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Constraining Air Pollutant Emissions through in situ Measurement and Novel Instrumentation

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Constraining Air Pollutant Emissions through in situ Measurement and Novel Instrumentation

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Chemistry by James M. Brady

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2015
The Dissertation of James M. Brady is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

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Co-Chair

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University of California, San Diego

2015
DEDICATION

Dedicated to Helene, Bernie, Joseph, Matthew, and Michaela - for always keeping me grounded and their never-faltering love and support.
EPIGRAPH

Strength does not come from winning. Your struggles develop your strengths. When you go through hardships and decide not to surrender, that is strength.

Arnold Schwarzenegger
# TABLE OF CONTENTS

Signature Page ................................................................................................................... iii  
Dedication .......................................................................................................................... iv  
Epigraph .............................................................................................................................. v  
Table of Contents ............................................................................................................... vi  
List of Figures .................................................................................................................... xi  
List of Tables .................................................................................................................. xvii  
Acknowledgements ........................................................................................................ xviii  
Vita....................................................................................................................................... xxi  
Abstract of the Dissertation ........................................................................................... xxiii  

1. Introduction ................................................................................................................ 1  
   1.1 Air Pollutants within the Troposphere .............................................................. 1  
   1.2 Uncertainty within Current Knowledge ........................................................... 3  
      1.2.1 Organic Acids ................................................................................................. 3  
         1.2.1.1 Isocyanic Acid ........................................................................................... 4  
         1.2.1.2 Formic Acid ............................................................................................... 5  
      1.2.2 The Salton Sea ................................................................................................ 5  
      1.2.3 Aerosol Measurements within the Lower Troposphere .............................. 7  
   1.3 Synopsis of Chapters ....................................................................................... 7  
   1.4 References ........................................................................................................... 9  


2. Real-time emission factor measurements of isocyanic acid from light duty gasoline vehicles .................................................................................................................... 12
2.1 Abstract............................................................................................................. 12
2.2 Introduction....................................................................................................... 13
2.3 Experimental ..................................................................................................... 19
2.3.1 Test vehicle selection and operation............................................................. 19
2.3.2 Vehicle exhaust handling and dilution systems ............................................ 21
2.3.3 CIMS measurements of HNCO .................................................................... 22
2.3.4 HNCO source output quantification ............................................................. 23
2.3.5 Measurements of NOx, CO and CO₂ mixing ratios........................................ 25
2.4 Results ............................................................................................................... 27
2.4.1 Real-time mixing ratios ................................................................................. 27
2.4.2 Real-time HNCO fuel based emission factors .............................................. 30
2.5 Discussions ....................................................................................................... 34
2.5.1 Mechanism for HNCO production............................................................... 34
2.5.2 Comparison with previous studies HNCO vehicle emissions studies .......... 38
2.6 Acknowledgements ........................................................................................... 41
2.7 References ......................................................................................................... 42
3. On the primary emission of formic acid from light-duty gasoline vehicles and ocean-going vessels ................................................................................................. 45
3.1 Abstract............................................................................................................. 45
3.2 Introduction....................................................................................................... 46
3.3.1 CI-ToFMS measurements of formic acid .................................................. 50
3.3.2 Emission factor measurements from LDGVs ............................................... 50

3.3.2.1 Test vehicle selection and operation at the Haagen-Smit Laboratory ..... 50

3.3.2.3 Measurements of NOx, CO and CO2 mixing ratios at the Haagen-Smit Laboratory ........................................................................................................ 53

3.3.3 Ship Plume Intercepts during CalNex 2010 .................................................. 53

3.4 Results and Discussion ..................................................................................... 55

3.4.1 Real-time emission factor measurements from light duty gasoline vehicles 55

3.4.2 Determination of formic acid fuel-based emission factors from ocean-going vessels ........................................................................................................ 61

3.5 Conclusions ....................................................................................................... 66

3.6 Acknowledgements ........................................................................................... 67

3.7 References ......................................................................................................... 69

4. Assessing the impact of the Salton Sea on local and regional air quality .......... 74

4.1 Abstract............................................................................................................. 74

4.2 Introduction ....................................................................................................... 75

4.3 Methods............................................................................................................. 86

4.3.1 Long Term Monitoring Networks ................................................................. 86

4.3.1.1 California Irrigation Management Information System (CIMIS) Stations ........................................................................................................ 86

4.3.1.2 Environmental Protection Agency (EPA) Air Quality Monitoring Sites 86

4.3.1.3 Salton Sea Surface Area Coverage .......................................................... 89

4.3.2 Wind Trajectory Analyses ............................................................................ 89

4.4 Results and Discussion ..................................................................................... 90
4.4.1 Air Quality Impact of Decadal Changes in Salton Sea Surface Area........... 90

4.4.2 Air Quality Impact of Episodic Wind Events in Populated Coastal Communities................................................................................................................................. 99

4.5 Acknowledgements......................................................................................... 109

4.6 References....................................................................................................... 110

5. Novel Implementation of a Quadrotor Unmanned Aircraft System for Aerosol Concentration Measurements within the Boundary Layer ......................... 114

5.1 Abstract........................................................................................................... 114

5.2 Introduction..................................................................................................... 114

5.3 Methods......................................................................................................... 120

5.3.1 Drone Sampling Platform........................................................................... 120

5.3.2 Sensor Packaging........................................................................................ 124

5.4 Results and Discussion ................................................................................ 127

5.4.1 Performance of the Drone Sampling Platform......................................... 127

5.4.2 Surf-zone Aerosol Production................................................................. 130

5.4.3 Vertical and Horizontal Flight Profiles.................................................... 134

5.4.4 Surf-zone Particle Emission Rate ............................................................ 139

5.5 Conclusions.................................................................................................. 141

5.6 Acknowledgements....................................................................................... 142

5.7 References..................................................................................................... 143

6. Development of a Forward-scattering Autonomous Low-cost Compact Optical-particle-counter (FALCON)............................................................ 147
LIST OF FIGURES

Figure 2.1: A) Vehicle speed (grey) and relative catalyst temperature (red) for the first Chevrolet Cavalier test with the four phases of the drive cycle depicted. Phase 1 (P1) is the cold start phase, Phase 2 (P2) is the first hot stabilized phase, Phase 3 (P3) is the hard acceleration phase, and Phase 4 (P4) is the second hot stabilized phase. B) Mixing ratios for modeled CO (green) as well as CO2 measured (blue circles) and modeled (blue lines) after the secondary dilution system for the first Cavalier test. C) Mixing ratios for modeled NOx (pink) after the secondary dilution system. D) Real-time post-SDS mixing ratios of HNCO for the Cavalier for both test 1 (red) and test 2 (blue). All gas concentration data has been time corrected to account for residence time in the dilution system........................ 20

Figure 2.2: Schematic of experimental setup depicting the primary and secondary dilution stages, RTC, and relative sampling locations............................................ 22

Figure 2.3: Measured mixing ratios of CO2 (2.3A), CO (2.3C), and NOx (2.3E) in the PDS, as well as the measured CO2 (2.3,teal) mixing ratios after the SDS for the first day of testing for the Chevrolet Cavalier. Modeled mixing ratios of HNCO post-SDS are also shown for CO2 (2.3B), CO (2.3D), and NOx (2.3F)............................................................................. 26

Figure 2.4: Fuel-based, real-time HNCO emissions factors for both test 1 (red) and test 2 (blue) for: A) the Chrysler Grand Cherokee, B) the Chevrolet Cavalier, and C) the Chevrolet S-10 Pickup. The dashed lines represent the divides between the four previously defined phases of the drive cycle................................................................. 32

Figure 2.5: Median HNCO emissions factors (red) for both test 1 and test 2 of the eight light duty gasoline vehicles including mean FBEF (purple), the interquartile range, and the range of FBEF measured for: A) the cold start phase, B) the first hot stabilized phase, C) the hard acceleration phase, D) the second hot stabilized phase, and E) the overall test run. Fleet averages for the first test do not include contributions from the Pathfinder. Error bars represent the interquartile range.............................................................................. 33

Figure 2.6: Dependence of the post-SDS average HNCO mixing ratios for the eight vehicles tested plotted vs. the product of the average loadings of NOx and CO for both the first and second days of testing. The data are color-coded by drive phase shown in Fig. 2.1. ........................................................................................................................................... 38

Figure 2.7: Comparison of the mean light duty gasoline vehicle HNCO emissions for the overall Unified Cycle (UC) and the four respective phases of the UC (blue) to the emission factors determined by Wentzel et al. for a light duty diesel engine operating under steady state conditions representative of the FTP75, USO6 and HWFET drive cycles and the engine running under idling conditions (grey). Error bars represent standard deviations of
the mean value reported. The y-axis is depicted with a split scale, the first from 0-2 mg kg\textsubscript{fuel}\textsuperscript{-1} and second from 2-6 mg kg\textsubscript{fuel}\textsuperscript{-1}

Figure 3.1: A) Real-time mixing ratios of formic acid (black; detected at m/z = 45) for the first Chevrolet S-10 test as measured after the secondary dilution system (SDS). The shaded region represents the propagated uncertainty in the HCOOH mixing ratio. The percent of maximum catalytic converter temperature is shown in red (right axis). B) Mixing ratios of modelled CO (red) and measured CO\textsubscript{2} (blue) post-SDS, for the first S-10 test. The “cold start” period, defined as the first 300 s following engine start and the “hot running” period, defined as the last 450 s of the test are shown with gray bars above panel A.

Figure 3.2: R/V Atlantis (solid black) and Margrethe Maersk (solid gray) ship tracks on 25 May 2010 (UTC) during CalNex 2010. Margrethe Maersk plume (4x) are shown in red overlaid on the R/V Atlantis ship track. Formic acid (HCOOH) mixing ratios during the Margrethe Maersk plume intercepts on top of the R/V Atlantis ship track.

Figure 3.3: Formic acid (A) and CO\textsubscript{2} (B) mixing ratios during a plume intercept of the Margrethe Maersk cargo ship of the coast of Southern California (33.6393, -118.5402) on 26 May 2010 (3:37 UTC). The squares in each figure represent the mean HCOOH concentration over the 30 seconds before and after the plume intercept and the dashed lines represent the interpolated baseline.

Figure 3.4: Correlation of one second measurements of formic acid and CO\textsubscript{2} mixing ratios during a plume intercept of the Margrethe Maersk cargo ship of the coast of Southern California (33.6393, -118.5402) on 26 May 2010 (3:37 UTC).

Figure 3.5: Dependence of the formic acid fuel-based emission factor as function of: A) estimated ship plume age, B) average CO/CO\textsubscript{2} ratio in the ship plume. Error bars represent $1\sigma$ standard deviation. Ship plume intercepts are colored by vessel type: tanker (red), cargo (black), passenger (yellow).

Figure 4.1: Locations of the EPA maintained and CIMIS maintained sampling stations used in this study.

Figure 4.2: Depiction of the Salton Sea surface elevation relative to NGDV 1929 since October 1\textsuperscript{st}, 1987, recorded at USGS site 10254005. The seasonal changes in the physical size of the Salton Sea stemming from the dependence of the Sea on agriculturally driven inflows is observed. It is also important to note the relatively stable surface elevation of the Salton Sea from the late 1980s to late 1990s and the beginning of a decline in the lake’s surface elevation beginning in 2000.

Figure 4.3: Map depicting the 6% decrease in surface area coverage of the Salton Sea from maximum coverage in 1999 (black) to minimum coverage in 2014.
Figure 4.4: Schematic depiction of the typical thermal profile expected for the Salton Sea based off of surface and base temperatures measured in 1999 [Holdren & Montaño, 2002]. The Salton Sea experiences prolonged thermal stratification during the summer and early fall and is more uniformly mixed during the winter and early spring. 80

Figure 4.5: A) Schematic of a thermally stratified lake with the arrangement of the epilimnion, metalimnion, and hypolimnion shown. The generic profiles for the temperature (red), DO concentrations (purple), and concentrations of reduced substances, e.g. hydrogen sulfide or ammonium, (green) within the lake. B) Generic depiction of the expected upwelling of the water column at the downwind end, resulting in a redistribution of reduced substances and low DO throughout the water column. Figure reproduced from Marti-Cardona et al. (2008). 82

Figure 4.6: A) Decrease in surface area coverage of the Salton Sea since maximum coverage in 1999. Averaged monthly means of measurements of PM10 (B), PM2.5 (C) and ozone (D) measured at EPA monitoring stations located in the local vicinity of the Salton Sea from 2000 to 2014. 92

Figure 4.7: A) Estimated number of days in the year that 24-hour national (150 μg m-3) and California state (50 μg m-3) PM10 standards would have been exceeded had sampling occurred every day of the year. B) Estimated number of days in the year that the national 24-hour PM2.5 standard of 35 μg m-3 would have been exceeded had sampling occurred every day of that year. C) Number of days in each year that the maximum 8-hour average ozone concentration at each specific monitoring station was greater than or equal to the national standard of 0.075 ppm (circles) and the California state standard of 0.070 ppm. Data provided by the California Air Resources Board. 95

Figure 4.8: Annual time series of monthly averages ± 1σ for temperature (A), wind speed (B), PM10 (C), PM2.5 (D), and ozone (E) collected at EPA monitoring stations during 2014. For criteria pollutants PM10, PM2.5, and ozone the NAAQS standards are also depicted. 96

Figure 4.9: Dependence of PM10 (A) and PM2.5 (B) emissions on Salton Sea size over the past 15 years. 98

Figure 4.10: Occurrence of an anomalous high speed sustained wind event on the evening of September 9th, 2012. The wind event last ca. 2 hours with sustained wind speeds ca. 10-20 mph faster than typical wind events for that period. 100

Figure 4.11: Forward trajectory analysis model results for air parcel trajectories between September 9, 2012 at 23:00 and September 10, 2012 at 17:00, demonstrating a strong outflow from the Salton Sea into San Bernadino and Riverside counties following the wind event that took place on the evening of September 9th. The model trajectories were calculated using the NOAA HYPLIT Trajectory Model [Draxler and Rolph]. Each
trajectory is calculated as an 8 hour run, with new trajectories starting every 2 hours. Times within the figure legend correspond to UTC. ................................................................. 103

Figure 4.12: Hourly measurements (blue) of temperature (A), PM$_{10}$ (B), and ozone (C) taken on September 10$^{th}$, 2012 at the Indio monitoring station. The monthly average for the hour ± 1σ is also depicted in red. .............................................................................. 105

Figure 4.13: Hourly measurements (blue) of temperature (A), PM$_{10}$ (B), PM$_{2.5}$ (C), and ozone (D) taken on September 10$^{th}$, 2012 at the Palm Springs monitoring station. The monthly average for the hour ± 1σ is also depicted in red. ............................................. 106

Figure 4.14: Hourly measurements (blue) of temperature (A), PM$_{10}$ (B), PM$_{2.5}$ (C), and SO$_2$ (D) taken on September 10$^{th}$, 2012 at the Riverside monitoring station. The monthly average for the hour ± 1σ is also depicted in red. ........................................................... 107

Figure 5.1: UAV flight paths during a representative vertical flight plan (A) and a representative horizontal flight plan (B) adjacent to the Scripps Institution of Oceanography (SIO) pier in La Jolla, CA. Vertical flights extended from the surface to approximately 100m, while horizontal flight plans extended to approximately 120m offshore. Note: the image in this figure was taken at low tide that may not necessarily reflect the conditions reported here. ................................................................................ 122

Figure 5.2: A) Close-up photograph of the 3DR Iris+ drone and attached sampling platform. B) In-flight photograph of the 3DR Iris+ drone and sampling package returning to the home location. ....................................................................................................... 126

Figure 5.3: Dependence of flight time of the 3DR Iris+ on payload weight. Blue squares are flight durations based on 3DR specifications and the red square is based on the observed flight durations in this study for a 510g payload. ........................................................... 127

Figure 5.4: A) Altitude precision of the 3DR Iris+ drone relative to the programmed waypoint altitude for both replicates of Flight Plan A. B) Horizontal precision of the 3DR Iris+ drone relative to the programmed waypoint position for all vertical profile flights. ......................................................................................................................................... 129

Figure 5.5: Time series of particle concentrations reported in the miniOPC small particle channel (A; 0.5 μm < $d_p$ < 1μm) and large particle channels (B; $d_p$ > 1μm) as measured from the SIO beach (dark red and dark blue) and at the terminal end of the SIO pier (light red and light blue) on 30 July 2015. ........................................................................................................................ 130

Figure 5.6: Frequency distributions of small (0.5 μm < $d_p$ < 1.0 μm) and large ($d_p$ > 1.0 μm) particle concentrations from continuous measurements conducted from the end of the SIO pier (A, C) and from the beach at the base of the SIO pier (B, D) as measured on 30 July 2015. ........................................................................................................................................ 131
Figure 5.7: Time series of particle concentration measurements taken during mobile measurements that span the SIO pier on 28 July 2015. .................................................. 132

Figure 5.8: Correlation of small (0.5 \( \mu m < d_p < 1 \mu m \)) and large (\( d_p > 1 \mu m \)) particle measurements as measured during the pier walk sampling measurements shown in Figure 5.7. ...................................................................................................................... 134

Figure 5.9: Particle concentration measurements (1Hz) as measured during research flight 1, for the large (blue; 0.5 \( \mu m < d_p < 1 \mu m \)) and small (red; \( d_p > 1 \mu m \)) particle sampling bins. .................................................................................................................................................. 136

Figure 5.10: Mean particle concentrations (and \( \pm 1 \sigma \)) for the large (blue; 0.5 \( \mu m < d_p < 1 \mu m \)) and small (red; \( d_p > 1 \mu m \)) size channels averaged for all 13 of the vertical flights sampled during this study. ........................................................................................................................................ 137

Figure 5.11: Horizontal flight profiles depicting the small (A) and large (B) particle channel counts at 5, 10, 15 and 25 meters. The wave breaking area was located at approximately 40-50 meters from the starting location of the horizontal flights. ......................................................... 138

Figure 5.12: Vertical profiles of the average small (A) and large (B) particle channel counts \( \pm 1 \sigma \) located before (gray circles) and after (red or blue squares) the breaking waves. The vertical profile for outside the breaking waves was constructed from the horizontal measurements shown in Figure 5.11. .............................................................................................................................. 139

Figure 6.1: Top Average ambient particle size distribution in Pacific Beach, CA. Bottom Modeled fractional deposition of inhaled particles as a function of particle diameter in the nasopharyngeal an laryngeal, the tracheobronchial and the alveolar regions of the human respiratory tract during nasal breathing. Data from: ICRP 1994. ................................................. 150

Figure 6.2: Average aerosol number distribution (Figure 4.2A) collected with a DMT UHSAS during the 2013 SARP campaign during multiple missed approaches at Los Angeles International Airport. The corresponding mass distribution was calculated using an average density for urban aerosol of 1.5 g cm\(^{-3}\) [Geller et al., 2006]. .......................... 152

Figure 6.3: Location of existing FRM PM\(_{2.5}\) measurements in San Diego County. The five R&P Partisol-Plus 2025 samplers (red star) are utilized for regulatory monitoring, measuring PM\(_{2.5}\) at hourly time resolution at a minimum of once every three days. The two BAM samplers are non-regulatory, have an hourly time resolution, and measure PM\(_{2.5}\) daily. ............................................................................................................................................. 154

Figure 6.4: Number of standard deviations either above or below the mean total particle concentration for the sample region for grid cells of ca. 100m x 100m. Data shown is calculated from the mobile measurements in Pacific Beach (shown in Fig. 6.1). This equates to 113 sensors km\(^{-2} \). ................................................................................................................................. 156
Figure 6.5: Dependence of Mie scattering efficiency on particle diameter, calculated at both 405 nm (purple) and 780 nm (red) for a spherical particle with a refractive index (m) = 1.5 – 0i. ................................................................. 158

Figure 6.6: Dependence of Mie scattering efficiency on particle diameter, calculated at 405 nm for spherical particles with refractive indices of: 1) (NH₄)₂SO₄ (green triangles), 2) carbon (purple circles) and 3) organic carbon (red squares). ........................................ 159

Figure 6.7: Simple polar graphs of the scattering patterns for a 100 nm (A) and 250 nm (B) sphere with a refractive index of 1.521 - 0i. The sphere is located at the center of the polar plot and the light is incident from the left. ................................................................. 161

Figure 6.8: Schematic of the laser diode driver circuit that incorporates the feedback of the laser diode’s internal photodiode to stabilize the power output of the laser diode producing a constant power output from a passively cooled laser diode. ................................. 164

Figure 6.9: Aerial view schematic the second generation FALCON depicting the laser diode mount, optics mounts, baffle tube, and scattering cavity. The cavity is designed such that two 405-nm V-Coat N-BK7 windows isolate the scattering cavity to improve aerosol stream through the laser beam path. The lenses, apertures, and windows are marked and correspond to the parts presented in Table 6.2. ................................................................. 166

Figure 6.10: A schematic detailing the experimental set-up utilized in the detection efficiency calibrations. ................................................................................................................. 170

Figure 6.11: Size dependent detection efficiency for the FALCON (blue), redOPC (red), and Shinyei PPD-60PV (green, right axis). .................................................................................. 171

Figure 6.12: Time series of the inverted scattering signal produced by a 101-nm ammonium sulfate particle (Figure 6.12A) and that produced by a 238-nm ammonium sulfate particle (Figure 6.12B). ................................................................. 173

Figure 6.13: Size dependent relative pulse height distributions to the mean baseline (-2.14 V) for filtered room air and 101 nm, 180 nm and 238 nm ammonium sulfate. ........................................ 174

Figure 6.14: Size dependent average pulse height distributions ± 1σ to the mean baseline (-2.14 V) for 101 nm, 180 nm and 238 nm ammonium sulfate (blue squares). Dependence of Mie scattering efficiency on particle diameter, calculated at 405 nm for spherical particles with refractive indices of (NH₄)₂SO₄ (green triangles). ........................................ 176

Figure 6.15: Relative pulse height distributions to the mean baseline (-2.14 V) for 101 nm ammonium sulfate particles and 104 nm sodium chloride particles. ................................. 177
LIST OF TABLES

Table 2.1: Manufacturer, Model, and Year of the Eight Light Duty Gasoline Vehicles Tested.......................................................................................................................................................... 18

Table 2.2: Mean HNCO Emissions Factors and Diluted Mixing Ratios of HNCO, CO, CO₂, and NOₓ for each vehicle test, with the 1σ standard deviation included in the parenthesis. The propagated uncertainty for the HNCO emissions factor is between 45-49%........... 29

Table 3.1: Manufacturer, model, and year of the eight light duty gasoline vehicles tested. ........................................................................................................................................... 49

Table 3.2: Formic acid (HCOOH) fuel-based emission factors and emission ratios for eight light duty gasoline vehicles during the “cold start” and the “hot running drive phase..... 56

Table 3.3: Formic acid (HCOOH) fuel-based emission factors for 12 ship plume intercepts as measured from the R/V Atlantis during the CalNex 2010 field campaign. .............. 64

Table 5.1: Flight plans for the 4 vertical flight profiles that were utilized during this study........................................................................................................................................... 123

Table 5.2: The average meteorological and swell conditions for each individual flight........................................................................................................................................... 135

Table 6.1: Currently available inexpensive, miniature instruments and sensors available for particle counting and the particle diameter based size range and resolution for each. ...................................................................................................................... 157

Table 6.2: Specific part descriptions and cost for complete build of the second generation FALCON (Figure 6.8). ...................................................................................................................... 167
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Constraining Air Pollutant Emissions Through in situ Measurement and Novel Instrumentation

by

James M. Brady

Doctor of Philosophy in Chemistry

University of California, San Diego, 2015

Professor Timothy Bertram, Chair
Professor Kimberly Prather, Co-Chair

Constraining air pollutant emissions is critical to assessing their impact on climate and public health and developing regulations to mitigate those effects. Despite all of the work done in atmospheric chemistry to date, there still exists significant uncertainties in emission inventories that can be addressed through direct measurement and study. While some emissions can be investigated with current instrumentation and technology, characterizing emissions in other areas is limited by the current sampling methods. This
dissertation aims to contribute to advancing the current emissions inventories through both direct measurement and study of specific emission sources, as well as the development of novel instrumentation and technology to provide a solution to current sampling method needs.

