of the four pesticides using the Iodide ToF-CIMS. Fit parameters are produced from the Gaussian Fit (black trace) function in Igor, where x0 is the Gaussian center, A is the amplitude, and width is the Gaussian standard deviation.
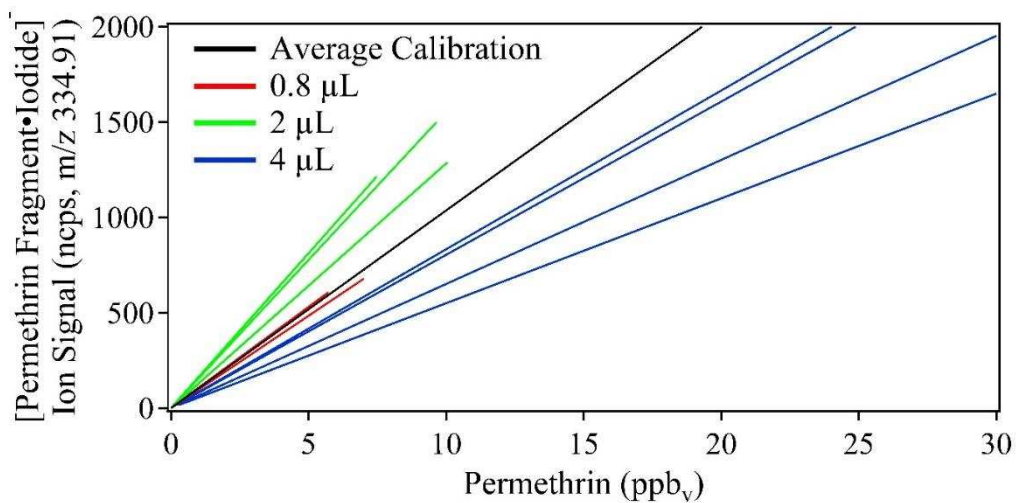
Figure A1.4. The average sensitivity for permethrin is 100 ± 40 ncps/ppb$_v$. However, the smallest injection volume (0.8 µL, red) has a greater average sensitivity (100 ± 10 ncps/ppb$_v$) than the largest volume (70 ± 10 ncps/ppb$_v$, 4 µL, blue), although the middle injection (2 µL, green) has the highest average sensitivity (150 ± 20 ncps/ppb$_v$).
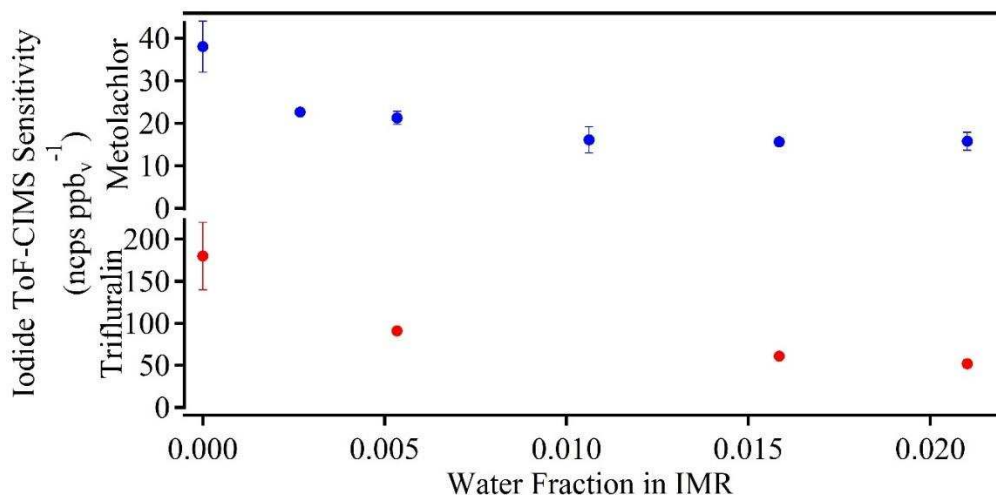
Figure A1.5. Changes in sensitivity as a function of humidity for metolachlor (blue) and trifluralin (red).

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.[1]

$$[I \cdot H_2O]^- + M \rightarrow [I \cdot M]^- + H_2O \qquad \text{(R2)}$$

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 A1.5 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.

$$M + I^- \rightarrow [M \cdot I]^- \qquad \text{(R3)}$$

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.[2] 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.
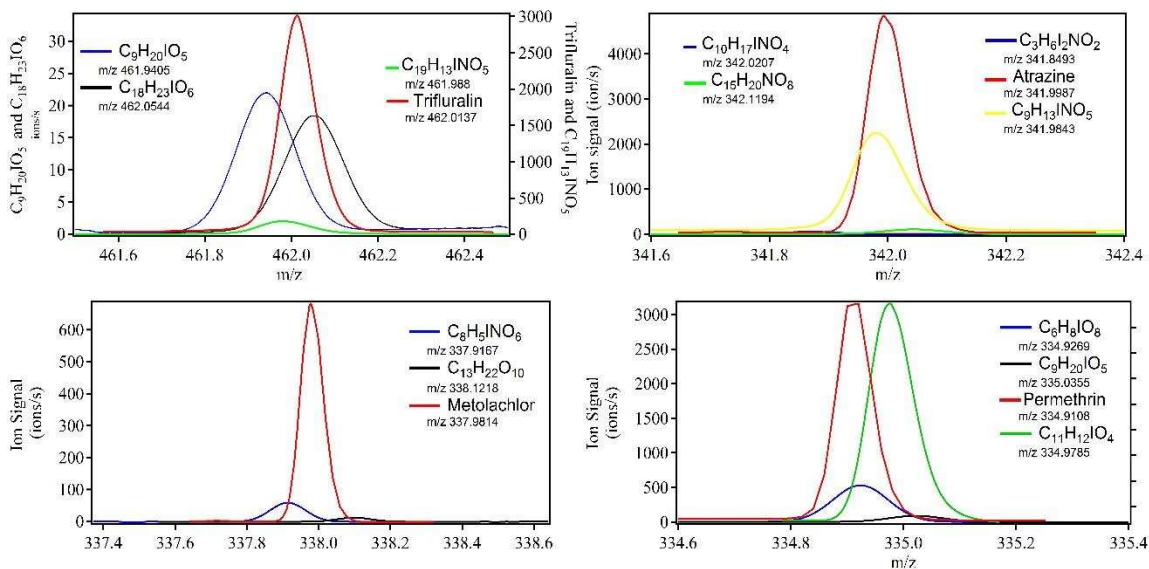
Figure A1.6. Exact locations of pesticides in the iodide ToF-CIMS mass spectra are compared with ions detected at the same nominal mass during two field campaigns, the Southern Oxidant and Aerosol Study (SOAS) and a local study in the Colorado Front Range (FRAPPE). Intensities of the pesticide peaks correspond to 1 ppb$_v$ during a calibration injection. Combined with isotope signatures shown in Figure A1.2, this figure illustrates the power of the iodide ToF-CIMS to separate and confidently identify pesticides.

