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RPPR Final Report
as of 27-Jun-2022

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INVESTIGATOR(S):

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Submitted By: Barbara Finlayson-Pitts Email: bjfinlay@uci.edu
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Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 2 **STEM Participants:** 2

Major Goals: The major goals were to elucidate environmentally relevant reactions of compounds that are structurally similar to insensitive munitions (IM). These data will provide a predictive capability that will facilitate defining the lifetimes and fates of both existing and proposed IM. The relevant structures include nitro-, amino- and alkene groups.

Accomplishments: The Xevo TQD triple quadrupole mass spectrometer with UPLC and a PDA (Waters) was acquired, set up, tested and applied in a wide variety of studies:

- Neonicotinoid pesticides (NN) contain many of the same functional groups and similar structures to IM. The photochemistry of two NN, dinotefuran and nitenpyram, was studied in the presence of a KBr matrix. Earlier studies had used thin films of the pure compounds but in actual usage, the NN are mixed at ~ 1-20% with a variety of surfactants, buffers, antioxidants and emulsifiers. It was not known how the presence of a matrix would affect the chemistry. The commercial formulations could not be studied in pure form for experimental reasons, so they were mixed with KBr and pressed into pellets that could be studied with transmission FTIR. For comparison, the pure compounds in KBr were also studied. These studies showed that the photochemistry of the NN was not affected by the presence of a matrix, so that results from experiments on the pure compounds could be extrapolated to environmental applications with confidence.
- Studies of the reactions of some NN (imidacloprid, dinotefuran and clothianidin) with the gas phase OH radical were carried out. The kinetics of these multiphase gas-solid reactions as well as the products were measured. The OH attack was mainly at the C-H groups in the NN, and the relative rates of loss were what is expected based on the relative reactivity of C-H groups from gas phase studies of alkanes. The absolute values of the reaction probabilities depend critically on the OH concentrations in the experiments. Studies are currently underway to measure these, but preliminary data suggest the reactions with OH will give lifetimes of the NN of a few days under typical atmospheric conditions.
- When the instrument was first installed, we had a collaborative opportunity to test the operational limits in a project involving the impacts of particulate matter (PM2.5) inhalation on reproductive parameters in mice. The aim of this collaboration was to develop a sensitive method to detect and quantify estradiol from ovaries of mice exposed to either clean air or concentrated PM2.5. The researchers had tried to use another instrument in our mass spectrometry facility to try to measure estradiol in exposed and control groups, but were not successful. For this analysis, an atmospheric pressure photo-ionization (APPI) source was used in combination with a derivatization step to achieve detection at the pg/mL level which couldn't be achieved using any other instrument available at the core mass spectrometry facility on campus.
- The instrument has been used routinely to quantify methanesulfonic acid (MSA), which is a strong acid formed

from the oxidation of dimethyl sulfide in air and which we have proposed may be an important contributor to new particle formation (NPF) in air when reacting with bases such as ammonia or small alkylamines. These airborne particles will eventually grow to become cloud condensation nuclei (diameter larger than 50-100 nm) by taking up surrounding molecules, and will ultimately affect cloud properties, visibility, climate and health. To elucidate the NPF potential of MSA, we studied its reaction with amines in presence or absence of water. The gas phase concentration of MSA as well as MSA present in the particles formed are measured using filter collection and subsequent extraction and analysis using the Acquity UPLC coupled with the Xevo TQD mass spectrometer. For this analysis, we designed a very sensitive method using the UPLC H Class Plus system coupled with electrospray ionization and tandem mass spectrometry (UPLC-ESI-MS/MS; Xevo TQD mass spectrometer; Waters) monitoring a specific MS transition for MSA (m/z 95 => 80, corresponding to CH3SO3- => SO3- ions). This method was a key analytical tool in undergraduate research projects investigating the reaction of MSA with methylamine, putrescine and monoethanolamine (an amine that is used in booming carbon capture technology).