The first section of this work focuses on investigating the emission of two specific organic acids from mobile sources. Emission of the potentially toxic trace gas isocyanic acid (HNCO) from light duty gasoline-powered vehicles (LDGVs) is investigated. The first real-time emission factor measurements for HNCO from a fleet of eight LDGVs are presented. In addition, this work also focuses on constraining the emissions factor of formic acid, one of the most abundant and ubiquitous organic acids in the atmosphere, for both LDGVs and ocean-going vessels. The second section of this dissertation assesses the impact of the Salton Sea, California’s largest body of water, on local and regional air quality. The impacts of the decrease in the size of the Salton Sea over the last 15 years and episodic, high-speed, sustained wind events at the Salton Sea are assessed. Finally, this work presents new advances in technology to close some of the current gaps in the existing sampling methods for aerosol measurement within the boundary layer. The novel implementation of a quadrotor unmanned aircraft system (UAS) drone and a custom sensor package is presented and utilized to generate vertical aerosol concentration profiles between 5 and 100 meters above sea level. The development of a novel small scale instrument for sizing and counting aerosol as small as 80 nm in diameter is also presented.
1. **Introduction**

1.1 **Air Pollutants within the Troposphere**

Earth’s atmosphere is a complex mixture of gases and aerosol particles, where the chemical composition of the atmosphere can vary on fine spatial and temporal scales. The vertical structure of the atmosphere is segmented into distinct layers set by the temperature profile of the atmosphere, with the lowest layer of the atmosphere classified as the troposphere. The troposphere is characterized by a decrease temperature with height and rapid vertical mixing, ranging in height from 10 to 15 kilometers in altitude depending on the latitude and time of year. Despite constituting only a small portion of the total height of the atmosphere, the troposphere contains 80% of the atmosphere’s mass and considering it is the closest layer to and interacts directly with the Earth’s surface, the troposphere is a region of specific interest to air quality. Although the bulk composition of the atmosphere remains nearly constant both spatially and temporally, comprised primarily of nitrogen (78%), oxygen (20.9%), argon (0.934%), and carbon dioxide (0.04%), trace gases and aerosol particles that comprise the remaining less than 1% of the atmosphere can have strong influences on climate and public health. Arising from both anthropogenic and natural sources, trace gases and aerosols present at concentrations higher than in the natural atmosphere with a potential for short- and/or long-term adverse effects are defined here as air pollutants. Developing a more complete understanding of the factors that control the concentrations and ultimate impact of air pollutants within the troposphere is a central driving force behind current atmospheric research.
Within the United States, the Environmental Protection Agency (EPA) under the direction of the Clean Air Act (CAA) aims to improve local and regional air quality through regulation of emissions. While ubiquitous air quality monitoring is impossible, the EPA has devoted significant efforts to developing air quality models that are used as tools for tracking trends, monitoring compliance, and making policy decisions [EPA]. Regional and global atmospheric chemistry models seek to investigate the role air pollutants play in and the impact air pollutants have on climate and public health. The dynamic nature of the atmosphere and the constant exchange and chemical processing with which air pollutants are subjected within the troposphere present a significant challenge to air quality models. Atmospheric chemistry aims to develop a quantitative understanding of how the concentrations of these air pollutants depend on emissions, transport, chemistry, and deposition within the troposphere. Regardless of the model’s spatial scale, if the troposphere is considered as a box model, the concentrations of the air pollutants within the box are controlled by emissions, transport, chemistry, and deposition of the pollutants within the model. Emissions control the initial flux of pollutants and their precursors into the troposphere and can originate from both anthropogenic and natural sources. Once in the atmosphere, trace gases and aerosol undergo chemical reaction and physical processing, leading to the formation and/or transformation of trace gases in the atmosphere. Within the troposphere, species are subject to vertical and horizontal transport. It is only through understanding all four processes that the concentrations of the species in air quality and climate models are fully constrained. As the collective knowledge of these four processes develops, the degree to which models can accurately predict the fate and impact of a particular pollutant within a given region improves. Although there is currently a great
deal of research dedicated to understanding the chemical processing that some air pollutants undergo within the troposphere, the emission inventories for a great deal of air pollutants is still lacking. In this work, I aim to contribute to the current understanding of primary emissions for both trace gases and aerosols by directly constraining the emission factors for gas-phase organic acids, investigating the impact of emissions from the Salton Sea on local and regional air quality, and developing both a novel sampling platform and a novel sizing instrument for improved measurements of aerosol emission.

1.2 Uncertainty within Current Knowledge

1.2.1 Organic Acids

Investigation of air pollution with regards to its sources, transport, and fate in the atmosphere is a significant area of environmental and atmospheric interest and while the number of individual air pollutants is vast, atmospheric organic acids are a category of specific emerging interest. Although strong inorganic acids, such as sulfuric and nitric acids, have been investigated extensively, investigations of organic acids are still emerging [Paulot et al., 2011; Khare, P. et al., 1999; Khwaja, 1995] Determining and constraining the sources of organic acids to atmosphere is critical for understanding their respective roles in a variety of atmospheric processes, such as secondary organic aerosol production, as well as the influence of these acids on air quality and public health. Arising from both anthropogenic and biogenic sources, organic acids are prevalent in a host of diverse environments, and characterizing the sources of these acids is of particular importance when modeling their effects on the environments in which they are emitted. With the
modern day growth and expansion of metropolitan areas there has been an increasing drive
to characterize and understand the role of atmospheric acids in urban environments.

1.2.1.1 Isocyanic Acid

Isocyanic acid (HNCO) is an acid of recent developing interest in the
characterization of urban emissions. The toxicity of isocyanates was demonstrated on a
large scale in Bhopal, India where the accidental release of highly concentrated methyl
isocyanate, CH₃NCO, killed thousands and injured hundreds of thousands [Mishra et al.,
2009]. Recent work has demonstrated the presence of HNCO in urban emissions, however
the sources of these emissions are not well characterized [Roberts et al., 2011; Wentzell et
al., 2013; Young et al., 2012]. Several controlled laboratory studies have observed the
formation of HNCO as a result of various forms of combustion, including biomass burning
and cigarette smoking [Roberts et al., 2011; Veres et al., 2010; Roberts et al., 2010].
Despite the abundance of automobiles in urban environments and the significant role of
vehicle emissions as a primary source of urban pollution, actual vehicle emission factors
(EFs) for HNCO are lacking [Wentzell et al., 2013; Austin et al., 1993]. In assessing an
urban environment’s potential risk of harmful exposure to HNCO as a result of vehicular
exhaust emissions, it is critical to determine EFs for HNCO using sensitive and selective
measurements of vehicle exhaust. HNCO EFs for light duty diesel vehicles have been
reported, however light duty gasoline vehicles (LDGVs) are not well characterized
[Wentzell et al., 2013]. To better constrain air quality model predictions of HNCO
emissions, a more complete inventory of vehicle based EFs is necessary, requiring the
measurement of EFs for light duty gasoline vehicles to be made.
1.2.1.2 Formic Acid

Formic acid (HCOOH) is among one of the most ubiquitous and abundant trace gases in the atmosphere and provides a significant contribution to the acidity of the troposphere [Paulot et al., 2011]. Produced by both primary and secondary anthropogenic and natural sources, measurements of the isotopic composition of HCOOH demonstrate a primarily modern carbon composition, consistent with major biogenic and biomass burning sources [Paulot et al., 2011; Glasius et al., 2000; Glasius et al., 2001]. Despite the abundance of formic acid in the troposphere, the sources of formic acid are still poorly understood and the emission sources are currently underestimated relative to reported measurements [Paulot et al., 2011; Ito et al., 2007]. Current constraints on HCOOH emissions from mobile vehicles are solely derived from measurements of the emission ratios of HCOOH relative to carbon monoxide performed in a bridge and tunnel study prior to 1988 [Talbot et al., 1998]. Since that time substantial changes in fuel composition and emissions control technology have occurred, yet there are no current experimental constraints on the HCOOH emissions rate from modern LDGVs. In addition, there are no experimental constraints on the emission rates of organic acids from ocean-going vessels. A more detailed knowledge of the contribution of both mobile vehicles and ocean-going vessels will further constrain our current formic acid emissions inventory and improve the current gap between measured and modeled formic acid concentrations in the troposphere.

1.2.2 The Salton Sea

The Salton Sea is a man-made, highly saline, terminal lake located in southern California. Since its initial formation in 1905 the Salton Sea has undergone significant
changes in both size and composition [Schroeder et al., 2002; Watts et al., 2001], prompting significant interest over the past decade in determining how biogeochemical changes in the Salton Sea may impact air quality in Southeastern California. The Salton Sea primarily serves as a sump for agricultural wastewater for the Imperial and Coachella valleys and as a result experiences high nutrient loadings, high algal biomass, high fish productivity, low clarity, frequent periods of anoxia, periods of strong thermal stratification, massive fish kills, and noxious odors [Holdren & Montaño, 2002]. While the majority of research regarding the Salton Sea has focused on issues regarding water quality, there are, to the best of our knowledge, very few published studies regarding the potential impact of the Salton Sea on local and regional air quality. In addition to the potential source for trace gases and aerosols out of the Salton Sea itself, drastic reductions in the Salton Sea’s size are expected to occur beginning in 2017 as a result of water transfers out of the Coachella and Imperial valleys to urban users. With the expected drastic decline in the Salton Sea’s size, there is rising concern over the potential threat the newly exposed lakebed poses to air quality. Current research regarding the threat the exposed lakebed may pose to local and regional air quality are limited to a few studies investigating the potential of dust emissions from various surface types at the Salton Sea [King et al., 2011; Buck et al., 2011]. Again, to our knowledge, there have been no long term, published studies investigating the potential effects a decrease in the size of the Salton Sea may have on air quality. Constituting the largest lake in California, the Salton Sea presents a potentially significant source of trace gas and aerosols to the troposphere that has yet to be fully constrained.
1.2.3 Aerosol Measurements within the Lower Troposphere

Aerosol particles are generated from natural and anthropogenic sources and can have significant impacts on public health and climate [Pöschl, 2005]. The emissions, chemical processing, physical transformations, and deposition of aerosol particles have been extensively studied with ground-based, aircraft and satellite remote sensing techniques. However, despite all of the studies to date, large uncertainties still remain in our understanding of the spatial and temporal variability of particle concentrations on the city-scale as well the vertical distribution of aerosol particles within the lower troposphere [Deshler, 2008; Ma & Yu, 2014]. The ability to measure the spatial and temporal variability of aerosols within the lower 300m of the troposphere is currently limited by the sampling platforms with which measurements are made. Currently the accuracy with which we are capable of predicting how changes in emissions at the surface will impact particle number and mass distributions within the troposphere is negatively impacted by the uncertainty that results from our lack of knowledge of the highly temporal and spatial variability that exists in the concentration, composition, and size distributions of aerosol particles in the lower troposphere [Pöschl, 2005; IPCC, 2007].

1.3 Synopsis of Chapters

The aim of this dissertation is to contribute to the current understanding of emission sources for both trace gases and aerosols through three distinct avenues of study. The first investigates direct measurements of organic acid emission from mobile sources. In the second part of this work I investigate the impact the Salton Sea, a potentially significant, yet unconstrained point emission source, has had on local and regional air quality. The
final portion of this work focuses on developing a novel sampling platform and a novel sizing instrument for improved measurements of aerosol emission within the lower troposphere.

Chapters 2 & 3 address the emission sources of organic acids into the troposphere. Chapter 2 reports the real-time first measurement of HNCO in the exhaust of light-duty gasoline vehicles (LDGVs) and investigates the dependence of HNCO emissions on the drive cycle of the vehicle. We report the first fuel-based emission factor (FBEF) for LDGVs and compare to previously reported FBEFs for diesel vehicles. Chapter 3 compares the emission of HCOOH from LDGVs and ocean-going vessels, reporting FBEFs for each mode of transportation.

Chapter 4 investigates the potential impact of the Salton Sea on local and regional air quality. Using publicly accessible datasets from air quality monitoring stations in the areas surrounding the Salton Sea we address the impact of the Salton Sea’s decreasing size on local air quality. In addition to addressing the potential impact of the Salton Sea’s size on air quality, we also address the impact of episodic high wind events at the Salton Sea on the air quality of both the local region and that of San Bernadino and Riverside counties.

Chapter 5 & 6 focus on the development of both a novel sampling platform and a novel sizing instrument to allow for improved aerosol measurements within the lower troposphere. Chapter 5 demonstrates a novel use of a quadrotor unmanned aircraft system (UAS) drone as a sampling platform for measurements of trace gas and aerosol within the boundary layer. In chapter 6 we focus on the development of a novel miniature sizing instrument capable of accurately counting and sizing particles in the size range between $0.1 < d_p < 1 \mu m$. 
1.4 References


2. Real-time emission factor measurements of isocyanic acid from light duty gasoline vehicles

2.1 Abstract

Exposure to gas-phase isocyanic acid (HNCO) has been previously shown to be associated with the development of atherosclerosis, cataracts and rheumatoid arthritis. As such, accurate emission inventories for HNCO are critical for modelling the spatial and temporal distribution of HNCO on a regional and global scale. To date, HNCO emission rates from light duty gasoline vehicles, operated under driving conditions, have not been determined. Here, we present the first measurements of real-time emission factors of isocyanic acid from a fleet of eight light duty gasoline-powered vehicles (LDGVs) tested on a chassis dynamometer using the Unified Driving Cycle (UC) at the California Air Resources Board (CARB) Haagen-Smit test facility, all of which were equipped with three-way catalytic converters. HNCO emissions were observed from all vehicles, in contrast to the idealized laboratory measurements. We report the tested fleet averaged HNCO emission factors, which depend strongly on the phase of the drive cycle; ranging from $0.46 \pm 0.13 \text{ mg kg}_{\text{fuel}}^{-1}$ during engine start to $1.70 \pm 1.77 \text{ mg kg}_{\text{fuel}}^{-1}$ during hard acceleration after the engine and catalytic converter were warm. The tested 8-car fleet average fuel based HNCO emission factor was $0.91 \pm 0.58 \text{ mg kg}_{\text{fuel}}^{-1}$, within the range previously estimated for light duty diesel-powered vehicles ($0.21-3.96 \text{ mg kg}_{\text{fuel}}^{-1}$). Our results suggest that HNCO emissions from LDGVs represent a significant emission source in urban areas that should be accounted for in global and regional models.
2.2 Introduction

Laboratory investigations have shown that cyanate anions (NCO⁻) can effectively modify protein structure and function through carbamylation of amino acid residuals [Wang et al., 2007]. Carbamylation of proteins by NCO⁻ has been implicated in several negative health effects ranging from cardiovascular and ocular impairments, to chronic diseases such as rheumatoid arthritis [Wang et al., 2007; Roberts et al., 2011; Lee et al., 1973; Mydel et al., 2010]. Recently, Roberts et al. reported the first atmospheric measurements of gas-phase isocyanic acid (HNCO), as well as showing that HNCO mixing ratios greater than 1 ppbv are high enough to cause protein carbamylation following accommodation and subsequent dissociation of HNCO into the blood stream [Roberts et al., 2011].

Real-time atmospheric measurements of HNCO mixing ratios are rare, thus limiting our ability to properly constrain HNCO sources and loss rates. The in situ measurements of Roberts et al. indicate that HNCO mixing ratios can exceed 200 pptv in air influenced by recent biomass burning, confirming laboratory investigations of HNCO production during the combustion and pyrolysis of nitrogen containing biomass (e.g. proteins) [Roberts et al., 2010; Hansson et al., 2004]. In the same publication, HNCO mixing ratios peaking at 100 pptv, and displaying strong diel variation, were reported for air sampled in Pasadena, CA during spring 2010. The sources of HNCO in Pasadena are less well understood, but have been hypothesized to be photochemical, potentially involving the oxidation of precursor amines and amides [Roberts et al., 2011; Borduas et al., 2013]. Recently, Wentzell et al. reported ambient HNCO mixing ratios in Toronto, ON., and demonstrated HNCO is highly correlated with benzene, suggesting a vehicular,
fuel combustion source [Wentzell et al., 2013]. To the best of our knowledge, these are the only published measurements of atmospheric HNCO mixing ratios.

Laboratory efforts have focused on determining emission factors or ratios for HNCO from a variety of combustions sources. Roberts et al. reported the first measurements of HNCO emissions from controlled biomass burning experiments, where the HNCO/CO ratios ranged between 0.1-0.6% during flaming stages of combustion and dropped by a factor of 5-10 during the smoldering stages [Roberts et al., 2011]. When scaled globally, biomass burning emissions of HNCO are estimated to be as large as 1.5 Tg yr⁻¹ [Young et al., 2012]. The atmospheric measurements of Wentzel et al. imply that vehicular emissions of HNCO are large, and could potentially surpass biomass burning emissions on a global scale. Wentzell et al. quantified HNCO emissions factors for a single light-duty diesel-powered engine, representative of light duty diesel-powered vehicles (LDDV) operating under 4 different steady-state driving modes [Wentzell et al., 2013], showing fuel based HNCO emission factors ranging between 0.21-3.96 mg kg⁻¹ fuel⁻¹. Further, HNCO emissions from diesel urea selective catalytic reduction (SCR) exhaust systems represent another potentially significant HNCO source. Average fuel based HNCO emissions factors for a diesel engine operating on the ISO8178/4 C1 cycle range from ca. 3.3 mg kg⁻¹ fuel⁻¹ when measuring direct engine exhaust, to 21.8-30.4 mg kg⁻¹ fuel⁻¹ when a combined diesel particle filter-deNOₓ system (DPN) is utilized. With the inclusion of the DPN in the exhaust line, the HNCO emission factor has a strong dependence on the amount of urea supplied to the system [Heeb et al., 2012; Heeb et al., 2011].

To date, there are no direct determinations of emission factors for HNCO from light-duty gasoline-powered vehicles (LDGVs), despite the fact that in 2009 on-road
gasoline vehicles accounted for the emission of 34,199 Gg of carbon monoxide (CO), an important precursor for HNCO in engines, in the US as compared to 524 Gg of CO emitted from on-road diesel vehicles [EPA, 2013]. On-road gasoline-powered passenger cars and light-duty trucks accounted for 32,666 Gg of the emitted CO, while diesel powered passenger cars and light-duty trucks specifically account for only 7 Gg of the total emitted CO [EPA, 2013]. Laboratory studies using FTIR to investigate the reactions of a tertiary gas mixture comprised of nitric oxide (NO), CO, and either hydrogen gas (H₂) or ammonia (NH₃) over precious metal catalysts have been used as proxy systems for LDGV engines and the associated catalytic converter systems. These laboratory measurements place an upper limit on the mixing ratios of HNCO emitted from LDGVs of 20 ppmv, the detection limit for the FTIR instrument used [Cant et al., 2003]. Mechanistically, these studies indicate that HNCO is formed in high yield when NO, CO, and either H₂ or NH₃ are reacted over precious metal catalysts (e.g., platinum, palladium, or rhodium) that are typically used in modern three-way catalytic converters (TWC) [Dümpelmann et al., 1995; Cant et al., 2000; Chambers et al., 2001; Cant et al., 2005].

The production of HNCO on precious metal catalysts is proposed to occur through the reaction between surface bound hydrogen atoms and NCO, where NCO comes from surface reactions involving adsorbed NO and CO [Cant et al., 2004]. The reactions proceed as follows, where surface bound species are denoted by (*) and surface sites are neglected.

\[
NO_{(g)} \rightleftharpoons *NO \rightarrow *N + *O \quad \text{(R1)}
\]

\[
CO_{(g)} \rightleftharpoons *CO \quad \text{(R2)}
\]

\[
*N + *CO \rightleftharpoons *NCO \quad \text{(R3)}
\]
The surface bound hydrogen can arise from either the dissociation of \( \text{H}_2 \) (R4) or \( \text{NH}_3 \) (R5) on the catalyst surface.

\[
\text{H}_2(g) \rightleftharpoons 2H^* \quad \text{(R4)}
\]

\[
\text{NH}_3(g) \rightarrow \text{*NH}_3 \rightleftharpoons \text{*NH}_2 + \text{H}^* \rightleftharpoons \text{*NH} + 2\text{H}^* \rightleftharpoons \text{*N} + 3\text{H}^* \quad \text{(R5)}
\]

For platinum catalysts the production of HNCO commences at relatively low temperatures, ca. 150°C, arising from reaction of NCO groups with adsorbed hydrogen [Chambers et al., 2001]. As the catalyst temperature increases, \( \text{H}_2 \) produced by the engine is consumed, and the majority of the surface bound hydrogen is formed following \( \text{NH}_3 \) dissociation. For the palladium catalyst, the production of HNCO commences at 235 °C, with surface bound hydrogen forming primarily from \( \text{NH}_3 \) [Chambers et al., 2001]. The different behavior of the two metals has been attributed to the relative adsorption strengths of CO and NO adsorption on the surface of each catalyst.

The surface bound hydrogen atoms and NCO groups react to form HNCO, which desorbs from the surface as HNCO(g) (R6).

\[
H^* + \text{*NCO} \rightarrow \text{HNCO(g)} \quad \text{(R6)}
\]

For the lower temperature regimes and typical of platinum-based catalytic converters, the production of HNCO can be summarized as:

\[
\text{NO} + \text{CO} + 1.5\text{H}_2 \rightarrow \text{HNCO} + \text{H}_2\text{O} \quad \text{(R7)}
\]

while at higher temperature regimes and typical of palladium catalyst the generalized reaction is:

\[
2\text{NO} + \text{NH}_3 + 5\text{CO} \rightarrow 3\text{HNCO} + 2\text{CO}_2 \quad \text{(R8)}
\]

The highest HNCO yield for R7 is observed over a silicon supported platinum catalyst (Pt/SiO2), peaking at 41% of the reacted nitrogen. The peak yield for HNCO from
R8 over a silicon oxide supported platinum catalyst is 70% of the reacted nitrogen, with the yield over a silicon oxide supported palladium catalyst reaching 46% of the reacted nitrogen.

Despite the relatively high yields of HNCO from nitrogen on the catalyst surfaces present in a modern TWC, a rapid and complete hydrolysis of HNCO has been suggested to occur (R9) on the oxide washcoat of the TWC, effectively removing HNCO from the exhaust [Dümpelmann et al., 1995; Cant et al., 2000; Chambers et al., 2001; Cant et al., 2005].

\[ HNCO + H_2O \rightarrow NH_3 + CO_2 \]  \hspace{1cm} (R9)

These studies suggest that the water concentration in the engine exhaust of a typical LDGV is sufficiently high such that any HNCO formed on the catalyst will be completely hydrolyzed on the washcoat before the exhaust can exit through the pores of the catalytic converter [Dümpelmann et al., 1995; Cant et al., 2000; Chambers et al., 2001; Cant et al., 2005]. If true, this would indicate that modern LDGVs would emit negligible concentrations of HNCO. However, while catalyst studies provide unique mechanistic information on the production and loss within an ideal catalytic converter, they do not provide constraints for the emission factors of HNCO from actual LDGVs and the associated range of catalytic converter functionality under a variety of real-world driving conditions.

Here, we report the first measurements of real-time, fuel-based HNCO emission factors from light duty gasoline vehicles. In this study, a fleet of eight LDGVs were driven under the California Unified driving cycle (UC) at the California Air Resources Board’s (CARB) Haagen-Smit Laboratory (HSL), where HNCO, CO and CO₂ were detected in
real-time in the diluted exhaust. The LDGVs were requisitioned by CARB from the current on-road vehicle fleet (Table 2.1). HNCO mixing ratios were determined via chemical ionization, time-of-flight mass spectrometry (CI-TOFMS) at 2 Hz, allowing for real-time measurement of HNCO mixing ratios throughout the drive cycle. In addition, the simultaneous measurement of CO and CO₂ allow for real-time fuel based emissions factors (FBEFs) to be calculated for the overall drive cycle, as well as for four specific phases of the UC as characterized by the catalytic converter temperature. The results indicate that HNCO production is highly dependent on the drive cycle and consequently on the efficiency with which the catalytic converter operates. This study establishes fuel based emissions factors for HNCO from LDGVs, while simultaneously providing a unique insight into the drive cycle dependency of HNCO emissions.