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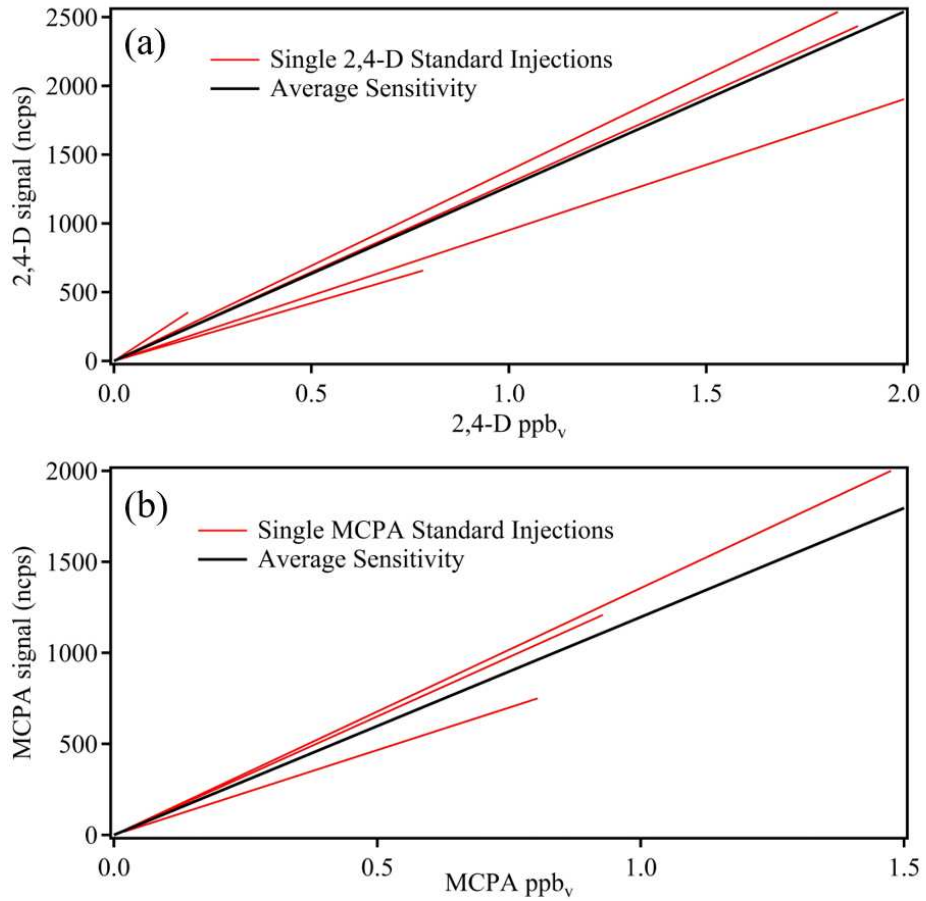
Figure A2.1. Calibration curves for 2,4-D (a) and MCPA (b) generated by heated standard solution injection method reported by Murschell et al.[1]
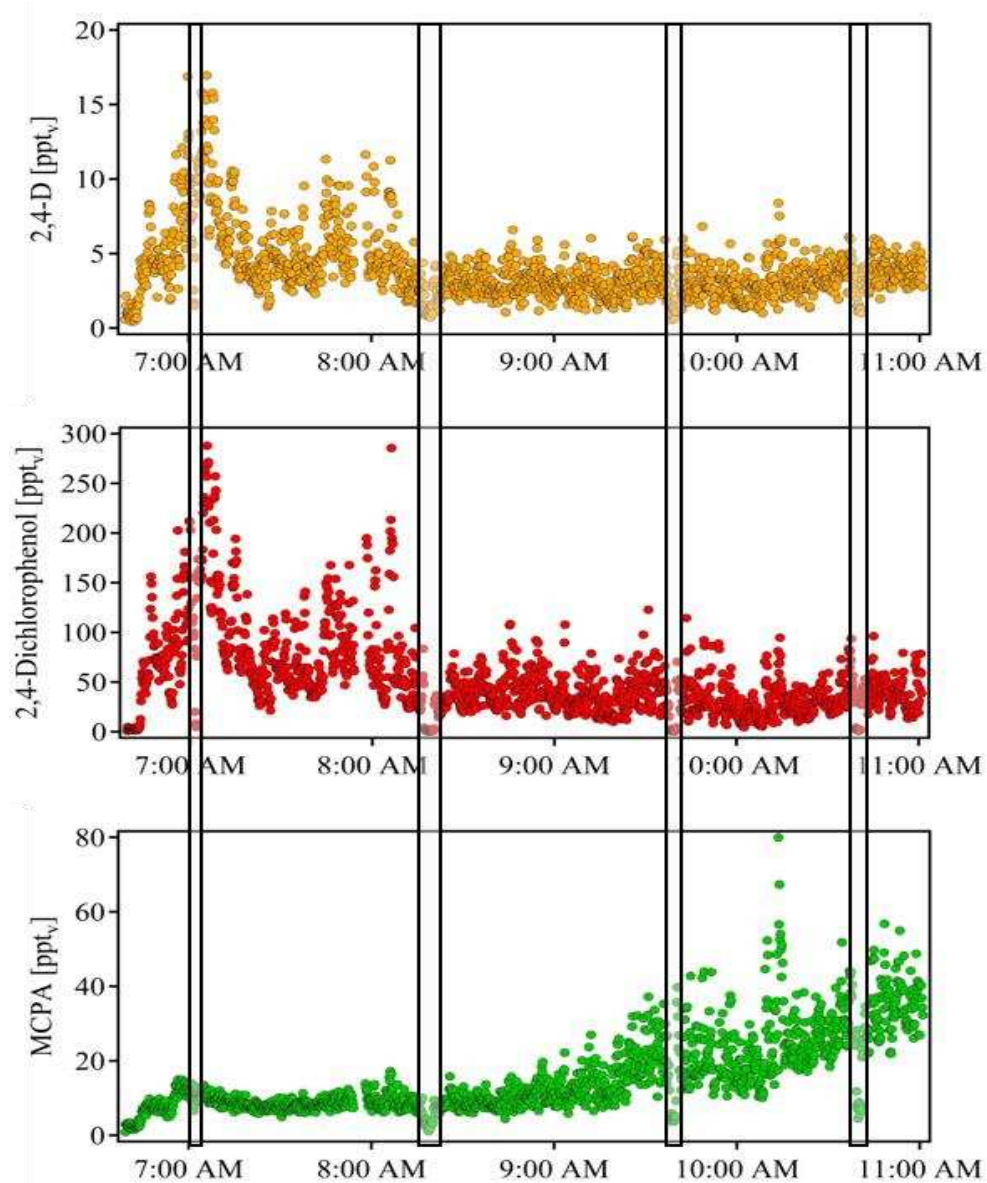
Figure A2.2. Averaged (10s) concentration time series of 2,4-D (top), 2,4-DCP (middle), and MCPA (bottom) with the four UHP zero backgrounds included in the shaded boxes. Application commenced around 6:42 am and finished around 7:08 pm.
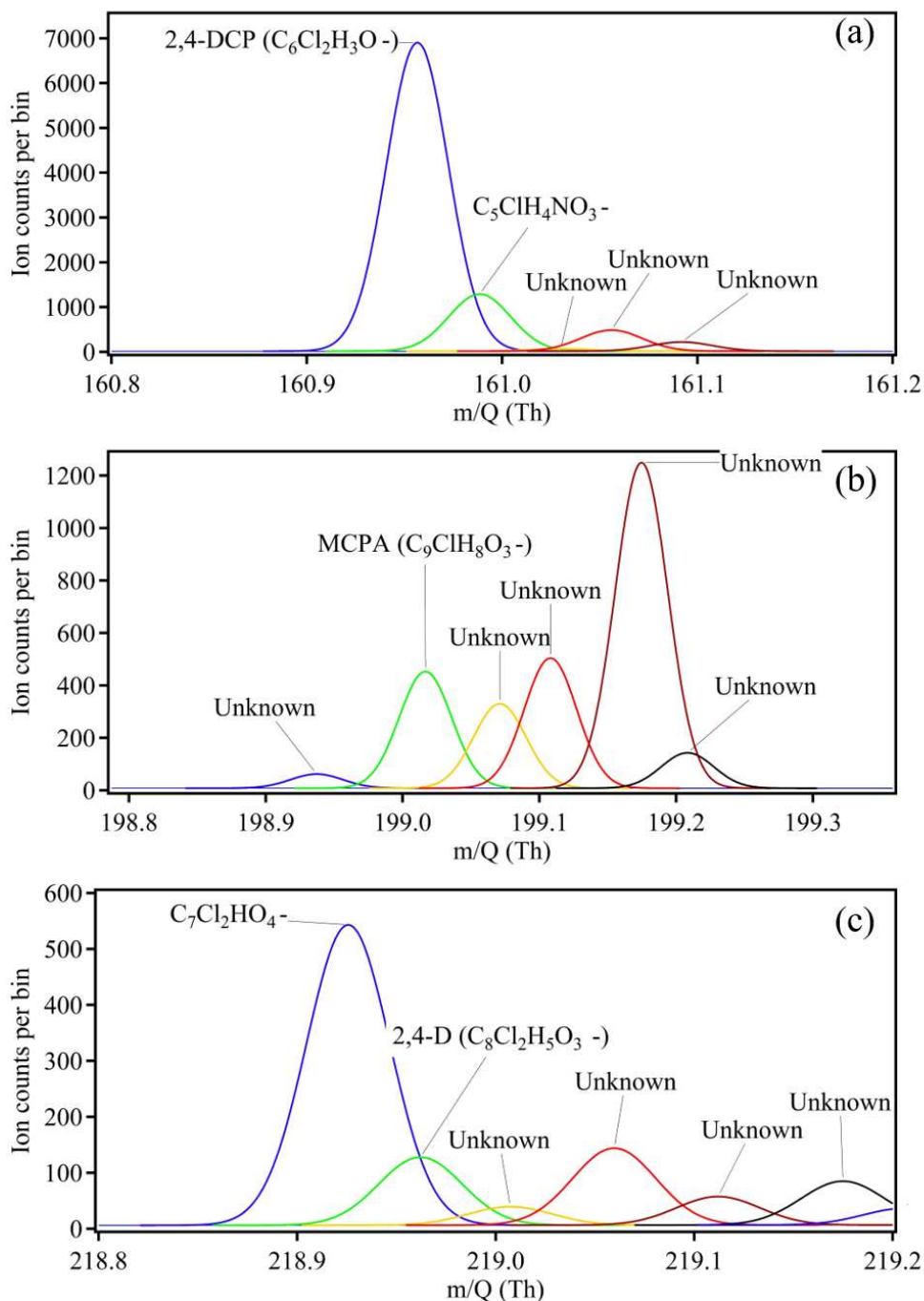
Figure A2.3. High resolution data peak fits and identification of 2,4-DCP (a), MCPA (b), and 2,4-D (c). While 2,4-DCP and MCPA are clear and well-resolved, 2,4-D quantification may suffer from an interference with what we tentatively identify as $C_7Cl_2HO_4^-$, which may be in the herbicide solution.