- Studies of the kinetics and mechanisms of the reactions of model compounds for IM with ozone were carried out in both the liquid phase and the gas phase, as well as in one case at the gas-solid interface. Kinetics studies were carried out in the liquid phase using a stopped flow apparatus at temperatures from 278 to 298 K. Carbon tetrachloride was used as the solvent in order to prevent OH radical production from interaction of ozone with water or a hydrocarbon solvent. The compounds studied were 2-methyl-1-nitroprop-1-ene, 4-methyl-4-nitro-1-pentene, E-N,N-dimethyl-1-propenylamine, N,N-dimethylallylamine, 1-dimethylamino-2-nitroethylene and nitenpyram. It was found that a vinyl nitro group significantly increased the activation energy compared to the simple alkenes and decreased the room temperature rate constant by about three orders of magnitude. In contrast, an amino group on the C=C increased the rate constant by more than two orders of magnitude. When both nitro and amino groups are attached to the C=C, the rate constants were similar to those of the simple alkenes. Products identified by mass spectrometry and FTIR suggested the site of initial ozone attack on the C=C and/or amine depended on the structure. Toxic products such as N-nitroso compounds were formed. Kinetics and mechanisms for nitenpyram were similar to the model compounds containing the same moieties. Thus, these data on model compounds provide a predictive basis for assessing environmental fates of emerging contaminants containing these multifunctional groups.
- Ozonolysis rate constants in the gas phase follow a similar trend to those in the liquid phase, with a nitro group significantly decreasing the rate constant, an amino group increasing it and the two together providing a counterbalancing effect. Interestingly, the rate constants were significantly smaller than those in the liquid phase, which was attributed to increased stabilization of an ozone-alkene complex that goes on to form products in the condensed phase. In the gas phase, all of the products that were identified were consistent with attack on the C=C, with no evidence for attack on the amine group as was the case in the liquid phase for some of the compounds. However, again some of the products such as formaldehyde and dimethylformamide have known health effects.

Training Opportunities: A number of students and postdoctoral fellows were trained using this instrument: two graduate students (estradiol project, Kelli Marlot; neonicotinoids project, Annie Rohrbacher/Anderson), a visiting undergraduate student from the University of San Diego and a UCI senior honors student (new particle formation from the reaction of methanesulfonic acid and amines project; Kanuri Roundtree and Cathy Wong), and a post-doctoral fellow (oxidation of model compounds for emerging contaminants project; Xinke Wang). Four of these researchers are female and one is African American. In addition, a number of students from other research groups have worked with two project scientists in my group, Dr. Veronique Perraud and Dr. Lisa Wingen, to apply this instrument for measurements in their research projects.

Results Dissemination: Three papers have been published, two have been submitted and one is in preparation. Due to COVID, presentations at meetings that would normally have happened were curtailed.

Honors and Awards: The PI received several awards during this period:
- 2018 Polanyi Medal, Royal Society of Chemistry
- 2019 Environment Prize, Royal Society of Chemistry
- 2021 Woman of the Year, 74th Assembly District, California

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

RPPR Final Report
as of 27-Jun-2022

Participant Type: PD/PI
Participant: Barbara Finlayson-Pitts
Person Months Worked: 1.00 **Funding Support:**
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ARTICLES:

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Volume: 3 Issue: 1 First Page #:
Date Submitted: 6/25/22 12:00AM Date Published: 8/1/20 7:00AM
Publication Location:
Article Title: Open questions on the chemical composition of airborne particles
Authors: Barbara J. Finlayson-Pitts, Lisa M. Wingen, Véronique Perraud, Michael J. Ezell
Keywords: Airborne particles, new particle formation and growth, atmospheric aerosols
Abstract: Airborne particles have significant impacts on health, visibility and climate. An overview of what is known about particle chemical composition is presented, along with open questions and challenges that are central to relating composition to their life cycles and impacts.
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Publication Location:
Article Title: Probing Matrix Effects on the Heterogeneous Photochemistry of Neonicotinoid Pesticides, Dinotefuran and Nitenpyram
Authors: Andrea Rohrbacher, Michael J. Ezell, Véronique Perraud, Barbara J. Finlayson-Pitts
Keywords: neonicotinoid, photochemistry, dinotefuran, nitenpyram
Abstract: Emerging contaminants are of concern due to their rapidly increasing numbers and potential ecological and human health effects. In this study, the synergistic effects of the presence of multi-functional nitro, amino and carbon-carbon double bond (C=C) groups on the gas phase ozonolysis in O2 or at the air/solid interface were investigated using five simple model compounds. A multiphase kinetics model was used to probe the gas-solid kinetics. A nitro group attached to the C=C lowers the gas phase rate constant by two to three orders of magnitude compared to te simple alkenes, while amino groups have the opposite effect. The presence of both groups provides counterbalancing effects. Products with deleterious health effects including dimethylformamide and formaldehyde were identified. This study provides a basis for predicting the environmental fates of emerging contaminants, and shows that both the toxicity of both the parent compounds and the products should be taken into account.
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Volume: 19 Issue: 1 First Page #:
Date Submitted: 6/25/22 12:00AM Date Published: 1/1/22 8:00AM
Publication Location:
Article Title: Exposure to environmentally relevant concentrations of ambient fine particulate matter (PM2.5) depletes the ovarian follicle reserve and causes sex-dependent cardiovascular changes in apolipoprotein E null mice
Authors: Ulrike Luderer, Jinhwan Lim, Laura Ortiz, Johnny D. Nguyen, Joyce H. Shin, Barrett D. Allen, Lisa S. Lia
Keywords: PM2.5, mice, reproductive effects
Abstract: Effects of inhalation of fine particulate matter (PM2.5) on the finite ovarian follicle pool in mice exposed to PM2.5 was measured.Primordial, primary and secondary ovarian follicle numbers were decreased in exposed mice compared to controls, suggesting signifcant impacts of inhaled particles on the reproductive system in mice.
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Journal: PNAS
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Date Submitted: 6/25/22 12:00AM Date Published:
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Article Title: Predicting the Environmental Fates of Emerging Contaminants: Synergistic Effects of Multi-Functional Groups on Their Ozone Reactions
Authors: Xinke Wang, Weihong Wang, Lisa M. Wingen, Véronique Perraud, Michael J. Ezell, Jessica Gable, Tho
Keywords: emerging contaminants; amine; nitro; nitroenamine; ozonolysis
Abstract: Effects of inhalation of fine particulate matter (PM2.5) on the finite ovarian follicle pool in mice exposed to PM2.5 was measured.Primordial, primary and secondary ovarian follicle numbers were decreased in exposed mice compared to controls, suggesting signifcant impacts of inhaled particles on the reproductive system in mice.
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Journal: Journal of Physical Chemistry A
Publication Identifier Type: Publication Identifier:
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Date Submitted: 6/25/22 12:00AM Date Published:
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Article Title: Gas Phase and Gas-Solid Interface Ozonolysis of Nitrogen Containing Alkenes: Nitroalkenes, Enamines, and Nitroenamines
Authors: Weihong Wang, Xinke Wang, Pascale S. J. Lakey, Michael J. Ezell, Manabu Shiraiwa, Barbara J. Finlay
Keywords: nitroalkene, enamine, nitroenamine, ozonolysis, gas phase, air-solid interface
Abstract: Effects of inhalation of fine particulate matter (PM2.5) on the finite ovarian follicle pool in mice exposed to PM2.5 was measured.Primordial, primary and secondary ovarian follicle numbers were decreased in exposed mice compared to controls, suggesting signifcant impacts of inhaled particles on the reproductive system in mice.
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RPPR Final Report
as of 27-Jun-2022

Partners

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I certify that the information in the report is complete and accurate:
Signature: B. J. Finlayson-Pitts
Signature Date: 6/25/22 9:59PM

Major Goals:

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Dissemination:

Two papers have been published, two have been submitted and one is in preparation. Due to COVID, presentations at meetings that would normally have happened were curtailed.

Honors:

The PI received several awards during this period:

- 2018 Polanyi Medal, Royal Society of Chemistry
- 2019 Environment Prize, Royal Society of Chemistry
- 2021 Woman of the Year, 74th Assembly District, California

Tech Transfer:

Nothing to report.

Participants/collaborators:

Since this is an equipment grant, there was no direct participant support provided. However, the following people were directly involved in the equipment purchase, setup and training, as well as application in a number of projects:

Dr Veronique Perraud, Dr. Lisa Wingen, Dr. Xinke Wang, Dr Weihong Wang, Kellie Marlot, Andrea Rohrbacher/Anderson, Kanuri Roundtree, Cathy Wong, Michael Ezell, Barbara Finlayson-Pitts.