Table 2.1: Manufacturer, Model, and Year of the Eight Light Duty Gasoline Vehicles Tested

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Model</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chevrolet</td>
<td>Cavalier</td>
<td>2001</td>
</tr>
<tr>
<td>Chevrolet</td>
<td>S-10</td>
<td>2002</td>
</tr>
<tr>
<td>Chrysler</td>
<td>Grand Cherokee</td>
<td>2002</td>
</tr>
<tr>
<td>Nissan</td>
<td>Pathfinder</td>
<td>2003</td>
</tr>
<tr>
<td>Toyota</td>
<td>Solara</td>
<td>2003</td>
</tr>
<tr>
<td>Toyota</td>
<td>Tacoma</td>
<td>2003</td>
</tr>
<tr>
<td>Ford</td>
<td>Taurus</td>
<td>1997</td>
</tr>
<tr>
<td>Ford</td>
<td>Windstar</td>
<td>1998</td>
</tr>
</tbody>
</table>
2.3 Experimental

2.3.1 Test vehicle selection and operation

The eight LDGVs tested here were sequestered from the current on-road fleet by the CARB and all met the current California vehicle emissions standards set by the LEV emission requirements. Before each day of testing, the eight LDGVs were stored overnight with a nominal cold soak engine temperature of 24 °C. The vehicles were then placed on a chassis dynamometer and driven according to the UC (Fig. 2.1.A). The UC is representative of a typical twenty minute trip taken by a California driver and is more aggressive than the current federal test procedure urban drive cycle, FTP-75 [Austen et al., 1993]. Each vehicle was driven under ambient conditions twice, with the exception of the Ford Windstar which was driven through the entire drive cycle only once due to an operation malfunction during the first day of testing.
Figure 2.1: A) Vehicle speed (grey) and relative catalyst temperature (red) for the first Chevrolet Cavalier test with the four phases of the drive cycle depicted. Phase 1 (P1) is the cold start phase, Phase 2 (P2) is the first hot stabilized phase, Phase 3 (P3) is the hard acceleration phase, and Phase 4 (P4) is the second hot stabilized phase. B) Mixing ratios for modeled CO (green) as well as CO\textsubscript{2} measured (blue circles) and modeled (blue lines) after the secondary dilution system for the first Cavalier test. C) Mixing ratios for modeled NO\textsubscript{x} (pink) after the secondary dilution system. D) Real-time post-SDS mixing ratios of HNCO for the Cavalier for both test 1 (red) and test 2 (blue). All gas concentration data has been time corrected to account for residence time in the dilution system.
2.3.2 Vehicle exhaust handling and dilution systems

The vehicle exhaust was sampled directly from the vehicle tailpipe and diluted in two stages prior to measurement. The exhaust dilution system has been described in detail elsewhere [Robert et al., 2007], and is only summarized briefly here. The primary dilution stage consisted of a standard constant volume sampler (CVS), operated by CARB, which fed directly into a secondary stainless steel dilution system (SDS) [Robert et al., 2007], achieving a total dilution factor of ca. 80. Secondary dilution air passed through a pre-filter, activated carbon, and a high-efficiency particulate air (HEPA) filter. Following dilution in a turbulent mixing chamber the sample was aged for approximately 60 seconds in a 0.10-m³ stainless steel residence time chamber (RTC) and then sub-sampled by the CI-TOFMS through a 2.24 meter long piece of perfluoroalkoxy (PFA) tubing with a 3.175 millimeter inner diameter. The transit time of the vehicle exhaust from tailpipe to instrument was ca. 80 seconds. A detailed schematic of the experimental setup is shown in Fig. 2.2.
2.3.3 CIMS measurements of HNCO

HNCO was detected in real-time using a chemical ionization time-of-flight mass spectrometer (CI-TOFMS). The instrument used here has been previously described for the detection of gas-phase formic acid \cite{Bertram2011} and details of acetate ion chemistry for the detection of HNCO can be found in Veres et al., \citeyear{Veres2010}. Here, we briefly describe the same instrument applied to the detection of gas-phase HNCO with additional details provided in the SI. The sample flow entering the CI-TOFMS ion-molecule reaction region (IMR) was restricted to 1.7 L min\(^{-1}\) using a critical orifice, with the remaining flow pulled through a sample bypass line. Utilizing acetate reagent ion chemistry, HNCO is detected as NCO\(^{-}\), following negative ion proton transfer.\(^2\) The acetate reagent ion was generated by mixing 10 sccm of ultra-high purity (UHP) nitrogen bubbled through a reservoir of acetic anhydride with 1.5 slpm of UHP N\(_2\) and subsequently passing the mixture through a \(^{210}\)Po ionization source (NRD P-2021) orthogonal to the IMR. The CI-
TOFMS duty cycle was held at 66 kHz for the duration of the study, and raw spectra were time averaged and saved at a rate of 2 Hz.

The CI-TOFMS was calibrated twice daily at the start and finish of each testing run using a calibrated formic acid (HCOOH) permeation source (Kin-Tek, SRT-2, 21.6 ng min\(^{-1}\) at 50º C) as a relative reference compound. After the study, the instrument was calibrated to HNCO, following the approach of Roberts et al. 2010. HNCO mixing ratios were calculated from the relative sensitivity of HNCO to HCOOH (\(F_{HNCO}\)) using Equation E2:

\[
[H\text{NCO}]_{pptv} = \frac{[NCO^-]}{F_{HNCO} \times c_{HCOOH}}
\]  

(E2)

where \([NCO^-]\) is the background corrected ion signal for isocyanic acid (measured at m/z = 42). \(F_{HNCO}\) was experimentally determined to be 1.02 ± 0.42, where the largest source of uncertainty in \(F_{HNCO}\) was the concentration of the HNCO primary standard (1.15 ± 0.41 ppm).

### 2.3.4 HNCO source output quantification

A system similar to Roberts et al., [Roberts et al., 2010; Roberts et al., 2011] was used to generate gas phase HNCO from the thermal decomposition of cyanuric acid (trimer of HNCO; Tokyo Chemical Industry Company, Lot TCKCC, >98.0%). Briefly, 4 grams of cyanuric acid were enclosed in a custom-built glass cell wrapped with heating tape. Decomposition of the cyanuric acid at \(T = 260^\circ C\) produced gas phase HNCO in the headspace of the cell that was diluted with 80 cm\(^3\) min\(^{-1}\) of synthetic air (Praxair, Ultra High Purity, 99.993%). The output from the source was directed into a 102-L borosilicate cylindrical cell equipped with White cell optics (33.6 m total path length) and interfaced to
a Thermo Nicolet Nexus 370 Fourier transform infrared (FTIR) spectrometer equipped with a liquid nitrogen-cooled Hg-Te detector [Ramazan et al., 2006]. All spectra were obtained at a resolution of 1.0 cm\(^{-1}\) with 2048 co-added scans. The gas phase concentration of HNCO generated by the source was quantified using the peak at 2281 cm\(^{-1}\). In order to observe the characteristic IR feature for HNCO at this wavelength, the contribution from CO\(_2\) present in the cell had to be subtracted out. The cross section of HNCO was determined using the PNNL database (apodization: Boxcar; resolution: 0.112 cm\(^{-1}\); 1 ppm-m) deresolved using the USEPA AEDC program [EPA Deresolution Program], to match the resolution of the experiments (1.0 cm\(^{-1}\)).

The flow from the source was either directly introduced into the chamber (Exp. #1) or was diluted with 500 cm\(^3\) min\(^{-1}\) of ultra high purity nitrogen (Praxair) prior to entering the evacuated IR cell (Exp. #2) until the total pressure reached 1 atm. At that point, an exhaust line from the cell was opened to maintain the pressure at 1 atm while HNCO continued to flow through the cell and spectra were recorded. Because some loss in the cell (wall loss and/or decomposition) was expected, the decay of HNCO was also measured by closing the cell and monitoring the loss of HNCO as a function of time (Exp #3). Temperature (T = 294 K) and relative humidity (RH < 3%) were monitored inside the chamber using a Vaisala gauge (model HMP-238).

The decay of HNCO in the IR cell was observed to be first order and the rate constant (\(k_{\text{loss}}, \text{in s}^{-1}\)) was calculated using Equation E3:

\[
\ln \left( \frac{[X_{\text{cell}}]}{[X_{\text{cell}}]_0} \right) = -k_{\text{loss}} \times t \tag{E3}
\]
In Equation E3, [X\text{cell}] and [X\text{cell}]_0 are the concentrations of HNCO at time t and t=0 respectively, where zero time is defined as that at which the flow was stopped. A decay rate constant of \((7.4 \pm 1.4) \times 10^{-5} \text{ s}^{-1}\) was experimentally determined from Exp#3. The output of the source was then calculated from the HNCO concentration measured when the cell reached 1 atm, corrected for the decay of HNCO that occurred during filling of the cell (~1082 min for the undiluted experiment, and ~251 min for the diluted experiment). Measurements from the undiluted (Exp#1) and diluted experiments (Exp#2) were in good agreement (0.87 and 1.44 ppm respectively), resulting in an average concentration of ~1.15 \pm 0.41 ppm (1s) for gas phase HNCO from the source before dilution.

2.3.5 Measurements of NOx, CO and CO2 mixing ratios

Real-time mixing ratios of nitrogen oxides (NOx ≡ NO + NO2), CO, and CO2 were measured in the CVS using a Horiba 7200-SLE. Because the HNCO measurements were made after the SDS+ RTC, the HNCO data is greatly smoothed relative to the measurements directly from the CVS. To facilitate comparison, measurements of gas-phase CO2 were also made after the SDS by a LI-6262 CO2/H2O gas analyzer (LI-COR Inc., USA). The measurements taken by the LI-6262 were compared to the mixing ratio of gas-phase CO2 measured by an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) using the Peak Integration by Key Analysis (PIKA) 1.10H toolpak [Collier et al., 2013; Aiken et al., 2008]. Good agreement between the CO2 from the CVS and CO2 from the HR-ToF-AMS, LI-6262, and SDS+RTC has been previously demonstrated [Forestieri et al., 2013]. Utilizing the CVS and post-SDS CO2 mixing ratios as constraints, dilution and mixing in the SDS were modeled with a continuously mixed
flow reactor model (Fig. 2.1.B). The same model was applied to the concentrations of CO and NO\textsubscript{x} measured in the CVS to give post-SDS mixing ratios for both CO and NO\textsubscript{x}. Representative modeled dilutions and mixings of CO\textsubscript{2}, CO, and NO\textsubscript{x} post-SDS are presented in Figure 2.3.

![Figure 2.3](image)

Figure 2.3: Measured mixing ratios of CO\textsubscript{2} (2.3A), CO (2.3C), and NO\textsubscript{x} (2.3E) in the PDS, as well as the measured CO\textsubscript{2} (2.3,teal) mixing ratios after the SDS for the first day of testing for the Chevrolet Cavalier. Modeled mixing ratios of HNCO post-SDS are also shown for CO\textsubscript{2} (2.3B), CO (2.3D), and NO\textsubscript{x} (2.3F).
2.4 Results

2.4.1 Real-time mixing ratios

Based on the real-time catalytic converter temperature data for each vehicle, the UC cycle was sub-divided into four phases (Fig. 2.1.A). In matching both vehicle speed and converter temperature data with the post-SDS gas-phase measurements, all gas-phase measurements were time adjusted by ca. 80 seconds to account for residence time in the dilution system. The first “cold start” phase is characterized by an increase in the catalytic converter temperature to a stable temperature (300 °C) at which the TWC should be operating efficiently. The second phase or “first hot stabilized” phase is characterized by a constant catalyst temperature (300 °C) that remains stable until reaching the third phase at ca. 840 seconds into the drive cycle. This third “hard acceleration” phase consists of vehicle acceleration from 0 to 65 miles per hour (mph) in approximately 40 seconds and is characterized by a subsequent rise in the average temperature of the catalytic converter (338 °C). The fourth and final “second hot stabilized” phase occurs as the car has come out of the hard acceleration and the catalytic converter temperature begins to stabilize again.

CO, CO₂, and NOₓ concentrations in the post-SDS diluted exhaust for the first day of testing for the Cavalier are shown in Fig. 2.1.B and Fig. 2.1.C. The profiles for CO₂ and NOₓ demonstrate a strong correlation with the drive cycle with increases in their respective mixing ratios corresponding to increases in vehicle speed and acceleration. The time trace of the CO concentration in the diluted exhaust gas depicts two significant spikes, the first at the start of the drive cycle during the cold start phase when the catalytic converter is not yet sufficiently heated to efficiently convert the CO produced by the engine into CO₂, and
a second occurring during the hard acceleration phase as would be expected for a vehicle entering a fuel rich state [EPA, 2013].

Contrary to the literature-based a priori assumption of negligible HNCO emissions from LDGVs, [Dümpelmann et al., 1995; Cant et al., 2000; Chambers et al., 2001; Cant et al., 2005] measureable and substantial HNCO mixing ratios were observed in the exhaust of all eight LDGVs tested. The median and mean mixing ratios of HNCO, CO, CO₂ and NOₓ measured after dilution are presented in Table 2.2. The interquartile range is also reported to demonstrate the variability of emissions in each phase and over the course of the entire drive cycle. As an example, real-time post-SDS mixing ratios of HNCO are shown in Fig. 2.1.D for the Chevrolet Cavalier. The concentration of HNCO steadily increases during the initial cold start phase of the UC and then reaches a local maximum 400-600 seconds after engine start. In the hard acceleration phase of the drive cycle the concentration of HNCO increases in lockstep with CO, reaching a maximum that directly follows peak acceleration. The maximum mixing ratios of HNCO in the post-SDS ranged from 0.7 to 15 ppbv depending on the vehicle. Following the hard acceleration, HNCO mixing ratios decay back toward their initial values through the hot stabilized phase of the drive cycle.
Table 2.2: Mean HNCO Emissions Factors and Diluted Mixing Ratios of HNCO, CO, CO₂, and NOₓ for each vehicle test, with the 1σ standard deviation included in the parenthesis. The propagated uncertainty for the HNCO emissions factor is between 45-49%.

<table>
<thead>
<tr>
<th>Drive Cycle Phase</th>
<th>HNCO Emissions Factor (mg kgfuel⁻¹)</th>
<th>HNCO (ppbv)</th>
<th>CO (ppmv)</th>
<th>CO₂ (%)</th>
<th>NOₓ (ppmv)</th>
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<tr>
<td>Chevrolet Cavalier</td>
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<tr>
<td>Cold Run</td>
<td>0.474 (0.11) 0.416 (0.094)</td>
<td>0.401 (0.11)</td>
<td>1.06 (0.15)</td>
<td>0.263 (0.11)</td>
<td>1.74 (1.1)</td>
</tr>
<tr>
<td>First Hot Run</td>
<td>0.619 (0.11) 0.567 (0.089)</td>
<td>0.263 (0.085)</td>
<td>2.18 (0.11)</td>
<td>0.192 (0.069)</td>
<td>0.447 (0.12)</td>
</tr>
<tr>
<td>Hard Acceleration</td>
<td>1.01 (0.13) 0.828 (0.15)</td>
<td>1.24 (0.36)</td>
<td>70.1 (1.29)</td>
<td>0.226 (0.03)</td>
<td>3.04 (0.84)</td>
</tr>
<tr>
<td>Second Hot Run</td>
<td>0.589 (0.18) 0.723 (0.21)</td>
<td>0.749 (0.16)</td>
<td>7.05 (1.26)</td>
<td>0.272 (0.064)</td>
<td>0.42 (1.02)</td>
</tr>
<tr>
<td>All</td>
<td>0.61 (0.21) 0.6 (0.21)</td>
<td>0.542 (0.32)</td>
<td>24 (1.35)</td>
<td>0.266 (0.093)</td>
<td>1.09 (0.89)</td>
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<tr>
<td>Chevrolet S-10</td>
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<tr>
<td>Cold Run</td>
<td>0.33 (0.092) 0.312 (0.063)</td>
<td>0.235 (0.054)</td>
<td>14.1 (0.15)</td>
<td>0.232 (0.073)</td>
<td>2.66 (0.27)</td>
</tr>
<tr>
<td>First Hot Run</td>
<td>0.406 (0.096) 0.429 (0.047)</td>
<td>0.25 (0.04)</td>
<td>26.6 (0.96)</td>
<td>0.176 (0.028)</td>
<td>0.654 (0.033)</td>
</tr>
<tr>
<td>Hard Acceleration</td>
<td>1.34 (0.73) 0.757 (0.4)</td>
<td>1.52 (0.76)</td>
<td>141 (9.7)</td>
<td>0.317 (0.086)</td>
<td>0.606 (0.014)</td>
</tr>
<tr>
<td>Second Hot Run</td>
<td>0.946 (0.52) 1.09 (0.2)</td>
<td>0.634 (0.33)</td>
<td>10.2 (0.94)</td>
<td>0.209 (0.04)</td>
<td>0.143 (0.16)</td>
</tr>
<tr>
<td>All</td>
<td>0.687 (0.55) 0.429 (0.079)</td>
<td>0.512 (0.53)</td>
<td>26.7 (5.6)</td>
<td>0.222 (0.076)</td>
<td>0.165 (0.21)</td>
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<tr>
<td>Chrysler Grand Cherokee</td>
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<tr>
<td>Cold Run</td>
<td>0.86 (0.26) 0.88 (0.31)</td>
<td>0.425 (0.063)</td>
<td>11.5 (2.4)</td>
<td>0.158 (0.024)</td>
<td>0.375 (0.15)</td>
</tr>
<tr>
<td>First Hot Run</td>
<td>1.56 (0.67) 1.56 (0.41)</td>
<td>0.941 (0.4)</td>
<td>22.6 (7.3)</td>
<td>0.185 (0.053)</td>
<td>1.25 (0.43)</td>
</tr>
<tr>
<td>Hard Acceleration</td>
<td>3.42 (0.6) 1.91 (0.4)</td>
<td>3.08 (1)</td>
<td>65 (27)</td>
<td>0.271 (0.066)</td>
<td>2.79 (1.0)</td>
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<tr>
<td>Ford Taurus</td>
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<tr>
<td>Cold Run</td>
<td>0.339 (0.15) 0.453 (0.2)</td>
<td>0.278 (0.12)</td>
<td>31.7 (43)</td>
<td>0.242 (0.097)</td>
<td>2.81 (2)</td>
</tr>
<tr>
<td>First Hot Run</td>
<td>1.04 (0.24) 1.04 (0.12)</td>
<td>0.603 (0.1)</td>
<td>59.8 (40)</td>
<td>0.231 (0.078)</td>
<td>2.57 (1.9)</td>
</tr>
<tr>
<td>Hard Acceleration</td>
<td>7.02 (1.2) 1.42 (0.39)</td>
<td>8 (2.1)</td>
<td>72 (5)</td>
<td>0.344 (0.091)</td>
<td>1.58 (0.7)</td>
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<td>Ford Windstar</td>
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<tr>
<td>Cold Run</td>
<td>0.359 (0.15)</td>
<td>0.278 (0.16)</td>
<td>41.5 (5.3)</td>
<td>0.237 (0.087)</td>
<td>2.06 (0.91)</td>
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<td>Nissan Pathfinder</td>
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<tr>
<td>Cold Run</td>
<td>2.81 (2) 1.23 (0.63)</td>
<td>1.56 (1.05)</td>
<td>46.8 (25)</td>
<td>0.179 (0.063)</td>
<td>4.89 (1.7)</td>
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</table>
Table 2.2 Continued: Mean HNCO Emissions Factors and Diluted Mixing Ratios of HNCO, CO, CO₂, and NOₓ for each vehicle test, with the 1σ standard deviation included in the parenthesis. The propagated uncertainty for the HNCO emissions factor is between 45-49%.

<table>
<thead>
<tr>
<th>Drive Cycle Phase</th>
<th>HNCO Emissions Factor (mg kgfuel⁻¹)</th>
<th>HNCO (ppbv)</th>
<th>CO (ppmv)</th>
<th>CO₂ (%)</th>
<th>NOₓ (ppmv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toyota Solara</td>
<td></td>
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</tr>
<tr>
<td>Cold Run</td>
<td>0.786 (0.2) 0.433 (0.074)</td>
<td>0.535 (0.061) 0.31 (0.05)</td>
<td>13.8 (15) 17.4 (18)</td>
<td>0.206 (0.074) 0.217 (0.067)</td>
<td>0.807 (0.8) 1.13 (1.2)</td>
</tr>
<tr>
<td>First Hot Run</td>
<td>0.676 (0.12) 0.519 (0.081)</td>
<td>0.386 (0.063) 0.286 (0.034)</td>
<td>0.37 (0.06) 0.47 (0.09)</td>
<td>0.175 (0.023) 0.169 (0.026)</td>
<td>0.103 (0.04) 0.103 (0.04)</td>
</tr>
<tr>
<td>Hard Acceleration</td>
<td>1.16 (0.26) 0.475 (0.13)</td>
<td>1.22 (0.38) 0.431 (0.051)</td>
<td>30 (24) 17.4 (14)</td>
<td>0.305 (0.07) 0.284 (0.068)</td>
<td>1.78 (1.3) 1.65 (1.1)</td>
</tr>
<tr>
<td>Second Hot Run</td>
<td>0.723 (0.26) 0.435 (0.11)</td>
<td>0.464 (0.18) 0.272 (0.066)</td>
<td>1.48 (1.7) 1.16 (0.93)</td>
<td>0.197 (0.031) 0.193 (0.031)</td>
<td>0.201 (0.11) 0.267 (0.11)</td>
</tr>
<tr>
<td>All</td>
<td>0.794 (0.26) 0.456 (0.1)</td>
<td>0.569 (0.31) 0.308 (0.073)</td>
<td>9.5 (16) 0.207 (0.071)</td>
<td>0.609 (0.86) 0.733 (0.99)</td>
<td></td>
</tr>
<tr>
<td>Toyota Tacoma</td>
<td></td>
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</tr>
<tr>
<td>Cold Run</td>
<td>0.522 (0.16) 0.396 (0.099)</td>
<td>0.34 (0.087) 0.274 (0.07)</td>
<td>17.2 (22) 24.4 (27)</td>
<td>0.209 (0.063) 0.209 (0.062)</td>
<td>1.01 (1.1) 1.06 (1.3)</td>
</tr>
<tr>
<td>First Hot Run</td>
<td>0.847 (0.077) 0.652 (0.091)</td>
<td>0.459 (0.05) 0.34 (0.042)</td>
<td>0.87 (0.5) 2.5 (0.6)</td>
<td>0.166 (0.023) 0.162 (0.026)</td>
<td>0.0862 (0.059) 0.0623 (0.034)</td>
</tr>
<tr>
<td>Hard Acceleration</td>
<td>0.846 (0.18) 0.465 (0.081)</td>
<td>0.718 (0.23) 0.413 (0.03)</td>
<td>2.74 (1.2) 3.12 (1.3)</td>
<td>0.274 (0.06) 0.262 (0.069)</td>
<td>1.07 (0.46) 0.591 (0.33)</td>
</tr>
<tr>
<td>Second Hot Run</td>
<td>0.624 (0.14) 0.526 (0.1)</td>
<td>0.396 (0.095) 0.311 (0.045)</td>
<td>0.824 (0.35) 1.12 (0.24)</td>
<td>0.19 (0.028) 0.18 (0.029)</td>
<td>0.181 (0.12) 0.239 (0.13)</td>
</tr>
<tr>
<td>All</td>
<td>0.67 (0.2) 0.502 (0.14)</td>
<td>0.425 (0.17) 0.313 (0.072)</td>
<td>7.41 (16) 10.6 (20)</td>
<td>0.201 (0.061) 0.196 (0.062)</td>
<td>0.589 (0.81) 0.56 (0.93)</td>
</tr>
</tbody>
</table>

2.4.2 Real-time HNCO fuel based emission factors

To capture the dependence of HNCO emissions on the vehicle drive cycle, we calculate fuel based emission factors (FBEFs) in real time for each of the eight LDGVs in two consecutive trials. For this work we define FBEFs for HNCO as the mass of HNCO (mg) emitted per kilogram of fuel burned by the LDGVs. The FBEFs were calculated as:

\[
FBEF_{\text{HNCO}} = \frac{[\text{HNCO}]}{[\text{CO}_2]} \times \frac{\text{MW}_{\text{CO}_2}}{\text{MW}_C} \times W_C
\]

(E3)

where \([\text{HNCO}]\) is the mass concentration of HNCO, \([\text{CO}_2]\) is the mass concentration of CO₂, \(\text{MW}_{\text{CO}_2}\) and \(\text{MW}_C\) are the molecular weights of CO₂ and carbon, and \(W_C\) is the mass fraction of carbon in the fuel, assumed to be 0.85 [Kirchstetter et al., 1999]. The FBEFs are calculated under the assumption that the carbon present in the fuel is converted to CO₂ with unit efficiency, where the contributions from other carbon species are negligible. The
mass concentrations of CO$_2$ were calculated using the real-time CO$_2$ measurements made by the HR-ToF-AMS (corrected for possible particle-phase CO$_2^+$ signal using the LI-6262) after the SDS.