Table A2.1. Chemical and physical properties of herbicides sprayed at Colorado State University and dichlorophenol, which was also observed.

Compound	Chemical Formula	Vapor Pressure (mmHg, 25C)	Henry's Law constant (atm m^3/mole)	Water Solubility (mg/L)	K_{OC}* (ml/g)
MCPA	$C_9H_9ClO_3$	5.9×10^{-62} [2]	4.8×10^{-10} [3]	630 (25ºC) [4]	52-60[5]
2,4-D	$C_8H_6Cl_2O_3$	1.4×10^{-7} [6]	9.8×10^{-8} [6]	851 (25ºC) [3]	72-135[7]
Triclopyr	$C_7H_4Cl_3NO_3$	1.2×10^{-6} [3]	9.7×10^{-10} [3]	440 (25ºC) [8]	12-134 [3]
Fluroxypyr	$C_7H_5Cl_2FN_2O_3$	3.7×10^{-7} [6]	1.7×10^{-11} [9]	3,300 (20ºC) [6]	100-700 [10]
2,4-DCP (dichlorophenol)	$C_6H_4Cl_2O$	0.09 [8]	3.5×10^{-6} [8]	4500 (20ºC) [4]	261-708 [8]

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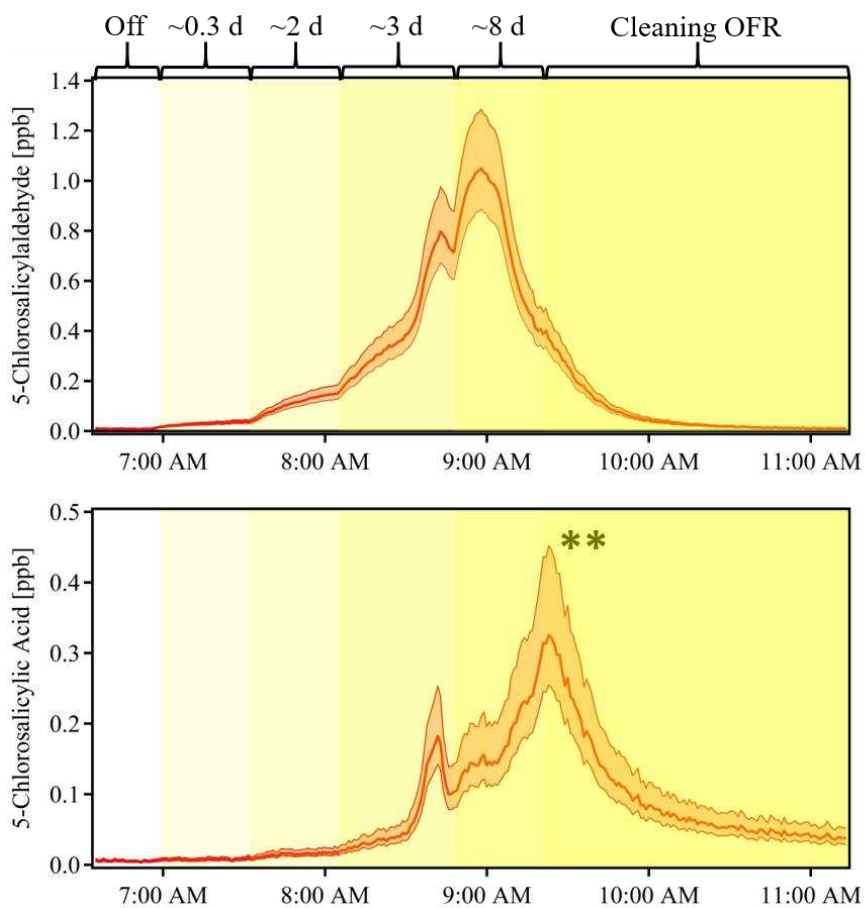
** End of solution injection