Real-time determinations of the fuel based emission factors for the duration of the drive cycle are shown in Fig. 2.4 for three representative LDGVs on both test days considered. Calculated fuel based emission factors are not constant during the drive cycle, but rather can vary by as much as a factor of 10, peaking during the hard acceleration phase of each vehicle’s drive cycle (Fig. 2.4). The differences in the FBEF between the two days of testing can be attributed to variations in HNCO production resulting from varying amounts of CO and NO$_x$, and is discussed in the following section. The average FBEF for each of the eight LDGVs are shown in Fig. 2.5 for the four phases of the drive cycle as well as averaged for overall test runs. While the absolute value of the FBEF displays vehicle-to-vehicle variability, a similar dependence on the drive cycle is observed for all vehicles, where the FBEFs reach a maximum during the hard acceleration phase and the lowest FBEF is observed during the cold start phase. For the four phases of the UC, we compute fleet averaged HNCO FBEFs of: 0.45 ($\pm$0.13) mg kg$^{-1}$ fuel (Phase 1), 0.70 ($\pm$0.2) mg kg$^{-1}$ fuel (Phase 2), 1.70 ($\pm$1.77) mg kg$^{-1}$ fuel (Phase 3), and 1.20 ($\pm$1.02) mg kg$^{-1}$ fuel (Phase 4). Values in parentheses reflect 1σ standard deviations. The propagated uncertainty for each individual car, which primarily reflects uncertainty in the concentration of the HNCO calibration sources, ranged between 45-49%. The LDGV tested fleet averaged HNCO FBEF for the entire drive cycle is 0.91 ± 0.58 mg kg$^{-1}$ fuel. The overall drive cycle average was calculated as the mean of the HNCO FBEFs for all of the cars for both days of testing, with the exception of the Nissan Pathfinder.
Figure 2.4: Fuel-based, real-time HNCO emissions factors for both test 1 (red) and test 2 (blue) for: A) the Chrysler Grand Cherokee, B) the Chevrolet Cavalier, and C) the Chevrolet S-10 Pickup. The dashed lines represent the divides between the four previously defined phases of the drive cycle.
Figure 2.5: Median HNCO emissions factors (red) for both test 1 and test 2 of the eight light duty gasoline vehicles including mean FBEF (purple), the interquartile range, and the range of FBEF measured for: A) the cold start phase, B) the first hot stabilized phase, C) the hard acceleration phase, D) the second hot stabilized phase, and E) the overall test run. Fleet averages for the first test do not include contributions from the Pathfinder. Error bars represent the interquartile range.
The Nissan Pathfinder was excluded from the LDGV fleet average as the emissions were highly anomalous compared with the vehicle fleet, with elevated FBEFs (a factor of 7 larger on day 1 as compared with day 2) observed during all phases of the drive cycle during the first day of testing. Further, on the second day of testing, the Pathfinder was observed to have maximum FBEF during the first hot stabilized phase and not the hard acceleration phase. At this time, we cannot confirm whether the Pathfinder itself or the measurement protocol caused the strong deviation from the fleet average state. If the Pathfinder is included, we compute fleet averaged HNCO FBEFs of the four phases as: 0.67 (±0.64) mg kg\textsubscript{fuel}\textsuperscript{-1} (Phase 1), 1.47 (±2.3) mg kg\textsubscript{fuel}\textsuperscript{-1} (Phase 2), 2.78 (±4.3) mg kg\textsubscript{fuel}\textsuperscript{-1} (Phase 3), and 2.07 (±3.2) mg kg\textsubscript{fuel}\textsuperscript{-1} (Phase 4). With the Pathfinder included, the tested fleet averaged HNCO FBEF for the entire drive cycle is 1.56 ± 2.2 mg kg\textsubscript{fuel}\textsuperscript{-1}.

2.5 Discussions

2.5.1 Mechanism for HNCO production

The dependence of the HNCO emission factor on the UC may provide further insight into the production mechanism of HNCO in the catalytic converter. The laboratory proxy-based studies on reactions of CO, NO, and either H\textsubscript{2} or NH\textsubscript{3} on precious metal catalysts have demonstrated that HNCO production is a complex function of the catalyst temperature and concentrations of CO, NO\textsubscript{x} and hydrogen. As the vehicle is driven through the UC, the production of HNCO by the vehicle is expected to reflect real-time changes in each of these factors.

The fleet averaged HNCO FBEF during the cold start period of the drive cycle was 0.46 ± 0.13 mg kg\textsubscript{fuel}\textsuperscript{-1}, a factor of 2 lower than the drive cycle average. During the cold
start phase, the temperature of the catalytic converter steadily increases as the vehicle is driven through the UC cycle. The coincident increase in HNCO mixing ratio, and hence FBEF, during the cold start phase is consistent with the mechanisms illustrated in Reactions 1-8, [Dümpelmann et al., 1995; Cant et al., 2000; Chambers et al., 2001; Cant et al., 2005; Cant et al., 2004] where the HNCO yield increases until the catalyst reaches an average temperature of 300°C (±82°C) at which point the yield of HNCO drops off as a result of limited CO coverage over the catalyst surface [Dümpelmann et al., 1995]. The local maximum in HNCO mixing ratio is achieved toward the end of the cold start phase and the FBEF decreases as the average catalytic converter temperature stabilizes at 300°C (±82°C).

As shown in Fig. 2.4 and 2.5, HNCO FBEFs are highest during the hard acceleration phase, with the fleet average FBEF 1.70 ± 1.77 mg kg\text{fuel}^{-1}, a factor of 1.86 higher than the overall drive cycle average. This increase in HNCO emission is accompanied by a simultaneous increase in the concentration of CO in the exhaust, consistent with the LDGV entering into a fuel rich state as a result of the hard acceleration. When fuel rich, engine emissions have insufficient oxygen for complete conversion to CO\textsubscript{2}, resulting in an increase in CO and the potential for a subsequent increase in the number of adsorbed CO on the precious metal catalyst surface. Previous work on model engine systems suggest a mechanism in which HNCO production is limited by the number of available adsorbed CO on the catalyst surface, with the formation of HNCO resulting from the hydrogenation of small concentrations of NCO groups under conditions of high CO coverage (R3 and R6) [Dümpelmann et al., 1995. With the increase in number of adsorbed CO on the catalyst during the hard acceleration, an increase in the yield of HNCO would be expected and is observed during our test runs. It is also plausible that HNCO is stored
on the catalyst as cyanuric acid or ammelide that thermally decomposes as the catalyst is heated or experiences a different chemical environment through the drive cycle.

During the second hot stabilized phase the vehicle ceases to operate under a fuel rich condition, leading to a decrease in CO emissions, and the catalyst returns to a steady-state temperature for efficient operation. Consequently, the concentration of adsorbed CO should decrease corresponding to a decrease in the yield of HNCO off the catalyst surface. This is consistent with the observed decrease in HNCO during the fourth phase of the drive cycle as the HNCO mixing ratios decline toward initial values. However, it is important to note that the production of HNCO is highly dependent not only on the CO concentration in the direct engine exhaust, but on the temperature of the catalytic converter denoted by suppressed HNCO production during the cold start phase, as well as the concentration of NOx.

For many of the vehicles tested, NOx and CO concentrations were not consistent between the two days of testing, permitting further assessment of the factors controlling HNCO production. For example, for the Chevrolet Cavalier there was a 39% decrease in the HNCO peak mixing ratio during the hard acceleration phase of the drive cycle on the second day of testing as compared to the first day of testing (1.24 ppbv as compared with 0.75 ppbv). This can be compared with the behavior of CO and NOx during the same phase, with the mixing ratio of CO in the diluted vehicle exhaust being 25% larger (60 ppmv as compared with 75 ppmv), and the diluted NOx mixing ratio being 46% smaller on the second day of testing (1.12 ppmv as compared with 0.60 ppmv). This result suggests that HNCO production for this vehicle was NOx limited. In contrast, HNCO production from the Chevrolet S-10 during the hard acceleration phase appears to be CO limited.
HNCO mixing ratios after the SDS were 46% lower (1.52 ppbv as compared with 0.82 ppbv) while diluted NOx concentrations were 233% higher (0.06 ppmv as compared with 0.20 ppmv) on the second day of testing. The production of HNCO in the catalytic converter appears to be CO limited with the second day of testing not having adequate CO concentrations to facilitate the formation of NCO groups on the catalyst surface. Despite the higher NOx concentrations on the second day of testing there was not a high enough concentration of adsorbed CO groups for efficient HNCO production.

The complexity of the HNCO production mechanism within the individual vehicles’ catalytic converters and the dependence of the HNCO production rate on catalyst temperature, CO, and NOx mixing ratios are illustrated in Fig. 2.6.

The dependence of the production of HNCO on the temperature of the catalytic converter is observed with the minimal production of HNCO in the first cold start drive phase, despite high concentrations of both CO and NOx. When the catalytic converter temperature is still cool, the production of HNCO is suppressed as CO and NOx in the engine exhaust are not able to efficiently adsorb to the catalyst surface (R1-5) and thus inhibit the efficient formation of HNCO. However, when the catalyst is at an efficient operating temperature (T > 300 °C), high concentrations of both NOx and CO are necessary to sustain a high yield of HNCO. It is important to note that the measurements of CO and NOx reported here were made after the catalytic converter. Given that the conversion efficiency of NOx and CO are likely also a function of drive cycle, future work on the dependence of HNCO production rates on NOx and CO between different phases of the drive cycle should include measurements of NOx and CO prior to the catalytic converter.
2.5.2 **Comparison with previous studies HNCO vehicle emissions studies**

The average fuel based emissions factors of HNCO for the LDGV fleet tested are shown in Fig. 2.7 alongside previously reported fuel based emissions factors for LDDVs.\(^8\) Emission factors reported for the LDDVs were calculated from HNCO mixing ratios measured using a 2001 Volkswagen Jetta turbo diesel injection engine equipped with a diesel oxidation catalyst (DOC) run under four different steady-state driving modes [Wentzell et al., 2013]. The FBEF for LDGVs under the UC is approximately 4.33 times that of the LDDVs run under steady-state conditions assumed to be representative of the
FTP-75 urban driving cycle (0.91 ± 0.58 mg kg\textsubscript{fuel}\textsuperscript{-1}, vs. 0.21 ± 0.14 mg kg\textsubscript{fuel}\textsuperscript{-1}, respectively). The precious metal catalysts in a typical diesel oxidation catalyst are usually either platinum or palladium [Wentzell et al., 2013], similar to that of a TWC in the tested LDGVs, and we would expect HNCO production to have a strong dependence on the availability of adsorbed CO. Since the typical diesel engine operates under lean burn conditions the concentration of CO in the direct engine exhaust is significantly lower for LDDVs when compared to LDGVs. With the higher direct CO emissions from the gasoline engine we would expect LDGVs to produce relatively higher concentrations of HNCO than LDDVs when driving under similar conditions assuming the converters are of a comparable size and oxide washcoat composition.

The fleet averaged overall fuel based emission factor for LDGVs is ca. 30 times smaller than that reported for diesel urea SCR exhaust systems (0.91 ± 0.58 mg kg\textsubscript{fuel}\textsuperscript{-1}, vs. 27.0 ± 4.6 mg kg\textsubscript{fuel}\textsuperscript{-1})\textsuperscript{10} While HNCO FBEFs are much smaller for LDGVs utilizing TWCs relative to diesel urea SCR systems, the large difference is due to the urea addition and subsequent HNCO formation from that addition in the SCR systems. Without the DPN included in the exhaust system the diesel engine emitted a reported FBEF of approximately 3.2 mg kg\textsubscript{fuel}\textsuperscript{-1}, a factor of 8.4 smaller.\textsuperscript{10-11} The variability in the calculated FBEFs for the LDGVs throughout the drive cycle (Fig. 2.7) suggests that FBEFs determined under steady-state testing conditions may underestimate the true average HNCO emission factor in urban regions as they do not capture accelerations. The fleet averaged FBEF for the hard acceleration phase was 1.70 ± 1.77 mg kg\textsubscript{fuel}\textsuperscript{-1} a factor of ca. 3.8 larger than that observed during the cold start (0.45 ± 0.13 mg kg\textsubscript{fuel}\textsuperscript{-1}). As a result, the fleet average FBEF for the entire drive cycle (0.91 ± 0.58 mg kg\textsubscript{fuel}\textsuperscript{-1}) is higher than that observed during the
steady-state hot run phases. As such, calculating FBEFs from one representative engine state may not fully capture the range in HNCO production rates or accurately represent the typical emissions of HNCO in urban areas.

Figure 2.7: Comparison of the mean light duty gasoline vehicle HNCO emissions for the overall Unified Cycle (UC) and the four respective phases of the UC (blue) to the emission factors determined by Wentzel et al. for a light duty diesel engine operating under steady state conditions representative of the FTP75, USO6 and HWFET drive cycles and the engine running under idling conditions (grey). Error bars represent standard deviations of the mean value reported. The y-axis is depicted with a split scale, the first from 0-2 mg kg\text{fuel}\textsuperscript{-1} and second from 2-6 mg kg\text{fuel}\textsuperscript{-1}. 
2.6 Acknowledgements

This research was supported by the California Air Resources Board (Contract No. 10-313). We thank Mang Zhang and the staff at the Haagen-Smit Vehicle Testing Facility in El Monte, CA, for their assistance in vehicle testing and for helpful discussions. We would also like to thank Barbara Finlayson-Pitts for her technical assistance in the calibration of our HNCO source, as well as Steven Sharpe and Timothy Johnson at the Pacific Northwest National Laboratory for their helpful consultations.

2.7 References


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3. On the primary emission of formic acid from light-duty gasoline vehicles and ocean-going vessels

3.1 Abstract

We present determinations of fuel-based emission factors for formic acid (EF\textsubscript{HCOOH}) from light duty gasoline vehicles (LDGVs) and in-use ocean-going vessels. Emission ratios, from which the emission factors were derived, were determined from LDGVs through measurement of HCOOH and carbon dioxide (CO\textsubscript{2}) in the exhaust of a fleet of eight LDGVs driven under the California Unified Cycle at the California Air Resources Board’s Haagen-Smit Laboratory. Emission ratios from in-use ocean-going vessels were determined through direct measurement of HCOOH and CO\textsubscript{2} in ship plumes intercepted by the R/V Atlantis during the 2010 California Research at the Nexus of Air Quality and Climate Change (CalNex) campaign within 24 nautical miles of the California coast. The eight car fleet average EF\textsubscript{HCOOH} was 0.94 ± 0.32 (1σ) and 0.57 ± 0.18 mg kg\textsubscript{fuel}\textsuperscript{−1} for the cold start and hot running phases of the drive cycle, respectively. This difference suggests that catalytic converter performance and the air/fuel equivalence ratio are important metrics contributing to EFHCOOH. EFHCOOH was determined to be 1.94 ± 1.06 mg kg\textsubscript{fuel}\textsuperscript{−1} for a single diesel vehicle driven under highway driving conditions, higher on average than any individual LDGV tested. In comparison, HCOOH primary emissions from in-use ocean-going vessels were substantially larger, averaging 20.89 ± 8.50 mg kg\textsubscript{fuel}\textsuperscript{−1}. On a global scale, HCOOH primary emissions from fossil fuel combustion are likely to be insignificant relative to secondary production mechanisms, however primary emissions may contribute more significantly on a finer, regional scale in urban locations.
3.2 Introduction

Field measurements have demonstrated that organic acids are ubiquitous in the troposphere and are present in both the gas and aerosol phase [Chebbi and Carlier, 1996; Keene and Galloway, 1988; Khare et al., 1999; Veres et al., 2011]. Organic acids can contribute to particulate and rain water acidity [Galloway et al., 1982] and have been shown to be a major component of secondary organic aerosol (SOA) mass loadings [Lee et al., 2003], thus impacting particle hygroscopicity. As a result, there is renewed interest in determining the relative strengths of primary and secondary sources of organic acids and the importance of anthropogenic and biogenic processes. Formic acid (HCOOH) has been shown to be ubiquitous in both remote and urban environments [e.g., Chebbi and Carlier, 1996]. Despite being one of the most abundant trace gases in the atmosphere, quantitative source attribution of HCOOH has remained elusive.

Laboratory measurements, confirmed by field observations indicate that HCOOH is directly emitted to the atmosphere from terrestrial vegetation [Kesselmeier, 2001], as a by-product of both biomass burning [Veres et al., 2010a] and biofuel and fossil fuel combustion [Kawamura and Kaplan, 1987; Kawamura et al., 1985], and from agricultural [Shaw et al., 2007] and soil emissions [Sanhueza and Andreae, 1991]. In addition, HCOOH has been shown to be produced in the photo-oxidation of a wide range of terrestrial, marine, and anthropogenic volatile organic compounds (VOC) [Butkovskaya et al., 2006a; Butkovskaya et al., 2006b; Larsen et al., 2001; Orlando et al., 2000; Paulot et al., 2009] as well as the direct ozonolysis of biogenic [Jacob and Wofsy, 1988] and anthropogenic alkenes [Hatakeyama et al., 1986; Herndon et al., 2007]. The production
of HCOOH following the heterogeneous reaction of hydroxyl radicals with organic aerosol has also been suggested to be an important, yet unconstrained source of HCOOH [Paulot et al., 2011a; Vlasenko et al., 2008]. The relative strength of any individual source is regionally specific, underlining the importance of quantitative source functions, reaction rates, and product yields.

Atmospheric observations have suggested that in urban locations, direct anthropogenic emission of HCOOH can comprise as much as 25% of the total production rate [Grosjean, 1992]. Radiocarbon analysis of gas-phase formic acid suggests that biogenic processes account for as much as 55% of HCOOH in urban regions and as much as 100% in remote areas [Glasius et al., 2001], although no distinction between primary and secondary processes could be made. On a global scale, Paulot et al. [2011a] constructed a bottom-up inventory for HCOOH sources and sinks that suggests that over 85% of the globally, annually averaged HCOOH source can be attributed to photochemical production, and direct anthropogenic emissions of HCOOH are insignificant on the global scale (< 1% of total sources). However, it is expected that direct emissions of HCOOH may play a more important role regionally, especially around mega-cities.

Here, we focus exclusively on the primary emission of HCOOH from light duty gasoline vehicles and in-use ocean-going vessels to provide directly measured, fuel-based emission factors for HCOOH (EF_{HCOOH}) for use in regional chemical transport models. The early measurements of Kawamura et al. [1987; 1985] describe primary emissions of organic acids from fossil fuel combustion but more recent measurements are not available to provide quantitative values for input into chemical transport models. Mechanistically, Zervas et al. [2001] demonstrated that HCOOH is produced in spark ignition engines from
fuel blends comprised of a wide range of aromatic and oxygenated compounds. The exhaust concentration was shown to increase with the air/fuel equivalence ratio suggesting that excess oxygen enhances HCOOH production. Zervas et al. [2001] suggested that HCOOH could be formed following the oxidation of formaldehyde and/or other volatile organic compounds in engine exhaust or in the 3-way catalytic converter. However, at present, EF$_{\text{HCOOH}}$ from light duty gasoline vehicles and in-use ocean-going vessels are not available to properly constrain HCOOH emission inventories. In their absence, current constraints on HCOOH emissions from mobile vehicles are mostly derived from measurements of the emission ratios of HCOOH relative to carbon monoxide (CO) in the Hampton Roads Bridge Tunnel studies of Talbot et al. [1988], where HCOOH emission was determined to be 2.1 x 10$^{-4}$ HCOOH per CO. It is important to note that these measurements were made prior to 1988. Substantial changes to fuel composition and emissions control technology in the past 15 years have almost certainly changed the HCOOH emissions rate. There currently are no experimental constraints on the emission rates of organic acids from ocean-going vessels.

In what follows we report the first measurements of real-time, fuel-based HCOOH emission factors from light duty gasoline vehicles and ocean-going vessels. In this study, a fleet of LDGVs were driven under the California Unified Cycle (UC) at the California Air Resources Board’s Haagen-Smit Laboratory, where HCOOH, carbon monoxide (CO) and carbon dioxide (CO$_2$) were detected with high time resolution ($\leq 1$ s) in the diluted exhaust. The study was conducted on eight LDGVs (Table 3.1) requisitioned from the California on-road vehicle fleet in 2011. The average age of the test fleet was approximately ten years. HCOOH mixing ratios were quantified via chemical ionization
time-of-flight mass spectrometry (CI-ToFMS) at 2 Hz, allowing for real-time measurement of HCOOH mixing ratios throughout the drive cycle. The simultaneous measurements of CO and CO₂ allow for fuel-based emission factors to be calculated for the overall drive cycle as well as for specific phases of the UC cycle.

Fuel-based emission factors for ocean-going vessels were determined from measurements of HCOOH and CO₂ within plumes intercepted during the 2010 CalNex campaign by the R/V Atlantis as it operated within the coastal waters of Southern and Northern California. The same CI-ToFMS instrument was used to make direct measurements of HCOOH both during day and night. Emissions from a total of 12 ship plumes are reported here, all of which were sampled within ten minutes of emission.

Table 3.1: Manufacturer, model, and year of the eight light duty gasoline vehicles tested.

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Model</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chevrolet</td>
<td>Cavalier</td>
<td>2001</td>
</tr>
<tr>
<td>Chevrolet</td>
<td>S-10</td>
<td>2002</td>
</tr>
<tr>
<td>Chrysler</td>
<td>Grand Cherokee</td>
<td>2002</td>
</tr>
<tr>
<td>Nissan</td>
<td>Pathfinder</td>
<td>2003</td>
</tr>
<tr>
<td>Toyota</td>
<td>Solara</td>
<td>2003</td>
</tr>
<tr>
<td>Toyota</td>
<td>Tacoma</td>
<td>2003</td>
</tr>
<tr>
<td>Ford</td>
<td>Taurus</td>
<td>1997</td>
</tr>
<tr>
<td>Ford</td>
<td>Windstar</td>
<td>1998</td>
</tr>
</tbody>
</table>
3.3 Experimental

3.3.1 CI-ToFMS measurements of formic acid

Formic acid was detected in real-time using a chemical ionization time-of-flight mass spectrometer (CI-ToFMS). The instrument used here has been previously described for the detection of gas-phase HCOOH [Bertram et al., 2011a] and details of the acetate ion chemistry can be found in Veres et al. [2010b]. The sample flow entering the ion-molecule reaction region (IMR) was restricted to 1.7 slpm using a critical orifice. Utilizing acetate reagent ion chemistry, HCOOH was detected as HCOO⁻, following negative ion proton transfer. Acetate reagent ions were generated by mixing 10 sccm of ultra-high purity (UHP) nitrogen that was bubbled through a reservoir of acetic anhydride with 1.5 slpm of UHP N₂ and passing the mixture through a ²¹⁰Po ionization source (NRD P-2021). Individual mass spectra were sampled at 66 kHz for the duration of the study and the raw spectra were time averaged and saved at a rate of 2 Hz. The CI-ToFMS was calibrated twice daily at the start and finish of each testing run using a calibrated HCOOH permeation source (Kin-Tek, SRT-2, 108 ng min⁻¹ at 70º C).

3.3.2 Emission factor measurements from LDGVs

3.3.2.1 Test vehicle selection and operation at the Haagen-Smit Laboratory

Eight LDGVs were requisitioned by the California Air Resources Board from the current on-road vehicle fleet. All eight vehicles were equipped with a three way catalytic converter (TWC) and met the current California vehicle emission standards set by the LEV emission requirements. Before each day of testing, the eight LDGVs were stored overnight
with a nominal cold soak engine temperature of 24 °C. The vehicles were then pushed onto a chassis dynamometer, started and driven through the first two phases of the UC cycle. The UC cycle is representative of a typical twenty minute trip taken by a California driver and is more aggressive than the current federal testing protocols urban drive cycle, FTP-75 [Austen et al., 1993]. Each vehicle was driven under these conditions twice on different days, with the exception of the Ford Windstar which was driven through the entire drive cycle only once due to a malfunction during the first day of testing. The eight vehicle fleet was fuelled with California summer blend gasoline containing ethanol (EtOH) as an additive to increase oxygen content.

3.3.2.2 Vehicle exhaust handling and dilution systems at the Haagen-Smit Laboratory

The vehicle exhaust was sampled directly from the vehicle tailpipe and diluted in two stages prior to measurement. The exhaust dilution system has been described elsewhere, and is only described briefly here [Kuwayama et al., 2015]. The primary dilution stage consisted of a constant volume sampler (CVS) which fed directly into the secondary dilution system (SDS) [Robert et al. 2007], achieving a total dilution factor of 60. For both the CVS and SDS, the exhaust was diluted using air passed through a pre-filter, high-efficiency particulate air (HEPA) filter, and activated carbon. Following secondary dilution, the sample was mixed under turbulent mixing conditions in a 0.10 cubic meter residence time chamber (RTC) and then sub-sampled by the CI-ToFMS through a 2.24 m long piece of perfluoroalkoxy (PFA) tubing with a 3.175 mm inner diameter. The transit time of the vehicle exhaust through the dilution system was approximately 80 s.
Direct addition of HCOOH to the inlet of the entire dilution system was not performed in this study, as such the emission factors reported here represent an upper limit. However, the fast time response in HCOOH mixing ratio as shown in Fig. 3.1 lends confidence that HCOOH losses in the dilution chamber were minimal.