Figure A3.1. Chlorosalicylic compounds detected with Acetate CIMS during MCPA oxidation. OH exposure in days are indicated above figure. We propose the chlorine on both compounds are at the 5th position, based on the MCPA precursor. The uncertainty band around the solid line indicates uncertainty in concentration propagated from errors in the calibration (18 and 28 % RSD for the aldehyde and acid, respectively). Lights in the OFR were turned on to full intensity to clean OFR.
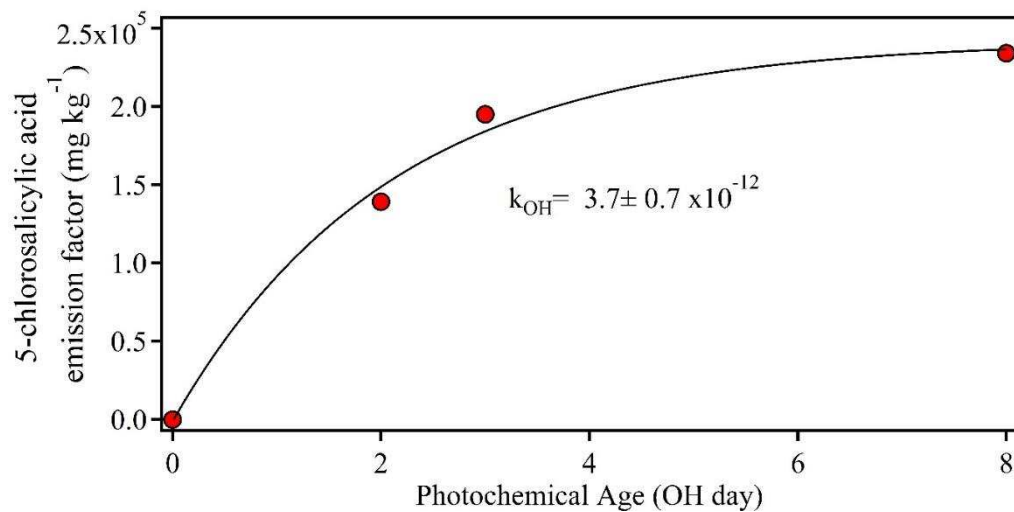
Figure A3.2. Fitting the increasing emission factor (mg of 5-chlorosalicylic acid over kg of MCPA) vs photochemical age (OH day) in Figure A.3.2, we can derive a precursor rate constant, k_{OH}, of 3.7 (0.7) x 10^{-12} cm^3 molecules^{-1} s^{-1}. In our proposed mechanism, this would most likely correspond to the OH abstraction of the hydrogen from the 5-chlorosalicylaldehyde.
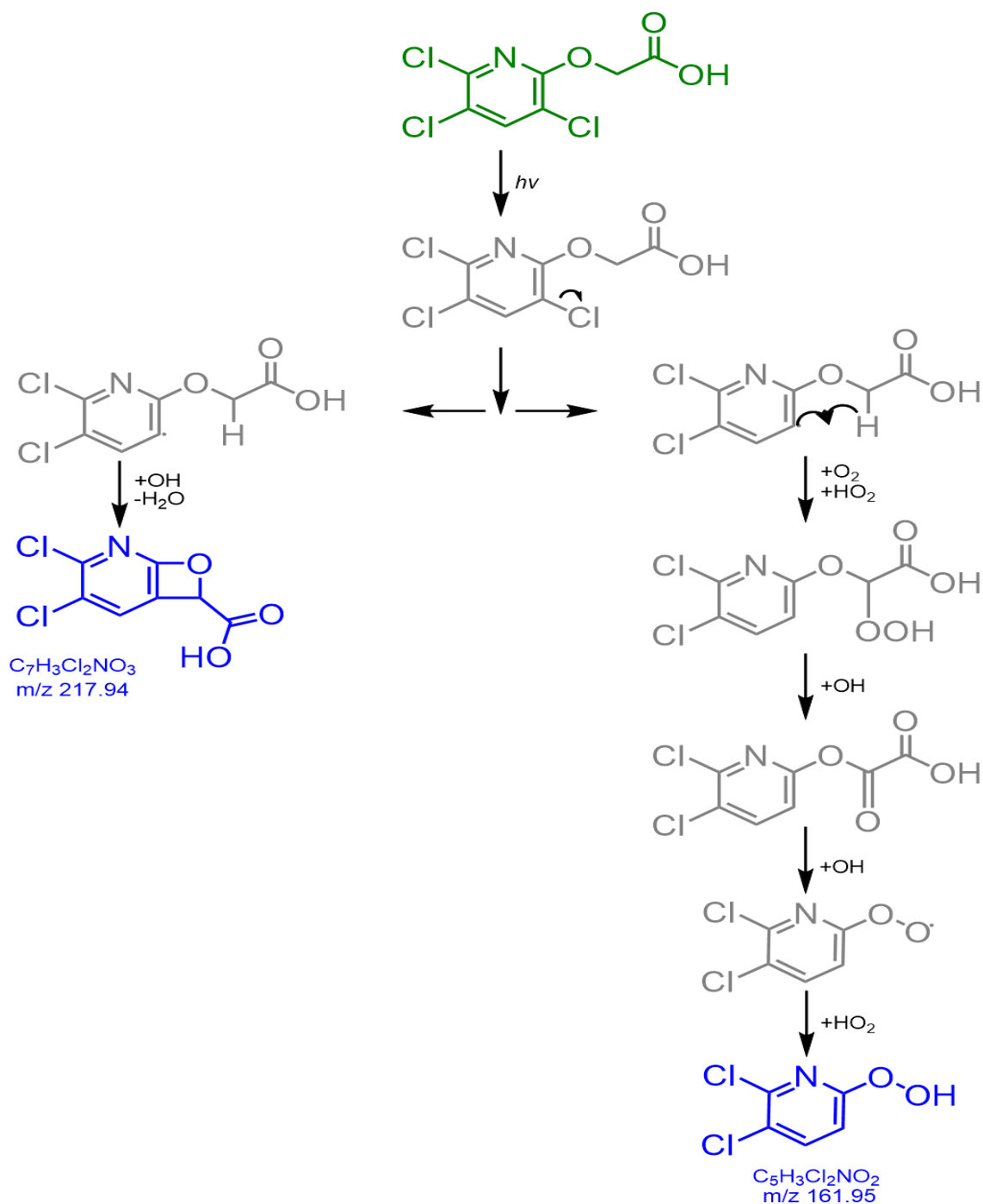
Scheme A3.1. Proposed triclopyr photolysis and OH oxidation. Two compounds with only 2 chlorines are measured using acetate CIMS, indicating photolysis of triclopyr (green), measured by both reagent ions. Compounds in gray are proposed intermediates that follow similar chemistry as that proposed in Scheme 2.
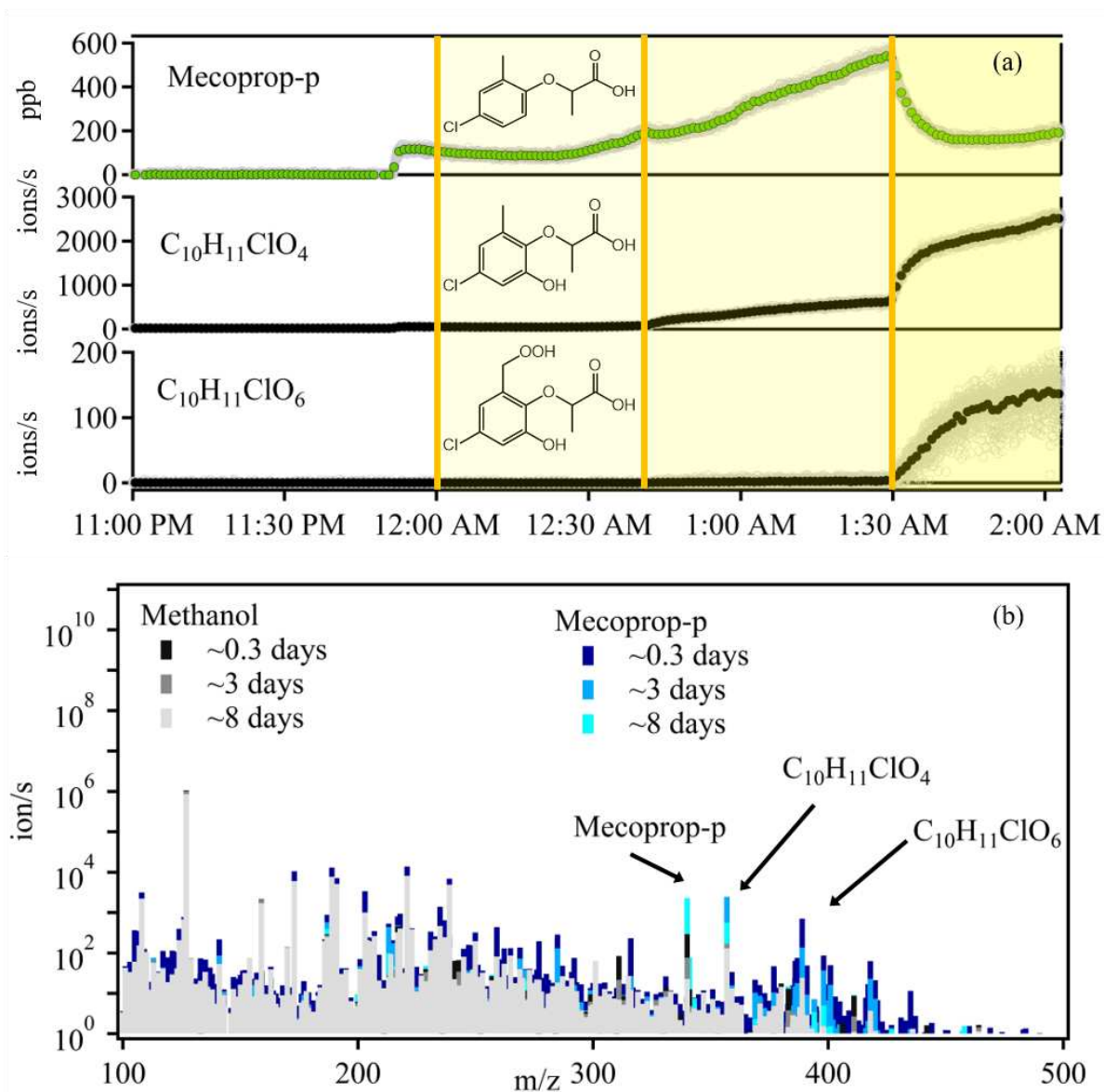