Figure 3.1: A) Real-time mixing ratios of formic acid (black; detected at m/z = 45) for the first Chevrolet S-10 test as measured after the secondary dilution system (SDS). The shaded region represents the propagated uncertainty in the HCOOH mixing ratio. The percent of maximum catalytic converter temperature is shown in red (right axis). B) Mixing ratios of modelled CO (red) and measured CO$_2$ (blue) post-SDS, for the first S-10 test. The “cold start” period, defined as the first 300 s following engine start and the “hot running” period, defined as the last 450 s of the test are shown with gray bars above panel A.
3.3.2.3 Measurements of NO\textsubscript{x}, CO and CO\textsubscript{2} mixing ratios at the Haagen-Smit Laboratory

Real-time mixing ratios of nitrogen oxides (NO\textsubscript{x}≡ NO + NO\textsubscript{2}), CO, and CO\textsubscript{2} were measured in the CVS using a Horiba 7200-SLE. CO\textsubscript{2} was also measured after the SDS by both a standard LI-6262 CO\textsubscript{2}/H\textsubscript{2}O Gas Analyzer (Licor, Inc.) and an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) using the Peak Integration by Key Analysis (PIKA) 1.10H toolpak [Collier and Zhang, 2013]. Due to a limited availability of the Licor, the CO\textsubscript{2} measurements utilized here were made with the HR-ToF-AMS. When both instruments were available, real-time measurements of CO\textsubscript{2} from the AMS compared well with those made with the Licor, within 6% on average [Collier and Zhang, 2013; Forestieri et al., 2013]. Utilizing the CO\textsubscript{2} mixing ratios measured in the CVS and post-SDS sampling line as constraints, dilution and mixing in the SDS were modelled with a continuously mixed flow reactor model. The same model was applied to the concentrations of CO and NO\textsubscript{x} measured in the CVS to determine post-SDS mixing ratios and time-series for both CO and NO\textsubscript{x}.

3.3.3 Ship Plume Intercepts during CalNex 2010

During the California Research at the Nexus of Air Quality and Climate Change (CalNex) Campaign, the R/V Atlantis intercepted 135 plumes from ocean-going vessels that were operating in the coastal waters of California [Ryerson et al., 2013a]. Regulations in effect in 2010 within CA required that vessels operating within 24 nautical miles of the CA coast utilize fuels with \( \leq 1.5\% \) sulphur by weight, which is less than that in “bunker
fuels” commonly used by larger ocean going vessels further off-shore and in unregulated waters. Measurements of SO2 within ship plumes confirmed that vessels within the regulated waters were using low sulphur fuels, with average fuel sulphur contents of 0.4%, 0.09% and 0.03% for vessels operating slow-speed, medium-speed and high-speed diesel engines, respectively [Buffaloe et al., 2014].

The R/V Atlantis provided a platform to measure the outflow of pollution in the marine boundary layer (MBL) along the coast of California during May and June 2010. Here, we concentrate on determining $EF_{HCOOH}$ for the ship plumes described in Table 3.3. Based on the plume selection criteria discussed in detail in Section 3, quantitative fuel-based emission factors were retrieved for 12 (ca. 10%) of the plumes sampled. The collection of plumes include: 1 passenger ship, 7 cargo ships, and 4 tanker plume intercepts, corresponding to a total of six independent vessels as the plumes from specific ships were sampled on more than a single occasion. The passenger ship was operating a high speed diesel engine whereas the other vessels were all operating slow speed diesel engines. The same CI-ToFMS used for vehicle testing was used during CalNex, with the primary difference being the inlet manifold. During CalNex, HCOOH and other trace gases were sampled by pulling ambient air through a 7.6 m long, 0.64 cm ID PFA heated inlet (temperature controlled to 35°C) at 10 standard L min$^{-1}$ (slpm) with a pressure of 933 mbar, resulting in an average residence time of 1.5 seconds. Calibrations to HCOOH were conducted every 90 minutes for a total of 293 calibrations during the campaign. Background determinations were conducted every 30 minutes by overflowing the inlet with UHP N$_2$ (882 total).
Near simultaneous measurements of CO₂ permit calculation of fuel-based emission factors for each plume sampled. During CalNex, CO₂ was measured using a Li-Cor Model Li-7000 non-dispersive infrared (NDIR) absorption instrument, sampling at 1 Hz, with an accuracy of ± 0.08 ppmv and a precision of 0.07 ppmv [Williams et al., 2009a].

3.4 Results and Discussion

3.4.1 Real-time emission factor measurements from light duty gasoline vehicles

A typical time series of the mixing ratio of formic acid, CO, and CO₂ over the drive cycle is shown in Figure 3.1. Through matching both vehicle speed and converter temperature data with the post-SDS gas-phase measurements, in particular CO₂, all gas-phase measurements were time adjusted by 80 seconds to account for the residence time in the dilution system. Here we concentrate on two specific periods of the drive cycle: 1) The “cold start” phase, characterized by an increase in the catalytic converter temperature to an initial stable temperature (300°C) at which point the TWC should be operating efficiently (we define this as the first 300 seconds of the second phase of the UC drive cycle), and 2) The final “hot running” phase, which occurs as the car has come out of a hard acceleration and the catalytic converter temperature begins to stabilize again (here we define this as the last 450 seconds of the drive cycle). The mixing ratio of formic acid was above the CI-ToFMS detection threshold for each of the eight cars studied.
Table 3.2: Formic acid (HCOOH) fuel-based emission factors and emission ratios for eight light duty gasoline vehicles during the “cold start” and the “hot running drive phase.

<table>
<thead>
<tr>
<th>Vehicle</th>
<th>Drive Cycle Phase</th>
<th>HCOOH Emission Factor $^{b}$ (mg (kg fuel)$^{-1}$)</th>
<th>[HCOOH] / [CO] (pptv/ppmv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ford Windstar</td>
<td>Cold Start</td>
<td>0.83 ± 0.24</td>
<td>6.23 ± 1.35</td>
</tr>
<tr>
<td></td>
<td>Hot Running</td>
<td>0.56 ± 0.66</td>
<td>96.5 ± 27.5</td>
</tr>
<tr>
<td>Toyota Solara</td>
<td>Cold Start</td>
<td>0.80 ± 1.1</td>
<td>17.3 ± 22.8</td>
</tr>
<tr>
<td></td>
<td>Hot Running</td>
<td>0.29 ± 0.87</td>
<td>N.A.</td>
</tr>
<tr>
<td>Ford Taurus</td>
<td>Cold Start</td>
<td>0.84 ± 0.43</td>
<td>5.71 ± 2.67</td>
</tr>
<tr>
<td></td>
<td>Hot Running</td>
<td>0.37 ± 0.65</td>
<td>11.2 ± 9.0</td>
</tr>
<tr>
<td>Chevrolet Cavalier</td>
<td>Cold Start</td>
<td>0.66 ± 0.42</td>
<td>5.41 ± 3.0</td>
</tr>
<tr>
<td></td>
<td>Hot Running</td>
<td>0.72 ± 1.16</td>
<td>49.7 ± 32.0</td>
</tr>
<tr>
<td>Nissan Pathfinder</td>
<td>Cold Start</td>
<td>0.85 ± 1.33</td>
<td>5.02 ± 11.8</td>
</tr>
<tr>
<td></td>
<td>Hot Running</td>
<td>0.75 ± 0.68</td>
<td>13.7 ± 9.5</td>
</tr>
<tr>
<td>Chrysler Grand Cherokee</td>
<td>Cold Start</td>
<td>1.06 ± 0.55</td>
<td>7.54 ± 2.67</td>
</tr>
<tr>
<td></td>
<td>Hot Running</td>
<td>0.62 ± 0.98</td>
<td>22.5 ± 20.3</td>
</tr>
<tr>
<td>Toyota Tacoma</td>
<td>Cold Start</td>
<td>0.82 ± 1.00</td>
<td>12.1 ± 11.4</td>
</tr>
<tr>
<td></td>
<td>Hot Running</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>Chevrolet S-10</td>
<td>Cold Start</td>
<td>1.68 ± 1.01</td>
<td>22.6 ± 14.2</td>
</tr>
<tr>
<td></td>
<td>Hot Running</td>
<td>0.69 ± 0.78</td>
<td>59.4 ± 32.5</td>
</tr>
<tr>
<td>LDGV Fleet Average</td>
<td>Cold Start</td>
<td>0.94 ± 0.32</td>
<td>10.2 ± 6.5</td>
</tr>
<tr>
<td></td>
<td>Hot Running</td>
<td>0.57 ± 0.18</td>
<td>42.2 ± 33.0</td>
</tr>
</tbody>
</table>

$^{a}$ All vehicles were driven through the UC twice, with the exception of the Ford Windstar.

$^{b}$ The reported error is the propagated uncertainty stemming from the 1 standard deviation of the HCOOH and CO$_2$ measurements during each drive phase.
Here, we define HCOOH fuel-based emission factors (EF_{HCOOH}) as the mass of formic acid (milligram) emitted per kilogram of fuel burned by the LDGV. The EFs were calculated using the following equation:

\[
EF_{HCOOH} = \frac{[HCOOH]}{[CO_2]} \times \frac{M_{CO_2}}{M_C} \times W_C
\]  

(E1)

where [HCOOH] is the mass concentration of formic acid, [CO_2] is the mass concentration of CO_2, \(M_{CO_2}\) and \(M_C\) are the molecular weights of CO_2 and carbon, respectively, and \(W_C\) is the mass fraction of carbon in the fuel, assumed to be 0.85 [Kirchstetter et al., 1999].

The EFs are calculated under the assumption that the carbon present in the fuel is converted to CO_2 with unit efficiency, where the contributions from other carbon species are negligible. Since CO is the second most abundant carbonaceous species emitted, and since the \([CO]/[CO_2]\) ratio is < 3\% for most periods of the drive cycle, this is a reasonable assumption. The mass concentrations of CO_2 were calculated using the real-time measurements of CO_2, measured by the HR-ToF-AMS after the SDS, constrained by CO_2 measurements in the CVS.

EF_{HCOOH} (in mg kg_{fuel}^{-1}) are shown in Table 3.2 for both the cold start and hot running periods of the drive cycle for all eight vehicles. Of the eight vehicles tested for the cold start phase, the Chevrolet S-10 displayed the highest EF_{HCOOH} (1.68 ± 1.01 mg kg_{fuel}^{-1}), while the Chevrolet Cavalier displayed the lowest EF_{HCOOH} (0.66 ± 0.42 mg kg_{fuel}^{-1}). The reported error is the propagated uncertainty stemming from the 1\(\sigma\) standard deviation of the HCOOH and CO_2 measurements during each drive phase. The eight car fleet average
$E_{\text{HCOOH}}$ were $0.94 \pm 0.32$ and $0.57 \pm 0.18$ mg kg$_{\text{fuel}}^{-1}$ for the cold start and the hot running phase of the drive cycle, respectively. Here, the reported uncertainty represents the 1σ standard deviation of the eight independent determinations. Looking in detail at the real-time HCOOH emission factor, HCOOH/CO$_2$ is largest during the first hard acceleration when the catalytic converter was below temperature. During the second hard acceleration (850 seconds after engine start) there is a large, short-lived increase in the concentration of CO along with a smaller increase in CO$_2$, suggestive of a decrease in the air/fuel equivalence ratio during this period. There is no corresponding increase in the concentration of HCOOH, consistent with the results of Zervas et al. [2001] for spark ignition engines, which suggested that excess oxygen enhances HCOOH production.

The emission ratio of formic acid relative to CO is also shown in Table 3.2. Emission ratios (HCOOH/CO) ranged from 5.02 to 96.5 pptv/ppmv. The eight car fleet average HCOOH/CO emission ratios were determined to be $10.2 \pm 6.5$ and $42.2 \pm 33.0$ pptv/ppmv for the cold start and the hot running phases of the drive cycle, respectively. A recent global analysis of HCOOH source attribution relied on results from the tunnel studies of Talbot et al. [1988] to estimate primary emissions of HCOOH from fossil fuel combustion [Paulot et al., 2011a]. In the Talbot et al. tunnel study, concentrations of HCOOH and CO were measured in air that was sampled from the exhaust ducts of the Hampton Roads Bridge Tunnel, which connects Hampton and Norfolk, VA. The resulting HCOOH / CO emission ratios ranged between 161.5 and 352.6 pptv/ppmv (mean ± 1σ of 232.7 ± 71, for 7 determinations). The emission ratios represent a composite mixture of both diesel and gasoline cars and trucks. The date of the Talbot experiment is not specifically mentioned, although it is assumed to be between September 1985 and
December 1986, the sampling period for the intensive measurements made in Hampton, VA. Given the expected driving conditions in the Hampton Roads Bridge Tunnel, it is most reasonable to compare the results of Talbot et al. (232.7 ± 71 pptv/ppmv) to the measurements made during the hot running phase of the UC drive cycle (42.2 ± 33 pptv/ppmv). The factor of five reduction in the HCOOH/CO emission factor between this study and that of Talbot may reflect a combination of factors: 1) the near 30 year difference between the measurements and improvements in catalytic converter technology, 2) differences in fuel composition used in this study as compared to that used in 1986, and/or 3) secondary production of HCOOH in the tunnel prior to sampling. Placing our results within the global framework of Paulot et al. [2011a], the substantially smaller HCOOH/CO emission ratios in this study compared to Talbot et al. (1988) suggests an even smaller global contribution of primary HCOOH emission from fossil fuel combustion (< 0.5% of the total primary emissions, instead of 2%, if HCOOH emissions scale linearly with CO). On a regional scale, especially near urban areas, primary emissions of HCOOH are likely to contribute to a greater extent. Assessment of the extent to which HCOOH primary emissions from fossil fuel combustion contribute to the observed mixing ratios of HCOOH are expected to be regionally specific and are beyond the scope of this analysis.
Figure 3.2: R/V Atlantis (solid black) and Margrethe Maersk (solid gray) ship tracks on 25 May 2010 (UTC) during CalNex 2010. Margrethe Maersk plume (4x) are shown in red overlaid on the R/V Atlantis ship track. Formic acid (HCOOH) mixing ratios during the Margrethe Maersk plume intercepts on top of the R/V Atlantis ship track.
3.4.2 Determination of formic acid fuel-based emission factors from ocean-going vessels

Figure 3.3: Formic acid (A) and CO$_2$ (B) mixing ratios during a plume intercept of the *Margrethe Maersk* cargo ship of the coast of Southern California (33.6393, -118.5402) on 26 May 2010 (3:37 UTC). The squares in each figure represent the mean HCOOH concentration over the 30 seconds before and after the plume intercept and the dashed lines represent the interpolated baseline.

During the CalNex 2010 field campaign, HCOOH fuel-based emission factors were determined for 12 ocean-going vessels. A sample ship plume intercept is shown in Figure 3.2, where the exhaust plume was sampled as the container ship (*Margrethe Maersk*) left the port of Long Beach. The concentration of HCOOH in the plume intercepts is shown in color on top of the Atlantis ship track. HCOOH mixing ratios during the fourth plume
encounter of the Margrethe Maersk (33.6393, -118.5402 at 3:37 UTC on 26 May 2010) is shown in Figure 3.3A and the corresponding CO₂ mixing ratio is shown in Figure 3.3B. A clear increase in both HCOOH and CO₂ above background levels within the plume is observed. Fuel-based emission ratios were calculated independently from both the slope of the correlation plot between CO₂ and HCOOH (e.g., Fig. 3.4) as well as from the ratio of the respective plume areas \( A_{HCOOH} \) and \( A_{CO2} \) as shown by the colored regions in Figure 3.3. Plume-specific EF\(_{HCOOH}\) values were calculated as:

\[
EF_{HCOOH} = \frac{A_{HCOOH}}{A_{CO2}} f_{fuel}
\]

(E2)

where, \( f_{fuel} \) is the fuel conversion factor that accounts for the unit conversions of CO₂ and HCOOH to mass loadings and the weight fraction of carbon in the fuel (here taken as 0.865) [Williams et al., 2009a]. Complete combustion to CO₂ is assumed in this calculation. Plume-specific background concentrations were determined by interpolating the average HCOOH from before and after the plume (Figure 3.3, black squares). Plume-specific detection limits were calculated for each plume intercept. The plume detection limit was determined as the area under a plume that was constructed as a boxcar of height +3σ of the HCOOH mixing ratio measured over the 30s prior to the plume intercept and length equal to that of the sample plume. Plume detection limits (DL) are reported in Table 3.3. All of the 12 reported plumes exceed the calculated plume detection limit. Further, for the plume to be considered in the analysis, the calculated emission factor from the regression and plume area methods were required to agree to within 30%.
Figure 3.4: Correlation of one second measurements of formic acid and CO$_2$ mixing ratios during a plume intercept of the Margrethe Maersk cargo ship of the coast of Southern California (33.6393, -118.5402) on 26 May 2010 (3:37 UTC). The data shown here is for the same plume intercept as shown in the time series in the previous figure (Figure 3.2).

The mean fuel-based emission factor for the 12 ship plumes sampled was determined to be 19.75 ± 7.63 mg kg$_{\text{fuel}}^{-1}$ from the regression analysis (R) and 20.89 ± 8.50 mg kg$_{\text{fuel}}^{-1}$ as determined from the plume area (A) method, where the uncertainties are the 1σ standard deviation. Of the 12 plumes intercepted, 1 originated from a passenger ship (Marin), 7 originated from 3 different cargo ships (Margrethe Maersk, Mol Endurance, and Sun Right), and 4 originated from 2 different tankers (British Purpose and Bunga Kelana 10), for a total of 6 individual vessels. With a limited collection of plume encounters, it is difficult to directly compare EF$_{\text{HCOOH}}$ between different ship classes. However, of the plumes sampled, EF$_{\text{HCOOH}}$ for the passenger ship (4.21 mg kg$_{\text{fuel}}^{-1}$) was significantly lower than the 7 plume average for cargo ships (18.90 ± 5.35 mg kg$_{\text{fuel}}^{-1}$) and
could either reflect class dependent emissions or engine load differences as the passenger ships speed during the plume intercept was 22.1 knots as compared with 12.1 knots for the average of the three cargo ships encountered.

Table 3.3: Formic acid (HCOOH) fuel-based emission factors for 12 ship plume intercepts as measured from the R/V Atlantis during the CalNex 2010 field campaign.

<table>
<thead>
<tr>
<th>Vessel Name</th>
<th>Vessel Typea</th>
<th>HCOOH Emission Factorb Mg kgfuel⁻¹</th>
<th>Estimated Plume Age (min)</th>
<th>Plume Intercept Time (Local)c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Margrethe Maersk</td>
<td>71</td>
<td>24. ± 2.28 (R)</td>
<td>4</td>
<td>5/24/2010 20:04 (N)</td>
</tr>
<tr>
<td></td>
<td>71</td>
<td>22.5 (A), 0.57 (DL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>71</td>
<td>17.6 ± 0.83 (R)</td>
<td>&lt; 1</td>
<td>5/24/2010 20:20 (N)</td>
</tr>
<tr>
<td></td>
<td>71</td>
<td>19.0 (A), 0.27 (DL)</td>
<td></td>
<td>5/24/2010 20:30 (N)</td>
</tr>
<tr>
<td></td>
<td>71</td>
<td>15.9 ± 0.49 (R)</td>
<td>&lt; 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>71</td>
<td>14.7 (A), 0.31 (DL)</td>
<td>4</td>
<td>5/24/2010 20:37 (N)</td>
</tr>
<tr>
<td></td>
<td>71</td>
<td>15.7 ± 0.61 (R)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>71</td>
<td>16.5 (A), 0.28 (DL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mol Endurance</td>
<td>70</td>
<td>26.1 ± 0.92 (R)</td>
<td>&lt; 1</td>
<td>5/25/2010 20:55 (N)</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>28.8 (A), 0.66 (DL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>12.4 ± 1.77 (R)</td>
<td>3</td>
<td>5/25/2010 21:02 (N)</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>12.9 (A), 2.07 (DL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sun Right</td>
<td>70</td>
<td>16.6 ± 2.23 (R)</td>
<td>7</td>
<td>5/25/2010 21:34 (N)</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>18.1 (A), 1.48 (DL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>British Purpose</td>
<td>89</td>
<td>31.3 ± 1.31 (R)</td>
<td>&lt; 1</td>
<td>5/27/2010 20:56 (N)</td>
</tr>
<tr>
<td></td>
<td>89</td>
<td>24.1 (A), 1.97 (DL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>89</td>
<td>17.4 ± 1.15 (R)</td>
<td>&lt; 1</td>
<td>5/27/2010 21:12 (N)</td>
</tr>
<tr>
<td></td>
<td>89</td>
<td>24.0 (A), 2.75 (DL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>89</td>
<td>26.8 ± 2.28 (R)</td>
<td>&lt; 1</td>
<td>5/27/2010 21:38 (N)</td>
</tr>
<tr>
<td></td>
<td>89</td>
<td>34.5 (A), 4.09 (DL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bunga Kelana 10</td>
<td>81</td>
<td>27.9 ± 1.30 (R)</td>
<td>1.5</td>
<td>5/28/2010 16:14 (D)</td>
</tr>
<tr>
<td>Marin</td>
<td>60</td>
<td>31.5 (A), 4.98 (DL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.79 ± 0.65 (R)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.21 (A), 2.38 (DL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>All Intercepts (N = 12)</td>
<td></td>
<td>19.8 ±7.63 (R), 20.9 ± 8.50 (A)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Passenger Ships (N=1)</td>
<td></td>
<td>4.79 ± 0.65 (R), 4.21 (A)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cargo Ships (N=7)</td>
<td></td>
<td>18.4 ± 4.97 (R), 18.9 ± 5.35 (A)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tanker Ships (N=4)</td>
<td></td>
<td>25.8 ± 5.93 (R), 28.5 ± 5.29 (A)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a The vessel codes are: Passenger (60), Cargo (70, 71), Tanker (81, 89)
b R = regression method, A = area method, DL = plume-specific detection limit
c N = nighttime, D = daytime
All but two of the plume intercepts were at night (Table 3.3), thus removing the potential for photochemical reactions post emission to contribute to the observed enhancements in HCOOH within those ship plumes. Nonetheless, there is potential for secondary HCOOH production from O3 initiated reactions with alkenes or NO3 radical chemistry to enhance HCOOH mixing ratios within the plume in addition to HCOOH uptake and/or phase partitioning to reduce HCOOH mixing ratios within plume. To assess the impact of post-emission processes, EF_{HCOOH} is shown as a function of the estimated ship plume age, as calculated from the observed wind speed, direction, and distance between the target vessel and the R/V Atlantis. As shown in Figure 3.5A, there is no significant positive correlation between EF_{HCOOH} and plume age over the time scales of 7 minutes, although this is difficult to assess because there may be ship-to-ship differences that confound any relationship with time. If the passenger plume is removed from the analysis, a linear regression indicates a negative correlation with a correlation coefficient (R^2 = 0.70), which could be interpreted as a net loss of HCOOH due to partitioning to aerosol in the plume.

Detailed studies of HCOOH production in spark injection engines (notably different than a marine diesel engine) suggested that HCOOH production is likely a product of formaldehyde oxidation and/or oxidation of other volatile organic compounds within the catalytic converter [Zervas et al., 2001]. As such it could be expected that EF_{HCOOH} may be correlated with EF_{CO} or CO/CO2 both markers for incomplete combustion of fuel carbon. Figure 3.5B shows the relationship between CO/CO2 and EF_{HCOOH} for each of the 12 plumes sampled. As shown, there is no correlation between CO/CO2 and EF_{HCOOH}
suggesting that factors beyond combustion efficiency are the source of the variability in \( \text{EF}_{\text{HCOOH}} \).

Figure 3.5: Dependence of the formic acid fuel-based emission factor as function of: A) estimated ship plume age, B) average CO/CO₂ ratio in the ship plume. Error bars represent 1σ standard deviation. Ship plume intercepts are colored by vessel type: tanker (red), cargo (black), passenger (yellow).

3.5 Conclusions

We present direct measurements of fuel-based emission factors for HCOOH from both light duty gasoline vehicles and underway ocean going vessels for use in regional and global assessments of HCOOH sources. The eight car average \( \text{EF}_{\text{HCOOH}} \) was \( 0.94 \pm 0.32 \) and \( 0.57 \pm 0.18 \) mg kg\text{fuel}^{-1} for the cold start and hot running phases of the drive cycle,
respectively, suggesting that catalytic converter performance and the air/fuel equivalence ratio are important metrics contributing to EF HCOOH. EF HCOOH was determined to be 1.94 ± 1.06 mg kg\textsubscript{fuel}\textsuperscript{-1} for a single diesel vehicle driven under highway driving conditions, higher on average than any individual LDGV tested. The HCOOH/CO emission ratio was 10.2 ± 6.5 and 42.2 ± 33.0 pptv/ppmv, more than a factor of 5 smaller than much older estimates that have formed the basis for estimating global primary HCOOH emissions from fuel combustion. HCOOH emission factors from ocean-going vessels averaged 20.89 ± 8.50 mg kg\textsubscript{fuel}\textsuperscript{-1}, substantially larger than the LDGV emission factors, although EF HCOOH between LDGVs and ocean-going vessels are not directly comparable due to significant differences in fuel composition, combustion temperatures, and post combustion air handling. It is important to note that the results of this study are based on the analysis of six ocean going vessels and eight light duty gasoline vehicles and may not be representative of all LDGV and ship emission factors. On a global scale, HCOOH primary emissions from fossil fuel combustion are likely to be insignificant relative to secondary production mechanisms, however primary emissions may contribute more significantly on a finer, local scale in urban locations.

### 3.6 Acknowledgements

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Chapter 3, in full, is a reprint of the material as it appear in Atmospheric Environment. Crisp, Timia A., Brady, James M., et al. "On the primary emission of formic
acid from light duty gasoline vehicles and ocean-going vessels." Atmospheric Environment 98 (2014): 426-433, doi:10.1016/j.atmosenv.2014.08.070. The dissertation author was one of the primary investigators and authors of this paper.
3.7 References


4. **Assessing the impact of the Salton Sea on local and regional air quality**

4.1 **Abstract**

The Salton Sea is a highly-saline, terminal lake located in Southeastern California. Despite constituting the largest body of water in California, the impact of the Salton Sea on local and regional air quality is not well detailed. We present here an assessment of the impact of the Salton Sea on local and regional air quality with respect to both long and short term influences through the use of publicly accessible air quality and meteorological data from the surrounding local and regional communities. A negligible impact on air quality was observed when assessing the impact of the shrinking of the Salton Sea over the past 15 years with no significances in PM$_{10}$ or PM$_{2.5}$ observed. High-speed, episodic wind events were determined to have a potentially negative impact on the air quality of both the local Salton Sea area as well as the San Bernadino and Riverside counties. Following a sustained, high-speed, episodic wind event on the evening of September 9th, 2012, significant emissions of hydrogen sulfide out of the Salton Sea resulted in both elevated H$_2$S and SO$_2$ as observed both at the Slaton Sea and in Riverside County. Although the Salton Sea does not currently pose a significant risk to local and regional air quality, the drastic changes in the size of the lake that are set to occur in 2017 have the potential to change the degree to which the Salton Sea impacts the air quality of the surrounding communities and further investigation is necessary.
4.2 Introduction

The Salton Sea, located between the agricultural fields of the Coachella and Imperial valleys, is the largest body of water in California (Fig. 4.1). The Sea is a highly saline, terminal lake formed over a 17 month period from October 1905 to February 1907, following an engineering accident by the California Development Company that resulted in water from the Colorado River breaching an irrigation channel levee and flooding into the Salton Basin [Robertson et al., 2008]. The Salton Sea originally formed as a fresh water lake, however since its formation the Sea has undergone significant changes in both its size and composition [Schroeder et al., 2002; Watts et al., 2001]. Over the past decade there has been renewed interest in determining how biogeochemical changes in the Salton Sea may impact air quality in Southeastern California. In the following chapter, we utilize long term measurements of criteria air pollutants to assess how the evolution of the Salton Sea has impacted air quality in this region.

Figure 4.1: Locations of the EPA maintained and CIMIS maintained sampling stations used in this study.
The Salton Sea is approximately 50 feet in depth (maximum) and covers a surface area of ca. 360 square miles (2015), measuring an average of 35 miles long and 15 miles wide at its widest point, constituting the largest body of water in California. The terminal nature of the Salton Sea has transformed the Sea into a highly saline lake. There are no drainage outlets for the Sea leaving continued evaporation the primary mechanism for water loss. This results in the retention and concentration of minerals and salts over time. As of 2007, the salinity of the lake is ca. 48 g L\(^{-1}\), roughly 37 percent saltier than the Pacific Ocean [Tetra Tech, 2007]. The Salton Sea receives on average less than 3 inches of direct precipitation annually while the net evaporation rate from the surface exceeds 70 inches per year [Robertson et al., 2002; Schroeder et al., 2002]. Direct flow of water from the Colorado River into the Salton Basin was arrested in 1907, leaving runoff of agricultural irrigation to the Salton Sea Basin (ca. 260 acre miles) primarily diverted from the Colorado River [Schroeder et al., 2002] the majority source for sustaining water levels. The majority of the inflow to the Salton Sea comes from the agricultural drain of the Imperial (Alamo and New rivers) and Coachella (Whitewater river) valleys, as well as municipal and industrial effluent from Mexicali, Mexico (New River) [Robertson et al., 2008; Chung et al., 2008; Schroeder et al., 2002]. By virtue of the dependence of the Salton Sea inflows on agricultural drainage, changes in the volume and size of the Salton Sea reflect the irrigation practices of the Coachella and Imperial valleys with the Sea reaching its maximum annual elevation during the spring and early summer (Fig. 4.2).
Immediately following the levee breach, the Salton Sea reached its maximum size, with a surface coverage of 520 sq. miles [Carpelan, 1958]. Following the canal repairs, evaporation rates at the Sea greatly exceeded agricultural drainage inflows and the lake experienced a drastic decline in size until 1925, at which time an increase in agricultural practices within the Salton Sea watershed and subsequent increase in agricultural drainage saw a rise in the surface elevation of the lake until the 1960’s [USGS]. The physical size of the Salton Sea remained constant until early 2000 when reductions in agricultural runoff from improved irrigation and water conservation practices within the watershed were observed [USGS; King et al., 2011]. The onset of the decline in the surface elevation of the Salton Sea beginning around early 2000 from its relatively stable average elevation of -228 feet above mean sea level [USGS] can be seen in Figure 4.2. In 2003, the size and
future of the Salton Sea was significantly influenced with the signing of the Quantification Settlement Agreement (QSA) by the Coachella Valley Water District, Imperial Irrigation District, and the Metropolitan Water District of Southern California. The QSA enables California the means to implement water transfers and supply programs such that California is able to remain within its 4.4 million acre-foot basic annual apportionment of the Colorado River Water [SDCWA]. The QSA adversely affects the future size of the Salton Sea by establishing a water transfer from agricultural water users of the Coachella and Imperial valleys to urban users [SDCWA]. With the transfer of water use out of the Coachella and Imperial valleys, the amount of agricultural drainage and subsequent inflow to the Salton Sea will drastically decrease, leading to a significant reduction in the physical size of the Salton Sea. While inflow reductions to the Salton Sea have already been observed, the QSA mandates that the surface water level of the Sea should be maintained at -227 feet above sea level or higher until 2018 [King et al., 2011]. However, the impact of the QSA on the Salton Sea is slated to significantly escalate starting in 2018, when water inflows to the Sea are to be significantly reduced [SDCWA; King et al., 2011]. Modeled projections estimate that surface of the Salton Sea will drop 20 feet in the 10 to 12 years following 2017, decreasing the volume of the lake by more than 60% and tripling the current salinity [Cohen & Hyun, 2006].
With the future physical size of Salton Sea set to decrease drastically in the coming years, there is concern regarding the potential impact these changes may have on local air quality [King et al., 2011; Cohen & Hyun, 2006]. During seasonal low water level periods at the Sea, a portion of the exposed areas can be described as playa-like due to their fine sediment composition, high salt content, close proximity to groundwater and susceptibility to wind erosion [King et al., 2011]. As demonstrated in the drastic case of Owens Lake, currently one of the largest single sources of dust pollution in the United States, quick, unmitigated exposure of larger areas of playas can lead to severe dust emissions [King et al., 2011; Reynolds et al., 2007; Pelletier et al., 2006]. As the surface area of the Salton Sea decreases and the exposed portion of the lake bed playa increases there is a potential
risk for an increase in dust emissions and subsequent PM$_{10}$ loadings within the local air
shed [King et al., 2011; Buck et al., 2011]. Over the past 15 years, the Salton Sea has
experienced a 6 percent loss in surface area since the maximum surface area coverage of
1999, as demonstrated by Figure 4.2 and Figure 4.3 [USGS]. In what follows, we first
assess the impact of decadal changes in the size and chemical composition of the Salton
Sea on regional air quality using long term, regional scale measurements of criteria air
pollutants. Second, we use the same observation based network to assess the role of
episodic emission events that have the potential to induce short term air quality
exceedances.

Figure 4.4: Schematic depiction of the typical thermal profile expected for the Salton Sea based off of surface
and base temperatures measured in 1999 [Holdren & Montaño, 2002]. The Salton Sea experiences prolonged
thermal stratification during the summer and early fall and is more uniformly mixed during the winter and
eyearly spring.

Since the mid-1920’s the Salton Sea has primarily served as a sump for agricultural
wastewater for the Imperial and Coachella valleys and as a result has experienced high
external nutrient loadings leading to the eutrophication of the Salton Sea. In its current condition, the Salton Sea is a highly eutrophic lake characterized by high nutrient concentrations, high algal biomass, high fish productivity, low clarity, frequent very low dissolved oxygen (DO) concentrations, periods of strong thermal stratification, massive fish kills, and noxious odors [Holdren & Montaño, 2002]. The water temperature of the Salton Sea follows expected seasonal patterns, typically reaching maximum water temperature in August and minimum water temperature in January [Arnal, 1961; Carpelan, 1958; Carpelan, 1961; Holdren & Montaño, 2002; Watts et al., 2001]. During the summer months, the Salton Sea experiences prolonged, persistent periods of thermal stratification during which temperatures of the top and bottom of the water column differ by as much as 9 °C, shown in Figure 4.4 [Holdren & Montaño, 2002; Watts et al., 2001]. During periods of thermal stratification, surface DO is observed to be frequently above saturation, while DO concentrations in the lower depths are often zero, the result of DO mixing into the lower, cooler, denser portions of the Sea being hindered [Chung et al., 2008] (Fig. 4.5A). The occurrence of low to nonexistent DO concentrations in the hypolimnion coupled with a high biological and chemical demand for oxygen results in the lower depths of the Salton Sea experiencing prolonged periods of anoxia during the summer months [Setmire et al., 2000]. Consequently, this leads to reducing conditions which affects any chemical changes within the lake depths, including the transformation of sulfates to sulfides (e.g. hydrogen sulfide) and the reduction of nitrate to ammonia [Setmire et al., 2000; Reese et al., 2008]. The occurrence of anoxia in the presence of high nitrogen and sulfate concentrations leads to an increase in the potential for the formation of ammonium (and ammonia) and hydrogen sulfide [Marti-Cardona et al., 2008]. These anaerobic byproducts remain confined to the
hypolimnion until the water column is mixed by a wind event of sufficient energy, releasing the accumulated H$_2$S and NH$_3$ (Fig. 4.5B) [Tiffany et al., 2009; Marti-Cardona et al., 2008], both of which can serve to initiate secondary aerosol formation.

Figure 4.5: A) Schematic of a thermally stratified lake with the arrangement of the epilimnion, metalimnion, and hypolimnion shown. The generic profiles for the temperature (red), DO concentrations (purple), and concentrations of reduced substances, e.g. hydrogen sulfide or ammonium, (green) within the lake. B) Generic depiction of the expected upwelling of the water column at the downwind end, resulting in a redistribution of reduced substances and low DO throughout the water column. Figure reproduced from Marti-Cardona et al. (2008).
Wind blowing over the long fetch of the lake is the primary driver for hydrodynamic behavior of the Salton Sea [Cook et al., 2002]. Wind forcing affects the water temperature, DO, and nutrient cycling of the Salton Sea [Carpelan, 1958; Watts et al., 2001]. The fetch of the wind, a function of wind speed and distance over which the wind blows across the surface, determines the depth and extent of mixing within the Sea [Cohen & Hyun, 2006]. Recent analysis of upwellings and wind patterns in the Salton Sea by Marti-Cardona et al. (2008) demonstrated that strong and persistent wind events are capable of inducing upwelling events in the Sea and typically proceed the majority of the massive fish kills that characterize the lake. When a wind event of sufficient fetch occurs over the thermally stratified lake, the large wind stress on the surface of the lake is balanced by a horizontal pressure gradient, triggering the colder, denser water of the hypolimnion to rise at the upwind lake boundary [Marti-Cardona et al., 2008; Farrow & Stevens, 2003]. Following the upwelling, the entire water column of the Sea is low in DO and high in concentrations of hydrogen sulfide and ammonium [Marti-Cardona et al., 2008; Watts et al., 2001]. Figure 4.5B demonstrates the expected upwelling and redistribution of DO and reduced substances that would occur in a thermally stratified lake under a constant wind event, with the upwelling occurring at the downwind end [Marti-Cardona et al., 2008].

The exchange of these redistributed pollutants across the air-water interface into the atmosphere is driven by a concentration gradient in which the aqueous phase and atmospheric concentrations seek to reach equilibrium [ATSDR, 2014]. The rate of evaporation depends on several factors such as temperature, humidity, pKa, and pH. The kinetics of the exchange across the air-water interface are similar to other unreactive gases at pH $\leq 6$, with hydrogen sulfide emission enhanced at higher pH [ATSDR, 2014]. Although
the major sink for H₂S in the water column is through O₂ oxidation, it has previously been demonstrated that following these mixing events DO concentrations are not sufficient for complete reduction of the sulfide and that even with adequate DO, the reduction can take weeks to complete, allowing for the volatilization of hydrogen sulfide to occur [Tetra Tech, 2007]. The upwelling events provide a potentially significant source of hydrogen sulfide emissions into the atmosphere, a precursor for SO₂ and ultimately sulfate aerosol production.

Once in the atmosphere, the emitted hydrogen sulfide may be oxidized by either oxygen or ozone to produce SO₂ and eventually sulfate compounds. Hydrogen sulfide is not expected to decompose via direct absorption of ultraviolet radiation and the reaction between H₂S is not expected to be a significant environmental fate due to its relatively long reaction time (k ≤ 2.0 x 10⁻²⁰ cm³ molecule⁻¹ s⁻¹) [Cox, 1975; ATSDR, 2014]. With a rate constant of 4.7x10⁻¹² cm³ molecule⁻¹ s⁻¹, the oxidation of H₂S by the hydroxyl radical is expected to dominate in the ambient atmosphere [Sander et al., 2011]. The production of SO₂ and H₂SO₄ from H₂S proceeds through the following series of homogeneous oxidation reactions.

\[
\begin{align*}
H₂S + OH & \rightarrow HS + H₂O \quad \text{(R1)} \\
HS + O₂ & \rightarrow SO₂ + H \quad \text{(R2)} \\
SO₂ + OH & \rightarrow HOSO₂ \quad \text{(R3)} \\
HOSO₂ + O₂ & \rightarrow HO₂ + SO₃ \quad \text{(R4)} \\
SO₃ + H₂O & \rightarrow H₂SO₄ \quad \text{(R5)}
\end{align*}
\]

The three-body reaction formation of H₂SO₄ from SO₂ (R3-R5) is rate limited by R3 [ATSDR, 2014] and can be simplified to:
SO$_2$ is also converted to sulfate through oxidation reactions in the aqueous phase. Based on summer daytime and yearly average hydroxyl radical concentrations, the effective lifetime of hydrogen sulfide is estimated to be 0.23 and 2.3 days respectively [Cox, 1975]. The lifetime of SO$_2$ in the atmosphere is estimated to be 1 day before it is deposited to the surface or oxidized to sulfate aerosol [Stevenson et al., 2003]. Once formed, H$_2$SO$_4$ forms sulfate aerosols either through condensation on preexisting nuclei or homogeneous nucleation mechanisms [Stevenson et al., 2003].

Episodic high wind events at the Salton Sea can produce a potentially significant source of H$_2$S, with subsequent increases in the production of SO$_2$, an EPA classified criteria pollutant, and sulfate particulate matter expected. To the best of our knowledge, there are no current assessments in the literature on the effects of these periodic high wind events and subsequent upwellings of the Salton Sea on regional air quality.

On September 10$^{th}$, 2012 a foul, “rotten egg” odor was reported throughout Riverside and San Bernadino counties [AQMD, 2012a]. The occurrence of the smell was reported by thousands of individuals over social media, with the AQMD receiving more than 200 complaints of sulfur and rotten-egg odors starting in the early morning hours of September 10$^{th}$ [AQMD, 2012a]. The AQMD later reported that the source of the odor was most likely the Salton Sea, and that there was no impact on air quality in the region other than the odor [AQMD, 2012a]. In this work we utilize this specific episodic wind event to assess the impact of a specific, high speed, sustained wind event occurring at the Salton Sea on September 9$^{th}$, 2012 on regional air quality.
4.3 Methods

4.3.1 Long Term Monitoring Networks

4.3.1.1 California Irrigation Management Information System (CIMIS) Stations

Meteorological data including air temperature, wind speed and wind direction was obtained from several CIMIS stations located around the Salton Sea. Locations of the CIMIS meteorological stations are shown in Figure 4.1. The CIMIS stations are maintained by the Department of Water Resources and use an onsite data logger to record meteorological data each minute. The data from each station is transmitted to a publicly accessible CIMIS database for long-term storage. Wind speed is calculated with a Met-One 014A three-cup anemometer that utilizes a magnet activated reed switch whose frequency is proportional to wind speed. The anemometer has a range of 0-100 mph and an accuracy of 0.25 mph. Wind direction is calculated with a 024A Met-One wind vane with an accuracy of ±5%.

4.3.1.2 Environmental Protection Agency (EPA) Air Quality Monitoring Sites

Criteria pollutant data for the local Salton Sea area and Riverside County were obtained from the EPA monitoring stations shown in Figure 4.1. The criteria pollutants measured varied with respective station, however all sampling methods were a Federal Reference Method or Federal Equivalent Method. A detailed list of the respective monitoring stations and method reference ID for each respective measurement is provided in Table 4.1, with the specific instrument descriptions for each method reference ID provided in Table 4.2. Although more detailed descriptions of each individual sampling method are provided in the literature, we provide here a brief overview of the various
sampling methods for each pollutant. Specific operating parameters and applicable quality assurance procedures for each method to achieve federal reference or equivalent method designation are provided by the EPA [US EPA:ORD, 2015].

The two PM$_{2.5}$ sampling methods utilized by the monitoring stations accessed in this study operate using a filter-based, gravimetric sampling method. The instruments draw particulate-laden ambient air sample streams through a size selective inlet to filter out particulate matter with a diameter larger than 2.5 microns. The air sample stream is then passed through a filter, onto which the particulate mass is collected and weighed to give the particulate mass for that sampling period [US EPA:ORD, 2015].

PM$_{10}$ measurements were made using either the FRM designated gravimetric analysis method, or by the FEM designated beta ray attenuation method. The operating principle of measurements made with the gravimetric method are similar to that utilized by the PM$_{2.5}$ sampling methods, except that inlet of the instrument is sized such that all particles up to 10 microns in size are sampled. The beta ray attenuation method measures and records airborne particulate concentration levels by measuring the attenuation of a beta ray signal through a piece of filter tape on which ambient dust is loaded. Comparing that to the number of beta rays transmitted through the clean filter tape at the beginning of the sample run allows for a calculation of the mass of the particulate matter on the filter tape, which can then be used to calculate the volumetric concentration of particulate matter in the ambient air [Met-One BAM1029 Datasheet].

Ozone measurements are made based on ultra violet absorption and the Beer-Lambert equation. The ozone analyzers operate by measuring the intensity of ultra violet light after it has passed through a sample of ambient air and comparing that to the intensity
of UV light through a sample that has been scrubbed of ozone. Coupling that with measurements of the ambient temperature and pressure of the sample gas, the Beer-Lambert equation is used to calculate the amount of ozone present in the sampler gas [Teledyne Technologies Model T400 Operation Manual].

The nitrogen dioxide measurements are based on the principle that nitric oxide (NO) and ozone react to produce a characteristic luminescence with an intensity that is linearly proportional to the NO concentration. After the ambient air sample is drawn into the instrument and filtered of particulate matter, the sample either flows directly to the sample chamber to measure the NO in the sample, or it flows through a molybdenum NO2-to-NO converter to measure the concentration of NOx in the sample. After calculating the concentrations of NO and NOx in the sample, the difference between the NOx and NO samples is calculate to give the concentration of NO2 in the sample [Thermo Environmental Instrument Model 42c Manual].

The SO2 measurements made at the Riverside monitoring site were made with a Thermo Scientific pulsed fluorescence SO2 analyzer. The analyzer operates under the principle that SO2 molecules absorb ultraviolet light and become excited at one wavelength, subsequently decaying to a lower energy state emitting UV light at a different wavelength. The air sample is sampled into the instrument, passed through a hydrocarbon kicker, and flowed into a fluorescence chamber in which a pulsating UV light is used to excite the SO2 molecules. The decay of the SO2 molecules to lower energy states results in an emission of UV light that is proportional to the SO2 concentration of the sample. Utilizing a bandpass filter, only the wavelengths emitted by the excited SO2 molecules reach the
photomultiplier tube detector whereupon the concentration of SO$_2$ can be calculated [Thermo Fisher Scientific Model 43i Trace Level-Enhanced Instruction Manual].

### 4.3.1.3 Salton Sea Surface Area Coverage

The surface elevation data utilized in this work was obtained from the United States Geological Survey (USGS) station 10254005. The station is managed by the Poway Field office and is funded by the Imperial Irrigation District and the Cooperative Water Program of the USGS. The station provides data on the surface elevation of the Salton Sea from October 1, 1987 until present day. The surface elevation data obtained from USGS station 10254005 was used to calculate the decline in surface area of the Salton Sea over the past 15 years. To calculate the surface area coverage of the Salton Sea from the surface elevation data, bathymetric one foot contours of the Salton Sea were obtained from the California Department of Fish and Wildlife, via the State of California Geoportal. Coupling the Salton Sea surface elevation with the bathymetric contours of the underlying topography of the Salton Sea we were able to calculate an estimated surface area coverage of the Salton Sea over the past 15 years.

### 4.3.2 Wind Trajectory Analyses

Analysis of the potential impact of the sustained, high-speed, anomalous wind event on September 9\textsuperscript{th}, 2012 at the Salton Sea on the regional air quality of San Bernardino and Riverside counties was furthered by wind trajectory analyses modeled using the National Oceanic and Atmospheric Administration’s (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT) [Draxler & Rolph; Draxler]. The HYSPLIT
trajectory analysis presented here was calculated for the time period between September 9th, 2012 at 23:00 PST and September 10th, 2012 at 17:00 PST. Trajectories were calculated over an 8-hour run time with new trajectories calculated starting every 2 hours.

4.4 Results and Discussion

4.4.1 Air Quality Impact of Decadal Changes in Salton Sea Surface Area

Over the past 15 years, the Salton Sea has gradually decreased in size (Fig. 4.3) reducing the surface area of the sea by 6% and in the process exposing an estimated 22 sq. miles of previously covered lake bed. With the future size of the Salton Sea predicted to rapidly decrease beginning in 2017 and model predictions estimating a 70% decrease in volume and the exposure of 134 sq. miles of lake bed by 2036, we assess the current impact of the Sea’s decreasing size on local air quality using data from local EPA monitoring sites [Cohen & Hyun, 2006].

A study by King et al. (2011) examined the relationship between surface type and dust emission variability at the Salton Sea. King et al. (2011) demonstrated that playa-like sites, considered to most closely resemble what the sediment in the Salton Sea would be like immediately after water levels recede, were a significant producer of dust during winter and early spring. During the cool, wet conditions of the winter season, the playa-like surfaces form a friable crust, becoming weaker during the winter as a function of temperature and humidity [King et al., 2011]. The salt-based crusts near the shoreline were concluded to be a significant but temporary source of dust, limited to cool wet months [King et al., 2011]. Silt/clay crusted sites and dry washes were proposed to be significant sources of dust at the Salton Sea throughout the year, with dry wash sites consistently
exhibiting the highest PM$_{10}$ emissions [King et al., 2011]. The results of King et al. (2011) would suggest that as the Salton Sea decreases in size and a larger percentage of the playa-like surface is exposed, enhancements in PM$_{10}$ emissions may be observed in the winter months.