Figure A3.3. Time series (top panel, a) of the OH oxidation of Mecoprop-p (green), during the iodide portion of the experiment, also showing the appearance of the two major products (black) as the OH exposure (yellow bars, shaded areas) increases. One minute averaged data is in color, while raw 1 s signal is shown in gray open circles. The bottom panel (b) shows averaged high-resolution Iodide mass spectra (between m/z 100-500). The gray scale mass spectra are taken from the methanol oxidation background, and blue-scale mass spectra are from the Mecoprop-p in methanol oxidation. Proposed products are indicated at the m/z of molecules clustered with iodide. Several peaks appeared during the oxidation experiments that were not clear products of mecoprop-p (e.g. C_7 and C_{11} species), and were not investigated in depth.

Table A3.1. Gas phase concentration enhancement (ppb) of four organic carboxylic acids detected during the pesticide oxidation experiments as a function of equivalent OH exposure time.

Herbicide	Formic Acid	Pyruvic Acid	Acetic Acid	Glycolic Acid‡
MCPA (~40 ppb) Acetate (0.3, 2, 3, 8 days)	0.25, 1.2, 3.1, 17	N/E, 0.31, 0.86, 4.4	N/E	N/E
Triclopyr (~29 ppb) Acetate (0.3, 8 days)	0.42, 1.1	0.065, 0.52	N/E	N/E
Mecoprop-p (~96 ppb) Iodide (0.3, 3, 8 days)	5.3**	0.12, 0.25, 0.26	0.88, 3.58, 10.6	0.014, 0.25, 1.6

*No enhancement observed
** Only observed at highest OH exposure
‡ Quantification of glycolic acid proved difficult, as high backgrounds were present in the solvent oxidation experiments, and the acid is ubiqutous in the OFR and IMR.