Serving as a sump for agricultural waste water, the Salton Sea contains a large supply of fine material and salts and as the lake shrinks in size the exposed dry playa-like lake bed poses as a significant emissions source for PM$_{10}$ [Baddock et al., 2011]. As the sea decreases in size, the exposed lake bed will be vulnerable to wind erosion by abrading saltating particles and a significant increase in PM$_{10}$ would be expected [Reid et al., 1994; Cahill et al., 1996]. The exposure of a similar playa-like lake bed at Owens Lake, California, demonstrates that aerosol generation from this type of exposed lake bed will potentially have a PM$_{10}$ mass median diameter between 2.5-5 μm [Reid et al., 1994; King et al., 2011]. As such we would expect the increase in exposed lake bed surface area to have a more significant impact on PM$_{10}$ than PM$_{2.5}$. 
Figure 4.6: A) Decrease in surface area coverage of the Salton Sea since maximum coverage in 1999. Averaged monthly means of measurements of PM10 (B), PM2.5 (C) and ozone (D) measured at EPA monitoring stations located in the local vicinity of the Salton Sea from 2000 to 2014.
Monthly averaged PM$_{10}$ at five monitoring stations within the local Salton Sea airshed are shown in Figure 4.6B. As shown in Figure 4.6B, observations of monthly averaged PM$_{10}$ mass concentrations dating back to 2000, show no statistical trend within the local air shed despite a concurrent increase in exposed playa-like surface area. When comparing the correlation between the measured PM$_{10}$ mass concentrations and increasing exposed surface area, linear regression analysis results in a 0.0094 $R^2$ value. Statistically there is no significant correlation between the increase in lake bed surface area exposure and PM$_{10}$ emissions within the surrounding airshed. To further investigate the potential relationship between the increase in lake bed exposure and impact on PM$_{10}$ emissions we also look at the estimated number of days in the year in which the air quality at the local monitoring stations would have been in exceedance of the 24-hour national (150 μg m$^{-3}$) and California state (50 μg m$^{-3}$) PM$_{10}$ standards (Fig. 4.7A). Paralleling the trends observed when detailing monthly means of PM$_{10}$ since 2000, no discernible increase in the number of days in exceedance of either the national or state standards is observed with the decreasing size of the Salton Sea. Taking a closer look at 2014, Figure 4.8B indicates that the highest monthly PM$_{10}$ is observed in May of 2014 and the lowest in December of 2014. Although a more detailed inventory of the PM$_{10}$ sources for each of these sites is necessary, based on the trends observed here, it appears that the current increase in the exposure of playa-like surfaces is not significant enough to impact local PM$_{10}$ mass concentrations in the region. Figure 4.9A demonstrates that there is no significant dependence of PM$_{10}$ emissions on the size of the Salton Sea. With no significant enhancement in PM$_{10}$ emissions with decreasing Salton Sea size, dry wash surfaces may still be the dominant
source of PM$_{10}$ emissions as the 22 sq. mile increase in playa-like surfaces is not large enough to affect the region.

The observed reduction in the surface area of the Salton Sea may also have direct impact on secondary aerosol formation rates following the oxidation of emitted trace gases such as H$_2$S. It has been postulated that a reduction in the volume of the Salton Sea will lessen stratification of the sea, leading to more oxygenated conditions and corresponding reduction in SOA precursor gases such as H$_2$S and NH$_3$.

Figure 4.6B does demonstrate an observed, albeit slight decrease in measured PM$_{2.5}$ since 2000. However, the availability of PM$_{2.5}$ data was limited to the Brawley and Indio sites, both of which are located in populated communities. Whether the slight reductions in PM$_{2.5}$ are entirely due to the shrinking of the Salton Sea over that 15 year time period or are in fact the mixed result of the shrinking Sea and improved PM$_{2.5}$ regulation and control in the area is not clear. When looking at PM$_{2.5}$ emissions in regards to days in exceedance of the 24-hour national standard of 35 $\mu$g m$^{-3}$ the paucity of data sites again limits our ability discern any concrete correlation between the shrinking Salton Sea size and PM$_{2.5}$ emissions (Fig. 4.7B). The dependence of PM$_{2.5}$ on the size of the Salton Sea is also depicted in Figure 4.9B, demonstrating again a slight decrease in PM$_{2.5}$ in the local area with decreasing Salton Sea surface area.
Figure 4.7: A) Estimated number of days in the year that 24-hour national (150 μg m⁻³) and California state (50 μg m⁻³) PM10 standards would have been exceeded had sampling occurred every day of the year. B) Estimated number of days in the year that the national 24-hour PM2.5 standard of 35 μg m⁻³ would have been exceeded had sampling occurred every day of that year. C) Number of days in each year that the maximum 8-hour average ozone concentration at each specific monitoring station was greater than or equal to the national standard of 0.075 ppm (circles) and the California state standard of 0.070 ppm. Data provided by the California Air Resources Board.
Figure 4.8: Annual time series of monthly averages ± 1σ for temperature (A), wind speed (B), PM10 (C), PM2.5 (D), and ozone (E) collected at EPA monitoring stations during 2014. For criteria pollutants PM10, PM2.5, and ozone the NAAQS standards are also depicted.
In the assessment of the Salton Sea’s decline on local air quality, ozone was also investigated. Although no distinct change in ozone concentrations is observed in the monthly means of ozone over the past 15 years, (Fig. 4.6C), a distinct decrease in the number of days in exceedance of the 8-hour national (0.075 ppm) and California (0.070 ppm) standards is observed in all of the 3 sites for which measurement data was available. The yearly profile for ozone in 2014 demonstrates an expected seasonality for ozone, with ozone concentrations peaking in the summer months and at their lowest in the winter months. The decrease in the size of the Salton Sea does not appear to have any effect on ozone in the local airshed.

Based on the available data for the past 15 years, it is not readily apparent that the current decrease in the physical size of the Salton Sea has had any adverse effects on local air quality. It is important to note however that while no impact has been observed over the past 15 years, the decrease in the lake’s size has been gradual over this time period. As part of the QSA, the estimated reduction in the Salton Sea’s volume of 60% over the 10 to 12 year period following the drastic reductions in Salton Sea inflows beginning in 2018 could potentially result in a more pronounced air quality impact, especially with consideration to PM₁₀ emissions [Cohen & Hyun, 2006]. As King et al. (2011) demonstrated, the playa-like surfaces present a significant, but temporarily short lived potential PM₁₀ emission source. The exposure of ca. 22 sq. miles of lakebed over the past 15 years may not fully capture the potential adverse implications of a more immediate and significant exposure of the lakebed. While no current correlation is observed between a decreasing lake size and decreasing air quality, the potential rapidness of the impending
estimated decline in the Salton Sea size beginning in 2018 could magnify the impact of the exposed lake bed on subsequent PM$_{10}$ emissions in the local airshed.

![Figure 4.9](image)

Figure 4.9: Dependence of PM$_{10}$ (A) and PM$_{2.5}$ (B) emissions on Salton Sea size over the past 15 years.

There is little to no observed correlation between emissions and current changes in the physical size of the Salton Sea. While the emissions do not track changes in the surface
area coverage of the Salton Sea, the emissions from the Salton Sea are episodic and are primarily driven by wind events. Although the changing sea size has had little effect on observed air quality metrics over the last 15 years, the actual impact of the Salton Sea on air quality may be more episodic and assessing that impact may require looking at specific episodic events.

4.4.2 Air Quality Impact of Episodic Wind Events in Populated Coastal Communities

The foul odor reported throughout San Bernardino and Riverside counties on September 10th, 2012 was suggested to have emanated from the Salton Sea, although a detailed look into the origin of the odor and possible air quality impact of the event have not been studied in detail [AQMD, 2012a]. An analysis of the wind speeds recorded at three CIMIS stations located around the Salton Sea during the month of September 2012 demonstrate that a sustained, high speed, anomalous wind event occurred on the evening of September 9th, 2012 (Fig. 4.10). Between 7-9:00 PM on the evening of September 9th a wind event was recorded with wind speeds ca. 10-20 mph faster than the average wind speed for the month of September. According to the CIMIS stations, the wind event reached average speeds as high as 23.3 mph and was elevated above 10 mph for a period of 3 hours beginning at 7 PM on the evening of September 9th. The AQMD reported much higher wind events of at least 50 mph [AQMD, 2012b]. The wind event took place in a parallel direction to the long axis of the Salton Sea. The high speed and sustained duration (ca. 3 hours) of the wind event coupled with the occurrence of the event over the long axis of the Salton Sea would have produced a fetch of significant intensity to induce an
upwelling within the previously thermally stratified lake. The upwelling event would have resulted in a thorough mixing of the water column with the byproducts of anaerobic activity, e.g. hydrogen sulfide and ammonium, that were previously confined to the hypolimnion being released from the lower depths and mixing throughout the water column.

Figure 4.10: Occurrence of an anomalous high speed sustained wind event on the evening of September 9th, 2012. The wind event last ca. 2 hours with sustained wind speeds ca. 10-20 mph faster than typical wind events for that period.

With the increase in surface water sulfide concentration as a consequence of the flux, an increase in the concentration of H$_2$S (g) is expected to occur directly above the Salton Sea. Although the primary loss mechanism for sulfide in the Salton Sea is through sulfide oxidation, losses at the air-water interface do occur, driven by a concentration gradient where in the aqueous phase concentration and the atmospheric concentration seek to reach an equilibrium. As demonstrated in a 2007 report prepared for the Salton Sea Authority, the concentration of H$_2$S in the air directly above the surface of the Salton Sea
increases dramatically with a rise in surface water sulfide concentrations resultant from upwelling events [Tetra Tech, 2007]. During that study, concentrations of H$_2$S above the Sea’s surface averaged 1.7 $\mu$g m$^{-3}$ through the winter and spring, increasing to concentrations as high as 34 $\mu$g m$^{-3}$ (24.4 ppb) following mixing events that saw a dramatic increase in surface water sulfide concentrations [Tetra Tech, 2007]. When compared to the average ambient levels of hydrogen sulfide found in typical urban environments (0.3 $\mu$g m$^{-3}$), upwelling events have the potential to produce hydrogen sulfide levels directly over the Salton Sea that are 10 times greater than what is seen in the typical ambient urban air shed. [Robinson and Robbins, 1970; Tetra Tech, 2007]. Following the widespread complaints of the foul odor emanating through Coachella Valley, the Banning Pass, and across the Los Angeles Basin, the AQMD dispatched technicians throughout the affected areas and sampled the local H$_2$S concentrations [AQMD, 2012b]. The AQMD (2012b) reported H$_2$S concentrations as high as 149 ppb Norwest of the Salton Sea. Since the September 10th odor event, the AQMD has installed H$_2$S monitors in the local vicinity of the Salton Sea and have since issued several odor advisories with reported H$_2$S concentrations ranging from 32-106 ppb [AQMD, 2014a; AQMD, 2014b]. The duration, speed, and direction of the wind event observed on the evening of September 9th at the Salton Sea, would have had a sufficient fetch to induce a mixing event within the Salton Sea that resulted in increased concentrations of hydrogen sulfide directly over the Salton Sea.

While the impact of hydrogen sulfide emissions from the Salton Sea are typically limited to the immediate area, wind trajectory analyses show a direct outflow of air from the Salton Sea into the San Bernadino and Riverside Counties. The results of a forward
trajectory analysis model are depicted in Figure 4.11, showing the modeled outflow of air parcels from the Salton Sea into San Bernadino and Riverside Counties. The model analysis reveals a direct path from the Salton Sea source to the affected counties in the time period immediately following the wind event into and through the next day. Over the timescales presented here, the hydrogen sulfide emissions occurring at the Salton Sea surface as a result of the upwelling events are capable of making it into San Bernadino and Riverside counties. Hysplit trajectory analysis estimates the emissions from the Salton Sea would reach Indio (Fig. 4.12) ca. 3-4 hours and Palm Springs (Fig. 4.13) 5-6 hours and Riverside (Fig. 4.14) ca. 10-12 hours after emission out of the Salton Sea.

Once in the atmosphere, hydrogen sulfide can degrade through oxidation by O₂ and O₃ to yield SO₂, or it can also react with hydroxyl radicals [Cox, 1975]. Decomposition by direct absorption of ultraviolet radiation is not expected and the effective lifetime of H₂S in the atmosphere is estimated to range from between 5.5 hours to 2.3 days [Cox, 1975]. Even with a conservative lifetime estimate of 5.5 hours, the hydrogen sulfide emitted by the Salton Sea will have reached San Bernadino and Riverside counties, carried by the air parcels depicted in Figure 4.11.
Figure 4.11: Forward trajectory analysis model results for air parcel trajectories between September 9, 2012 at 23:00 and September 10, 2012 at 17:00, demonstrating a strong outflow from the Salton Sea into San Bernadino and Riverside counties following the wind event that took place on the evening of September 9th. The model trajectories were calculated using the NOAA HYSPLIT Trajectory Model [Draxler and Rolph]. Each trajectory is calculated as an 8 hour run, with new trajectories starting every 2 hours. Times within the figure legend correspond to UTC.
Observations at the Riverside sampling site (Fig. 4.14) demonstrate a significant increase in the SO₂ observed on September 10th, 2012 as compared to the monthly average (Fig. 4.14.E). The SO₂ is observed to peak at ca. 10am in the morning, which would correlate to approximately 3.5 hours of daylight with which the transported H₂S plume could be oxidized by OH. Utilizing a simple box model with a constant [OH] of 1×10⁶ molecules cm⁻³, we calculate that a concentration of ca. 85 ppb H₂S would be required to produce the 4.3 ppb SO₂ observed at Riverside. With the AQMD reported H₂S at the Salton Sea of 149 ppb there should be sufficient H₂S within the air mass reaching Riverside from the Salton Sea to result in the observed SO₂ peak.

While this episodic H₂S emission plume from the Salton Sea is expected and observed to have an impact on SO₂ in the areas affected by the wind event, formation of particulate mass from H₂S is not expected to have as readily of an apparent impact. The kinetics of the oxidation of SO₂ to sulfate aerosols are too slow with respect to the transport times of the emission plumes through the affected communities. Assuming all of the SO₂ formed undergoes oxidation to H₂SO₄ and subsequently forms ammonium sulfate, we calculate that after 4 hours the total SOA formed would be 0.50 μg m⁻³; after 12 hours the total SOA formed would be 4.2 μg m⁻³. The available PM₂.₅ measurements at Palm Springs (Fig 4.13) and Riverside (Fig 4.14) demonstrate no significant increases in PM₂.₅ over the average monthly mean for September 2012. A significant enhancement in PM₁₀ is observed however. The enhancement in PM₁₀ and lack of increase in PM₂.₅ suggests that the increase in PM₁₀ is mechanically driven and is not related to the upwelling events that occurred at the Salton Sea.
Figure 4.12: Hourly measurements (blue) of temperature (A), PM$_{10}$ (B), and ozone (C) taken on September 10th, 2012 at the Indio monitoring station. The monthly average for the hour $\pm 1\sigma$ is also depicted in red.
Figure 4.13: Hourly measurements (blue) of temperature (A), PM$_{10}$ (B), PM$_{2.5}$ (C), and ozone (D) taken on September 10th, 2012 at the Palm Springs monitoring station. The monthly average for the hour ± 1σ is also depicted in red.
Figure 4.14: Hourly measurements (blue) of temperature (A), PM$_{10}$ (B), PM$_{2.5}$ (C), and SO$_2$ (D) taken on September 10$^{th}$, 2012 at the Riverside monitoring station. The monthly average for the hour ± 1σ is also depicted in red.
The olfactory impact of this isolated episodic wind event was clearly demonstrated by both media reports and the large number of complaints issued to the AQMD by the public. Aside from the unpleasant odor from the hydrogen sulfide, this event had a very slight impact on the air quality of Riverside with respect to a clearly demonstrated enhancement in SO$_2$ over the monthly average for Riverside. While the raised SO$_2$ mixing rations significantly below the current 1 hour NAAQS for SO$_2$ of 75 ppb, the influence of this episodic event at Salton Sea on the air quality metrics of a community ca. 100 miles away is noteworthy.

Utilizing publicly available data from the EPA monitoring sites within the Salton Sea air shed and surrounding counties it is evident that the ca. 7 foot drop in the lake’s surface elevation and a 6% reduction in the surface area coverage of the Salton Sea has had no major impact on air quality metrics as currently measured within the local airshed. Although a more rapid reduction in surface area coverage in the near future could potentially have a more significant impact air quality, the current gradual decline in size does not. Episodic wind events at the Salton Sea, especially those following relatively long periods of thermal stratification can potentially influence the air quality of communities outside of the immediate Salton Sea area in a negative manner, increasing SO$_2$ concentrations as well producing an unpleasant and offensive odor. As the Salton Sea shrinks, prolonged periods of stratification within the lake should lessen and the occurrence of these types of episodic hydrogen sulfide emissions should potentially decrease as well.
4.5 Acknowledgements

We thank the EPA, CARB, CIMIS, and the USGS for providing and maintaining the publicly accessible databases of air quality and meteorological data utilized within this investigation. We also gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.ready.noaa.gov) used in this study.
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Thermo Environmental Instrument Model 42C Operations Manual

Thermo Fisher Scientific Model 43i Trace Level-Enhanced Instruction Manual


5. Novel Implementation of a Quadrotor Unmanned Aircraft System for Aerosol Concentration Measurements within the Boundary Layer

5.1 Abstract

We present here the novel implementation of a quadrotor unmanned aircraft system (UAS) as a sampling platform to measure the vertical and horizontal concentration profiles of aerosol particles within the boundary layer. A 3D Robotics Iris+ (Iris) autonomous quadcopter was outfitted with a custom built sensor package consisting of a MetOne 80080 two channel particle counter, a K-30 CO2 sensor, a micro air pump, and the power sources and electronics necessary for the operation of whole sensor package. The Iris flew 13 vertical and 4 horizontal flights adjacent to the Scripps Institution of Oceanography (SIO) to assess the platform’s performance as well as measure sea spray aerosol concentrations between 5-100m above sea level. The Iris demonstrated high precision in both vertical (±0.5m) and horizontal positioning (±1m) and highlights the future potential of quadrotor UAS drones for aerosol and trace gas measurements within the boundary layer. Vertical profile measurements of aerosol demonstrated an aerosol plume height of 30-35 m above the surf zone. Ambient humidity emission rates for small (0.5 \( \mu \)m < \( d_p \) < 1\( \mu \)m) and large (\( d_p > 1\mu \)m) particles were calculated to be 416 and 187 particles cm\(^{-2} \) s\(^{-1} \) and we estimate an ambient humidity mass flux of 285 \( \mu \)g m\(^{-2} \) s\(^{-1} \).

5.2 Introduction

Atmospheric aerosol particles play a central role in Earth’s radiation budget [IPCC, 2007], act to limit visibility through the scattering and absorption of radiation /Seinfeld, J.,
Pandis, S., 1998], enable the spreading of biological organisms and pathogens [Pöschl, 2005], and present a significant health hazard in urban environments [Lave et al., 1973; Bernstein et al., 2004, Turóczi et al., 2012]. Aerosol particles are generated from both natural and anthropogenic sources, and either emitted directly into the atmosphere as primary particles, or formed in the atmosphere by gas-to-particle conversion. Ground-based, aircraft, and satellite remote sensing techniques have been utilized extensively to characterize the emission, chemical and physical transformation and removal of aerosol particles in Earth’s atmosphere. The vast majority of information on particle spatial distributions comes from routine ground-based observations of aerosol particle mass loadings and satellite observations of aerosol optical thickness (AOT). Despite decades of aircraft measurements of aerosol particle number and mass distributions, large uncertainties still exist in our understanding of the vertical distribution of aerosol particles in the lower troposphere [Deshler et al., 2008; Ma & Yu, 2014] and the spatial and temporal variability in particle concentrations on the city-scale. As a result, our ability to predict how changes in emissions will impact particle number and mass distributions is subject to significant uncertainties resultant from a current lack of knowledge regarding the highly temporal and spatial variability that exists in the concentration, composition and size distributions of atmospheric aerosol particles within the lower troposphere [Ma & Yu, 2014; Pöschl, 2005; IPCC, 2007]. In this manuscript we assess the potential for unmanned aircraft systems (UAS) for sampling aerosol particle number concentrations in the lower troposphere.

The Planetary Boundary Layer (PBL) constitutes the lowest most region of the troposphere in which flow is strongly influenced by interaction with the surface of the
Earth, responding to surface forcings with a timescale of approximately 1 hour or less [Holton & Hakim, 2013]. Due to ground-level heating, the boundary layer is typically very turbulent during the day, where surface heating can sustain high boundary layer heights (ca. 1-3 km), and the entirety of the PBL is assumed to be well mixed during the day. Deep surface cooling after sunset creates a much shallower stable nocturnal boundary layer (ca. 100-200 m), where the remainder of the daytime PBL is decoupled from the surface layer forming a nocturnal residual layer [Holton & Hakim, 2013]. Within the PBL the vertical concentration profiles of aerosols and trace gases are normally non-linear as a result of the natural air turbulence caused by wind and/or temperature gradients [O'Dowd & Wagner, 2007]. At present there is a paucity of measurements of aerosol and trace gas concentration gradients within the lowest 300m of the PBL. Accurate representation of the vertical distribution of aerosol in the PBL is critical in order to assess the accuracy of model representations of surface air quality and their response to changing emissions. Further, accurate assessment of the degree to which surface measurements represent the entire PBL are required to validate the use of remote sensing techniques for surface air quality predictions. Current research initiatives, including the NASA based Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) project, demonstrate the necessity to constrain aerosol and trace gas profiles within the troposphere for improved interpretation of satellite observations and ultimately improve the accuracy with which near-surface air quality conditions can be diagnosed from space.

Capturing the spatial and temporal variability of atmospheric aerosols and trace gases between the surface and 300m is currently limited by the sampling platforms with
which measurements are made. Measurement of particle number and mass distributions above the surface, but below 300m are very limited due to the paucity of sampling platforms that can perform controlled horizontal and vertical translations within the lower troposphere. These measurements are even more restricted within the dense, complex and constantly evolving nature of urban environments. Current measurement platforms that allow for vertical profiling of the lower troposphere are primarily limited to fixed tall towers [e.g. Brown et al., 2013; Clarke et al., 2006], research vessels over open ocean waters [e.g. Petelski & Piskozub, 2006; Petelski, 2003], tethered balloons [e.g. Hara et al. 2013], winged UAV’s [e.g. Holland et al., 2001; Clarke et al., 2002; Ramanathan et al., 2007; Bates et al., 2013], and large scale research aircraft such as airplanes [e.g. Buzorius et al., 2006; Li et al., 2015; Hara et al., 2006] and Zeppelins [Li et al., 2014]. Tower measurements provide a sampling platform with limited vertical translations set by the physical tower itself and no horizontal translation, with larger regional scale applications requiring the impractical or impossible relocation of the tower [Buzorius et al., 2006]. Research vessels provide a mobile sampling platform over open water that has limited vertical translation (typically < 25m) and requires a relatively high measurement height in order to avoid influence from the ship hull [Petelski, 2003]. The vertical range of tethered balloons allows for measurements over the entire troposphere, though are limited in horizontal translation and fixed horizontal position accuracy over the course of the vertical measurement [Hara et al. 2013]. Winged unmanned aircraft systems and large scale research aircraft are both limited by increased uncertainties in measurements as a result of the airplane motion itself [Buzorius et al., 2006]. Large research aircraft are also limited with respect to their vertical range as altitude restrictions are strictly enforced over
populated areas. Typically low flight paths (<150 m above sea level) are capable over open water [Buzorius et al., 2006], however flights below 300m over more populated areas are typically limited to missed approaches at airports [Jacob et al., 2010]. Measurements of specific emission point sources, e.g. smoke stacks, are also limited with both UAS and large scale research airplanes as these aircraft are unable to fly to and remain stationary at a specific point and must instead fly multiple passes over the area of interest.

Recent advancements in quadrotor UAS present an attractive solution to the current problem surrounding measurements of aerosols and trace gases within the lower troposphere, providing a sampling platform capable of both horizontal and vertical translation within the boundary layer. The quadrotor UAS can be flown autonomously with preprogrammed electronic flight plans. Here we present the novel use of a quadrotor UAS as a sampling platform to measure vertical and horizontal profiles of particle and CO2 concentrations at a coastal site in Southern California.

In the following manuscript, we assess the viability of using UAS for measurement of aerosol concentrations above the surface, then apply the measurements to the study of marine aerosol particles generated in the surf zone. With over 70% of the Earth’s surface covered by oceans, wind-driven particle production at the ocean surface represents one of the most abundant natural aerosol sources to the atmosphere globally [Quinn et al., 2015; de Leeuw & O’Dowd, 2007]. The generation of marine aerosols by processes associated with breaking surface waves and the formation of bubble plumes and foams is well understood [Blanchard, 1954; Blanchard, 1989; Cipriano et al., 1983; Stokes et al., 2012]. Recent studies have demonstrated that the surf-zone, characterized by abundant wave breaking, is a high-intensive production zone for sea spray aerosol (SSA) relative to the
near open ocean [Monahan, 1995; de Leeuw et al., 1997]. Further work has been dedicated to characterizing a surf source function; Chomka and Petelski (1997) suggest a function relating the total aerosol flux to wave energy dissipation ($WED$) to the $\frac{3}{4}$ power, whereas Clarke et al. (2006) calculated a universal function for the surface flux of aerosols for a whitecap coverage of 100% that scales with the whitecap coverage. Although the surf source function is still an area of relatively high uncertainty, assessment of surf aerosol effects is also dependent on the transport of aerosols both horizontally and vertically within the boundary layer; an area in which the literature is even sparser [van EijK et al., 2011]. In addition to the scarcity of literature, the existing literature provides contradicting information. Hooper and Martin (1999) used lidar to demonstrate surf-aerosol plumes as high as 20 m above sea level, with de Leeuw et al. (1997) later reporting similar plume heights of 20-25 m, inferred from gradient functions based on in situ measurements made at ca. 5 and 15 m above sea level. Clarke et al. (2006) utilized a 20 m tower to collect aerosol samples at 5, 10 and 20 m above sea level and based on their observations suggest that the aerosol plumes generated in the surf zone did not exceed 5 m. Assessing the vertical transport of sea spray aerosol within the first 100 m of the boundary layer provides a solid framework for an initial assessment of the novel quadroto UAS sampling platform as a means for aerosol concentration measurements within the lower portion of the boundary layer.
5.3 Methods

5.3.1 Drone Sampling Platform

Measurements of particle number concentrations \((d_p > 500\text{nm})\) and CO₂ within the boundary layer at various vertical and horizontal locations were made by mounting two commercial sensors to a 3D Robotics Iris+ autonomous quadcopter (Iris). The Iris uses two 10 × 4.7 push propellers and two 10 × 4.7 puller propellers powered by 850 kV motors to create lift and provide maneuverability for the platform. The telemetry range of the Iris is 1 km, more than sufficient to cover the desired sampling window (5-100m). The Iris is powered by a 3 cell, 11.1 V, 3.5 Ah lithium polymer battery providing a flight time of 10-13 minutes at the manufacturer suggested payload capacity of 400 g. The exact flight time achieved is highly dependent on the weight and size of the attached sensor package and is further discussed in section 5.4.1.