The enhancement concentration is calculated as the difference between concentration during the OH+pesticide+solvent experiment and the equivalent OH+solvent experiment. Calculated concentrations between the methanol oxidation and herbicide oxidation that are either not significantly different or negative are considered to have no enhancement (N/E).

Text A3.1. OFR Experimental Note

Several experimental limitations with the OFR were apparent in this work. While often presented as a "wall-less" chamber, residues from previous a day's experiments deposited on the walls, hindering our ability to quantify compounds of interest. Cleaning the OFR with solvents followed by lengthy clean-out days with zero air + UV lights was often inadequate, and caused significant down time between experiments of several days without fully scrubbing residues. We also note that compounds adsorbed to the IMR of the CIMS can contribute to signals for days-weeks, depending on solution concentrations and CIMS sensitivities. Previous studies have reported that as much as 77% of organic compounds produced in the OFR can be lost to the walls of the IMR due to the geometry and flow turbulence.[1] Closing the CIMS inlet and powering the IMR body heater to 80-90℃ for several days facilitated the return of mass spectral signal to a reasonable, albeit not entirely clean, starting point for the next experiment.

We also note that methanol reacts with OH to form carbon monoxide, thus was determined to not be a large source of any interferences. However, impurities, albeit at low concentrations in the solvent, will participate in oxidation chemistry, creating artificially high backgrounds and complicating yield calculations. We did observe that compounds formed in the methanol oxidation could carry over to the next experiment if the system was inadequately cleaned. We recommend careful experimental planning, adequate time between experiments, and a standard OFR cleaning procedure for future experiments using the OFR coupled to multifunctional and low volatility precursors.
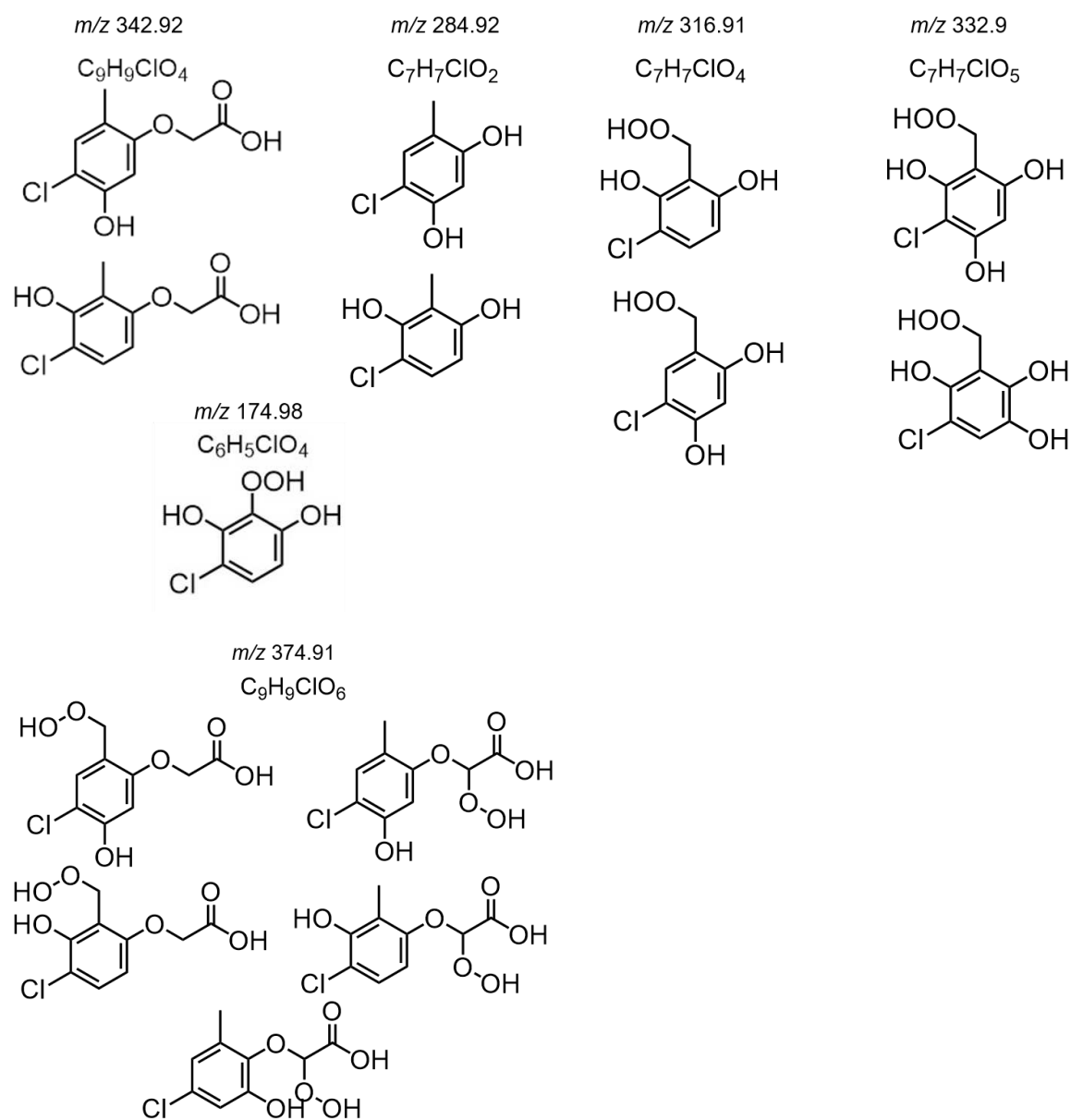
Figure A3.4. Since the CIMS is unable to determine specific structural isomers, we include possible isomers of the measured compounds during the MCPA oxidation experiment, shown in the manuscript, Scheme 4.1.
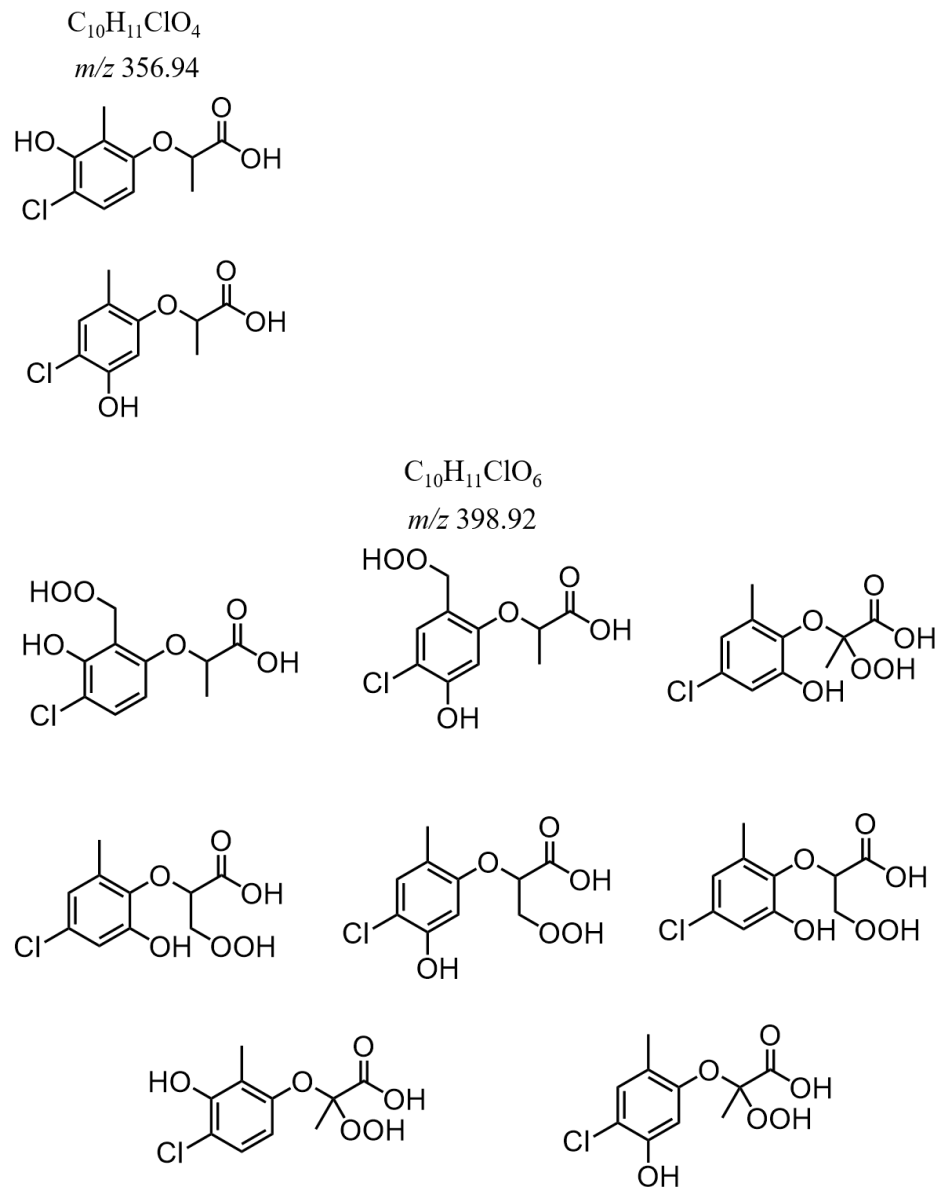
Figure A3.5. Similar to Figure A.3.4, we include possible isomers of the proposed compounds in the Mecoprop-p mechanism scheme in the manuscript, Scheme 4.3.

APPENDIX 3 REFERENCES

1. Krechmer, J. E.; Pagonis, D.; Ziemann, P. J.; Jimenez, J. L., Quantification of Gas-Wall Partitioning in Teflon Environmental Chambers Using Rapid Bursts of Low-Volatility Oxidized Species Generated in Situ. *Environmental Science & Technology* **2016,** *50* (11), 5757-5765.

*Start of Injection
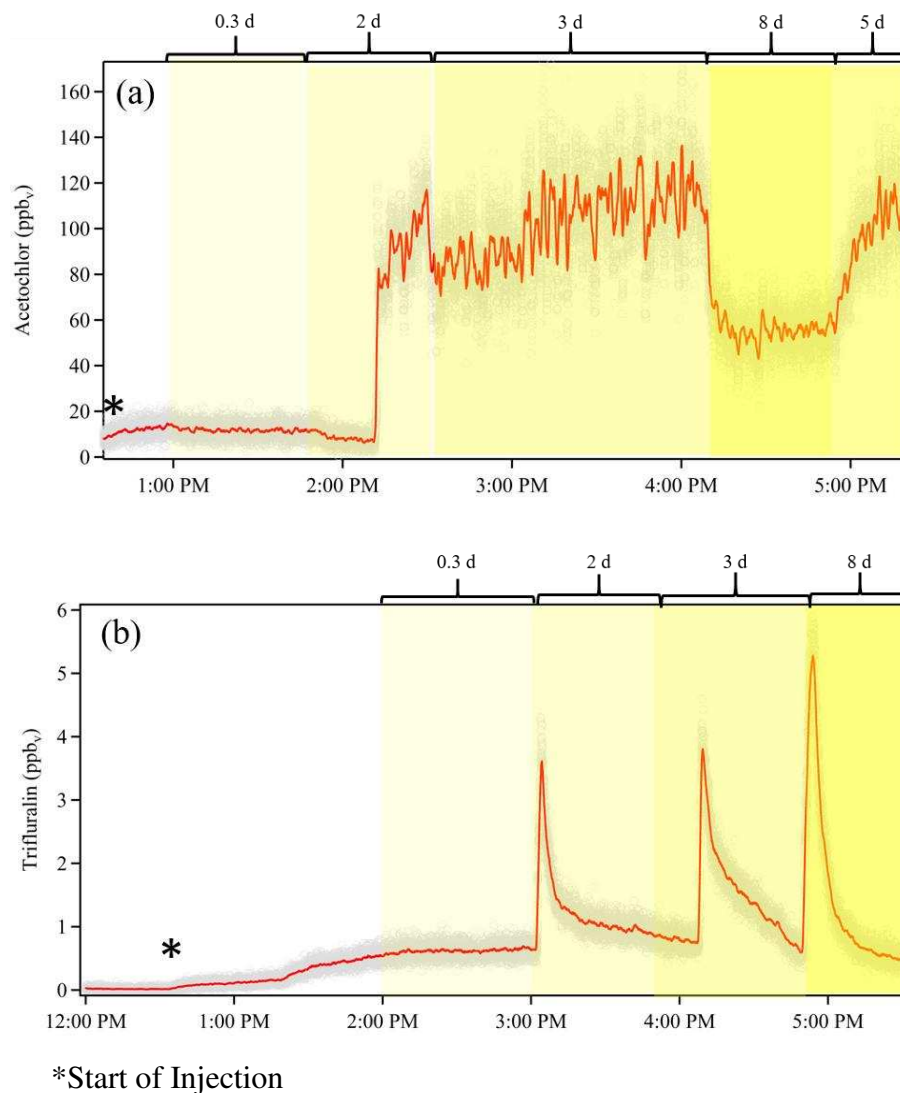
Figure A4.1. Time series of acetochlor (a) and trifluralin (b) during oxidation experiments with shaded boxes indicating OH exposure days. Red solid lines are 1 minute averages (1 Hz data in gray open circles). Expected concentrations in the OFR for both herbicides were ~20ppb$_v$. Acetochlor volatilized from the OFR halfway through the 2 OH exposure day step.
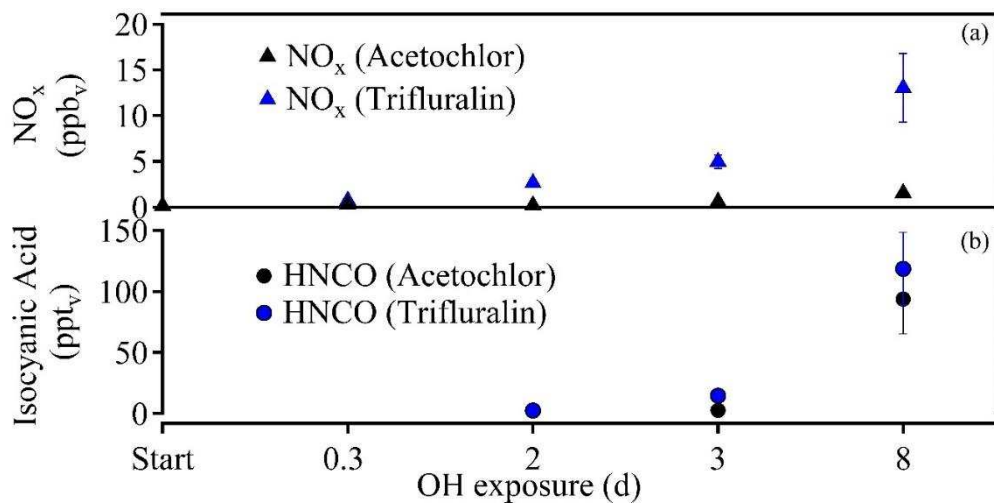
Figure A4.2. Concentrations of NO_x (top) and HNCO (bottom) produced at each oxidation step during acetochlor (black) and trifluralin (blue) experiments. Production yields ($[x]/\Delta[pesticide]$) are nearly incalculable because of OFR and IMR wall effects.
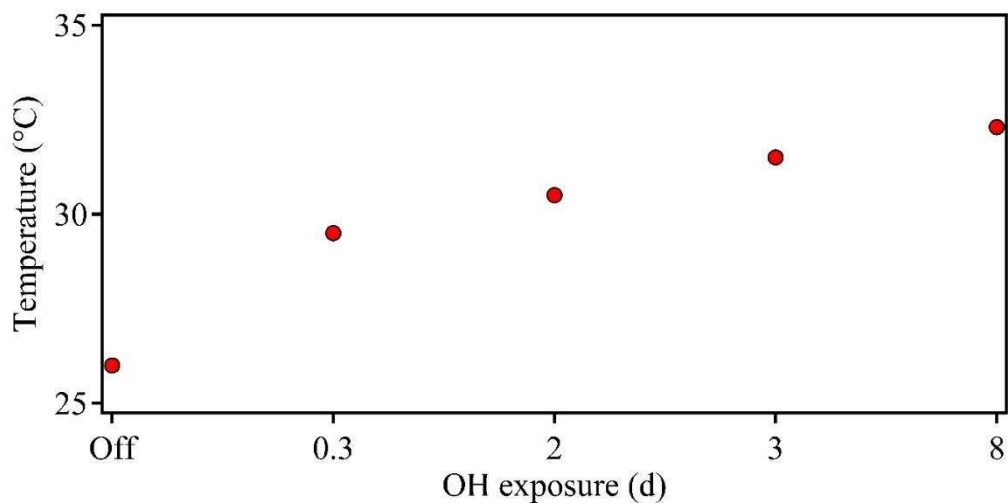
Figure A4.3. Temperature changes occuring in the OFR as voltage supply to the UV lamps increased. Temperature was measured (a) in the center of the air flow, directly in the middle of the reactor, and (b) adjacent to the UV lamps.
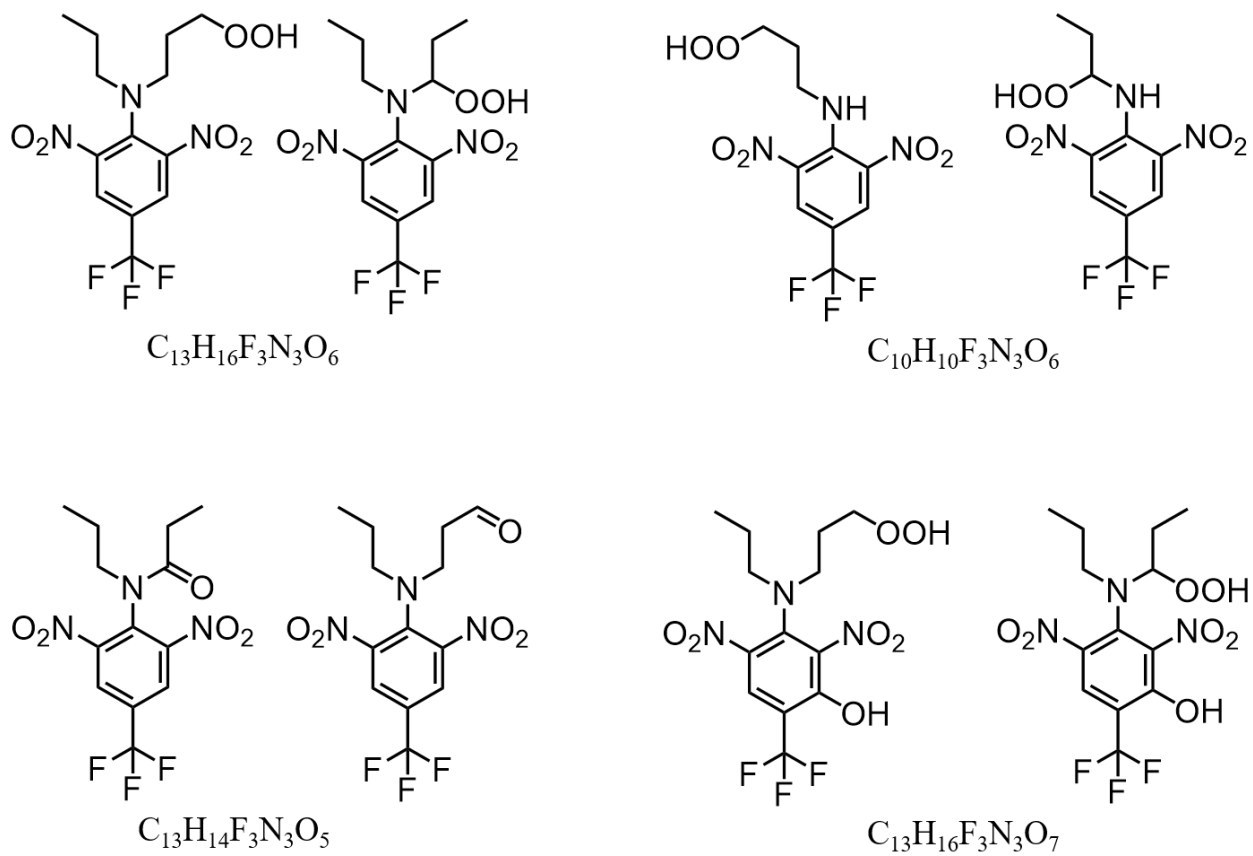
Figure A4.4. Possible isomers for trifluralin oxidation products presented in Scheme 5.1.