The Iris is capable of being flown both manually and autonomously. As an added safety precaution and to account for the unpredictability of a beach environment, initial take-offs and landings were performed using the manual flight mode. Once the Iris had taken off however, the unit was switched into full autonomy (AUTO) mode, where in the Iris executes the stored mission, progressing through a series of waypoint commands. The waypoints are GPS-positioned points that describe the 3 dimensional location of the drone at that point in the flight path, with a latitude, longitude, altitude, and radius. The waypoint commands detail the action of the drone with respect to said waypoint and range from simple navigation, e.g. go here, to more detailed commands including the ability to have the drone loiter for a specified duration of time. Representative vertical and horizontal
flight paths are presented in Figure 5.1 and detailed descriptions of the flight plans flown during this study are provided in Table 5.1.

The waypoints and flight plans for each flight were programmed using the open-source Mission Planner software. Mission Planner is an open-source, full featured ground station for the APM autopilot platform developed by Michael Osborne*. Mission Planner software provides an intuitive and simple interface with which autonomous mission plans can be planned, saved, and loaded to the drone. In addition to planning the specific flight paths, Mission Planner allows for continuous, real time monitoring of the status of the Iris+ during operation. Telemetry logs for all of the flights are recorded and processed by Mission Planner providing easy access to information such as altitude, acceleration, ground speed, latitude, longitude, roll, and pitch. The on-board autopilot records flight log data an average of 7 times a second, providing a clear, detailed, and accurate log of the aircraft’s sampling profile.

* Mission Planner software and a more detailed description of the software are provided at http://planner.ardupilot.com/
Figure 5.1: UAV flight paths during a representative vertical flight plan (A) and a representative horizontal flight plan (B) adjacent to the Scripps Institution of Oceanography (SIO) pier in La Jolla, CA. Vertical flights extended from the surface to approximately 100m, while horizontal flight plans extended to approximately 120m offshore. Note: the image in this figure was taken at low tide that may not necessarily reflect the conditions reported here.
Table 5.1: Flight plans for the 4 vertical flight profiles that were utilized during this study.

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5.3.2 Sensor Packaging

As previously discussed, the weight and size of the payload attached to the Iris is critical to maximizing total flight and sample times. To minimize the weight and size of the payload, a custom sensor package was assembled from an existing commercially available particle counter and CO2 sensor.

The particle counter used in this study is a MetOne 80080 two channel particle counter. Here, we provide a brief description of the operating principles of the 80080 particle counter, however more detailed descriptions are provided elsewhere in the literature [Clarke et al. 2002]. The 80080 particle counter is an optical particle counter that uses scattered light from a 670-nm laser to detect and count particles in two size ranges. The size ranges for the counter are set at 0.5-1μm (channel one) and greater than 1μm (channel two). The count period of the counter is set at 1 second. The 80080 particle counter provides reliable, real-time measurements of particle counts for particles greater than 0.5 μm.

The CO2 sensor is a K-30 sensor manufactured and sold by CO2Meter. The K30 is a low cost, low power, accurate CO2 meter that utilizes non-dispersive infrared (NDIR) waveguide technology and an automatic background calibration algorithm to detect CO2 between 0-10,000 ppm. The K-30 has a sensitivity of ± 20 ppm ± 1 % of measured value with an accuracy of ± 30 ppm and ± 3 % of measured value within specifications. Although originally designed as a diffusion-type sensor, incorporation of the CM-0114 tube cap adapter kit to the K-30 transforms the sensor into a remote sensor capable of actively measuring CO2 levels in ambient air samples in real time. The K-30 provides a relatively accurate CO2 measurement in a small, compact, lightweight package.
The MetOne particle counter and CO$_2$ sensor are not standalone instruments and do require interfacing with a computer to collect and record measurements. A Raspberry Pi 1 Model B computer provides an inexpensive, compact, light-weight computing solution. At the start of each sampling flight, the user executed a custom, python based program to initialize the sensors and begin an 8 minute sampling period during which particle and CO$_2$ measurements are continuously recorded. The 8 minute sampling window was chosen to account for any potential delays in flight start time to ensure that the sample flight window would be captured. After each flight, the data files were collected and transferred to a long term storage location.

A Sensidyne A120INSNF63VN1 micro air pump provided sample flow for both the MetOne particle counter and K-30 CO$_2$ sensor. Powered using an Energizer LA522 Advanced Lithium 9V battery, the micro air pump provided a consistent sample flow of 4.88 slpm through both sensors for the duration of each sample flight. Although tests on the battery power demonstrated a constant sample flow for time periods greater than 1 hour, the lithium 9V batteries were swapped out every 2 sample flights to ensure consistent sample flow across all sampling flights.

The components of this sensor package require relatively low power and the entire package was powered using a 9V lithium battery and a Mophie powerstation. The Metone particle counter and Sensidyne pump were powered with the Energizer Lithium 9V battery and the battery was swapped following every 2$^{nd}$ flight. The Mophie powerstation was used to provide continuous mobile power to the Raspberry Pi and CO$_2$ sensor over the entire respective sampling period.
All of the individual components were assembled together into a compact package that weighed 490 grams (Fig. 5.2). The entire unit was mounted to the undercarriage of the Iris with the sampling inlet mounted to the front of the drone extending above the props to avoid sampling contamination.

Figure 5.2: A) Close-up photograph of the 3DR Iris+ drone and attached sampling platform. B) In-flight photograph of the 3DR Iris+ drone and sampling package returning to the home location.
5.4 Results and Discussion

5.4.1 Performance of the Drone Sampling Platform

Figure 5.3: Dependence of flight time of the 3DR Iris+ on payload weight. Blue squares are flight durations based on 3DR specifications and the red square is based on the observed flight durations in this study for a 510g payload.

The total weight and size of the sensor package has a direct and significant impact on the total flight time which can be achieved with the Iris. The manufacturer recommends a payload of 400 grams for flight times of ca. 10-13 minutes, with flight times of ca. 18-20 minutes achieved with no payload attached. The sensor package, inlet tube, and mounting hardware used during this study weighed a total of 510 g, ca. 28% heavier than the recommended payload. Despite being slightly heavier than the manufacture recommended payload of 400 grams, the sensor package size still allowed for a conservative flight time
of 5 minutes. Figure 5.3 shows the non-linear dependence of the Iris’ flight time on payload weight and demonstrates the critical need for light payloads to ensure maximum flight time. With time considerations for take-off and landing, the Iris is capable of providing 4 minutes of onsite sampling flight time at a payload of 510 g. Although this initial sensor package was relatively light, future work will look to decrease the weight of the package in an attempt to increase total flight time and ensure a longer sampling duration per sample flight.

Future applications of UAS in atmospheric research will necessitate extreme vertical and horizontal flight precision for studies conducted within a forest canopy or an urban street canyon. During the vertical flight profiles, the altitude precision of the Iris drone relative to the programmed way point altitude was extremely high. The Iris drone was capable of holding within 0.35 m of the programmed altitude. Figure 5.4.A demonstrates the vertical precision of the Iris drone for both replicate flights of Flight Plan A, with the drone flying as low as 5 m and has high as 100 m above sea level. The horizontal precision of the Iris drone was also high, with the Iris typically holding within 1 m of the preprogrammed location. The horizontal precision of the drone relative to the programmed waypoint position for all vertical profile flights is shown in Figure 5.4.B. Overall the drone demonstrated a high precision with regard to both vertical and horizontal position that showcases the potential utility of these sampling platforms for aerosol and trace gas measurements in the boundary layer within various complex environments.
Figure 5.4: A) Altitude precision of the 3DR Iris+ drone relative to the programmed waypoint altitude for both replicates of Flight Plan A. B) Horizontal precision of the 3DR Iris+ drone relative to the programmed waypoint position for all vertical profile flights.
5.4.2 Surf-zone Aerosol Production

Figure 5.5: Time series of particle concentrations reported in the miniOPC small particle channel (A; 0.5 μm < $d_p$ < 1μm) and large particle channels (B; $d_p$ > 1μm) as measured from the SIO beach (dark red and dark blue) and at the terminal end of the SIO pier (light red and light blue) on 30 July 2015.

Aerosol production was observed to be enhanced within and downwind of the surf-zone, consistent with previously reported observations of surf-zone enhancement [eg. de Leeuw et al., 1997]. A time series of particle concentrations measured at the SIO beach and at the terminal end of the SIO pier are shown in Figure 5.5. In both the small particle channel (0.5 μm < $d_p$ < 1μm) and large particle channel ($d_p$ > 1μm) the surf-zone influenced
beach measurements show a distinct enhancement and higher variability as compared to the measurements at the end of the pier over the ocean. The frequency distributions of the small and large particle concentrations (Figure 5.6) further demonstrate not only an enhancement in particle concentrations within the surf-zone but also a high degree of variability in both small and large particles when compared to the open ocean.

![Frequency distributions of small and large particle concentrations](image)

Figure 5.6: Frequency distributions of small ($0.5 \mu m < d_p < 1.0 \mu m$) and large ($d_p > 1.0 \mu m$) particle concentrations from continuous measurements conducted from the end of the SIO pier (A, C) and from the beach at the base of the SIO pier (B, D) as measured on 30 July 2015.

The highly intensive production of aerosol in the surf-zone as compared to the near open-ocean is also observed in the horizontal profiles of aerosols measured while walking along the SIO pier on July 28th, 2015, shown in Figure 5.7. The horizontal profiles
demonstrate that aerosol production in and downwind of the wave breaking region is significantly enhanced for both small and large particle channels when compared to the aerosol concentrations over the open ocean, i.e. the end of the pier. In the large particle channels we observe enhancements by as much as a factor of 4.2 in the surf-zone over that of open-ocean. An enhancement factor of 2.3 over the open ocean small particle concentration is observed in the surf-zone. The results agree with those presented by van Eijk et al. (2011) who reported a surf-zone enhancement factor of 3 to 5 particles at smaller diameters (0.5 μm) increasing to a factor of 10 at larger (10 μm).

Figure 5.7: Time series of particle concentration measurements taken during mobile measurements that span the SIO pier on 28 July 2015.
Although the magnitude of our observed enhancement is not as large, it holds with the observed increasing enhancement factor with increasing particle size. The discrepancies between the magnitudes in the surf-zone enhancement are most likely influenced by wind-wave energy dissipation in the surf zone, controlled by the bathymetry of the underlining surf zone and changes in the wave motion, the width of the breaker zone, and increased transport efficiency of the aerosol [Neele et al., 1998; Chomka & Petelski, 1997]. Figure 5.8 demonstrates a correlation of the small and large particle measurements made during the July 28th pier walk. Comparing the slope of this correlation (5.29 ± 0.04) to the ratio of small (0.5 μm < dp < 1μm) to large (dp > 1μm) particles measured in nascent sea spray (1.6) we find that the two are in relatively good agreement [Prather et al., 2013]. Although the nascent sea spray distribution would predict a much shallower slope with a ratio of 1.6 small particles per big particle, the deposition loss bias of large particles as compared to small within the first 10 m would suggest that a slight increase in the slope be observed. Further investigation into the processes controlling the particle production within the surf-zone was beyond the scope of this work, as this manuscript focuses primarily on assessment of UAS for atmospheric measurement.
Figure 5.8: Correlation of small \((0.5 \, \mu m < d_p < 1 \, \mu m)\) and large \((d_p > 1 \, \mu m)\) particle measurements as measured during the pier walk sampling measurements shown in Figure 5.7.

### 5.4.3 Vertical and Horizontal Flight Profiles

Thirteen separate vertical sampling flights were flown between July 29\(^{th}\) and July 30\(^{th}\), 2015. The vertical sampling flights took place on the SIO beach and were flown according to the flight paths presented in Table 5.1 under the ambient conditions presented in Table 5.2. Multiple flight plans were flown to both assess the performance capabilities of the Iris as a sampling platform, discussed previously in section 5.4.1, as well as to effectively constrain the aerosol concentration measurements within the first 100 m of the boundary layer. Figure 5.9 is a representative figure depicting the raw particle concentration measurements for both the large and small particle channels collected during the first research flight from July 28\(^{th}\). The raw, unprocessed data demonstrates not only a vertical concentration gradient for both small and large channels but also clearly shows the
Table 5.2: The average meteorological and swell conditions for each individual flight.

<table>
<thead>
<tr>
<th>Flight</th>
<th>Orientation</th>
<th>Wind Speed ± 1σ (kn)</th>
<th>Wind Direction ± 1σ (deg)</th>
<th>Air Temperature ± 1σ (°F)</th>
<th>Swell Height ± 1σ (m)</th>
<th>Swell Period ± 1σ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Vertical</td>
<td>2.68 ± 0.03</td>
<td>265.03 ± 1.51</td>
<td>70.3 ± 0.02</td>
<td>0.63 ± 0.002</td>
<td>4.6 ± 0.005</td>
</tr>
<tr>
<td>2</td>
<td>Vertical</td>
<td>3.05 ± 0.16</td>
<td>290.57 ± 0.20</td>
<td>71.7 ± 0.12</td>
<td>0.61 ± 0.002</td>
<td>4.5 ± 0.004</td>
</tr>
<tr>
<td>3</td>
<td>Vertical</td>
<td>3.99 ± 0.08</td>
<td>282.46 ± 1.92</td>
<td>71.7 ± 0.08</td>
<td>0.63 ± 0.002</td>
<td>4.4 ± 0.004</td>
</tr>
<tr>
<td>4</td>
<td>Vertical</td>
<td>5.03 ± 0.11</td>
<td>275.43 ± 1.75</td>
<td>70.8 ± 0.04</td>
<td>0.65 ± 0.002</td>
<td>4.4 ± 0.004</td>
</tr>
<tr>
<td>5</td>
<td>Vertical</td>
<td>5.34 ± 0.04</td>
<td>270.06 ± 0.81</td>
<td>70.5 ± 0.08</td>
<td>0.67 ± 0.002</td>
<td>4.3 ± 0.004</td>
</tr>
<tr>
<td>6</td>
<td>Vertical</td>
<td>5.46 ± 0.04</td>
<td>270.58 ± 0.42</td>
<td>70.3 ± 0.01</td>
<td>0.7 ± 0.00</td>
<td>5.0 ± 0.004</td>
</tr>
<tr>
<td>7</td>
<td>Vertical</td>
<td>5.98 ± 0.17</td>
<td>272.74 ± 2.25</td>
<td>70.3 ± 0.01</td>
<td>0.7 ± 0.00</td>
<td>5.0 ± 0.003</td>
</tr>
<tr>
<td>8</td>
<td>Vertical</td>
<td>6.23 ± 0.12</td>
<td>271.91 ± 0.63</td>
<td>70.3 ± 0.00</td>
<td>0.7 ± 0.00</td>
<td>4.9 ± 0.010</td>
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<tr>
<td>9</td>
<td>Vertical</td>
<td>5.14 ± 0.09</td>
<td>259.72 ± 2.09</td>
<td>70.2 ± 0.01</td>
<td>0.7 ± 0.00</td>
<td>4.8 ± 0.010</td>
</tr>
<tr>
<td>10</td>
<td>Vertical</td>
<td>5.22 ± 0.33</td>
<td>247.13 ± 0.75</td>
<td>70.3 ± 0.05</td>
<td>0.7 ± 0.00</td>
<td>4.7 ± 0.009</td>
</tr>
<tr>
<td>11</td>
<td>Vertical</td>
<td>5.80 ± 0.14</td>
<td>266.69 ± 1.62</td>
<td>70.2 ± 0.01</td>
<td>0.7 ± 0.00</td>
<td>4.6 ± 0.009</td>
</tr>
<tr>
<td>12</td>
<td>Vertical</td>
<td>4.11 ± 0.03</td>
<td>308.96 ± 1.51</td>
<td>72.6 ± 0.06</td>
<td>0.60 ± 0.001</td>
<td>4.5 ± 0.004</td>
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<tr>
<td>13</td>
<td>Vertical</td>
<td>3.85 ± 0.14</td>
<td>296.54 ± 0.77</td>
<td>73.2 ± 0.05</td>
<td>0.58 ± 0.002</td>
<td>4.4 ± 0.006</td>
</tr>
<tr>
<td>14</td>
<td>Horizontal</td>
<td>3.64 ± 0.12</td>
<td>305.78 ± 0.07</td>
<td>72.5 ± 0.01</td>
<td>0.50 ± 0.00</td>
<td>4.2 ± 7e-04</td>
</tr>
<tr>
<td>15</td>
<td>Horizontal</td>
<td>3.36 ± 0.04</td>
<td>305.65 ± 0.29</td>
<td>72.5 ± 0.00</td>
<td>0.50 ± 0.00</td>
<td>1.2 ± 9e-04</td>
</tr>
<tr>
<td>16</td>
<td>Horizontal</td>
<td>4.19 ± 0.05</td>
<td>309.87 ± 1.29</td>
<td>72.5 ± 0.00</td>
<td>0.50 ± 0.00</td>
<td>4.2 ± 9e-04</td>
</tr>
</tbody>
</table>
influence of the surf-zone source variability on measurements at each altitude. To account for the surf-zone variability and provide a representative profile of the aerosol concentration gradients between the surface and 100 m, Figure 5.10 shows the mean particle concentrations (and ±1σ) for all 13 of the vertical flights sampled during this study. A plume height of 30-35 m was observed and is in relatively good agreement with previously calculated surf-zone plume heights of 20-25 meters presented by de Leeuw et al. (1997) and Hooper and Martin (1999).

Figure 5.9: Particle concentration measurements (1Hz) as measured during research flight 1, for the large (blue; 0.5 μm < \(d_p\) < 1μm) and small (red; \(d_p\) > 1μm) particle sampling bins.

The vertical profile also demonstrates a turnover in the small channel particle concentrations at an altitude of 70 m. A more detailed analysis of the meteorological
conditions than is currently available is necessary to comment with certainty, though it is likely that this increase in small particle concentration may reflect the transition from the constant-flux surface layer to the mixed layer of the boundary layer. The surface layer typically accounts for the lowest 10% of the boundary layer and a boundary layer height of 700 m is highly probable and an impact on aerosol concentration profiles at that transitional point would not be unexpected. While a more quantitative assessment of this turnover in the small particle channel concentration is outside of this work, it does provide an interesting science question that future flights and studies may be capable of addressing.

Figure 5.10: Mean particle concentrations (and ±1σ) for the large (blue; 0.5 μm < d_p < 1μm) and small (red; d_p > 1μm) size channels averaged for all 13 of the vertical flights sampled during this study.
In addition to the vertical flights, horizontal flight profiles were also flown from the beach, over the surf-zone. A visual representation of the horizontal flight paths is depicted in Figure 5.1.B. The horizontal flight paths were flown at 5, 10, 15 and 25 m to provide both horizontal and vertical measurements of the aerosol plume. The horizontal flight profiles are shown in Figure 5.11 and demonstrate both the vertical concentration gradient observed in the strictly vertical flight profiles, as well as the horizontal gradient expected between the surf-zone and open-ocean.

Figure 5.11: Horizontal flight profiles depicting the small (A) and large (B) particle channel counts at 5, 10, 15 and 25 meters. The wave breaking area was located at approximately 40-50 meters from the starting location of the horizontal flights.
5.4.4 Surf-zone Particle Emission Rate

![Figure 5.12: Vertical profiles of the average small (A) and large (B) particle channel counts ±1σ located before (gray circles) and after (red or blue squares) the breaking waves. The vertical profile for outside the breaking waves was constructed from the horizontal measurements shown in Figure 5.11.](image)

Vertical profiles of the average small and large particle channels (±1σ) located before and after the breaking waves were constructed from the aerosol concentration data collected during the vertical and horizontal flights (Figure 5.12). Utilizing the vertical profiles of the particle concentrations for both the open-ocean and surf-zone we can calculate the SSA emission rate at the Scripps Pier using a simple column model. The mass balance equation for the time rate of change in particle number concentration (N_p) is defined as:

\[
\frac{d[N_p]}{dt} = \frac{E}{h} + P - L - D \tag{1}
\]
where \( h \) is the mixing height of the column (27.5 m), \( P \) is the chemical production, \( L \) is the chemical loss, and \( D \) is deposition. Here we take \( P \), \( L \), and \( D \) to be zero and rearrange the equation using the chain rule to introduce \( U \) (mean wind seed; \( \frac{dx}{dt} \)).

\[
\frac{d[N_p]}{dx} U = \frac{E}{h} 
\]  

(2)

We can then solve for \( E \) with our measurement of \( d[N_p] \), the change in the column averaged particle concentration, and \( dx \), the length of the surf zone (taken to be 30 m). Using this simplified column model we calculate ambient humidity emission rates for small and large particles in the surf zone to be 416 and 187 particles \( \text{cm}^2 \text{s}^{-1} \) respectively. Utilizing the large channel particle flux and weighting mass calculations by a representative aerosol size distribution between 1 and 10 \( \mu \text{m} \) for a breaking wave [Prather et al., 2013], we estimate an ambient humidity mass flux of 285 \( \mu \text{g m}^{-2} \text{s}^{-1} \). This represents a conservative and potentially lower end estimation of mass flux as influence of particles larger than 10 \( \mu \text{m} \) was not considered. Comparing to the two previously reported literature values of mass flux for Scripps Pier of 1500 \( \mu \text{g m}^{-2} \text{s}^{-1} \) [van Eijk et al., 2011] and 562-1034 \( \mu \text{g m}^{-2} \text{s}^{-1} \) [de Leeuw et al.; 2000], the calculated flux is within agreeable range. In their work van Eijk et al. [2011] present the following approximate relation between \( WED \) and the average wave height, \( H_{rms} \):

\[
WED = -3 + 35 \cdot H_{rms} 
\]  

(3)

Using equation 3 we estimate that the \( WED \) during the course of this study was ca. 19 W \( \text{m}^{-2} \), a factor of ca. 1.6-2.6 smaller than the \( WED \) interval (30-50 W\( \text{m}^{-2} \)) for which van Eijk et al., presented their mass flux. Assuming the 3/4 power dependence between mass...
flux and $WED$ is reasonable that we would observe a significant decrease in mass flux at our lower $WED$.

5.5 Conclusions

The primary objective of this work was to assess the application of a quadrotor UAS as a sampling platform with which aerosols and trace gasses within the lower troposphere can be measured. The 3D Robotics Iris+ autonomous quadcopter demonstrated high precision in both vertical and horizontal positioning and showcased the future potential of these sampling platforms for measurements of aerosol and trace gas measurements within various complex environments in the boundary layer.

Utilizing the Iris sampling platform, vertical profile measurements of aerosol number were made between 5 and 100 m above the surf zone. The vertical profiles demonstrated a maximum aerosol plume height of 30-35 m above the surf zone. Based on the horizontal and vertical aerosol profiles measured in this work, ambient humidity emission rates for small and large particles in the surf zone were calculated to be 416 and 187 particles cm$^{-2}$ s$^{-1}$ respectively with an estimated ambient humidity mass flux of 285 $\mu$g m$^{-2}$ s$^{-1}$. The Iris UAS provided an efficient and precise sampling platform for measuring the vertical and horizontal profiles of sea spray aerosol generated within the boundary layer.
5.6 Acknowledgements

This research was primarily supported by the Environmental Protection Agency and the Science to Achieve Results (STAR) Program through a grant awarded to T.H.B. (EPA-G2011-STAR-B2).

The authors would like to thank Jim Bonnardel of Radio Control Specialties for his valued insight and guidance with respect to quadrotor UAS drones, as well as his time and expertise in piloting the drone throughout the course of this study.
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6. Development of a Forward-scattering Autonomous Low-cost Compact Optical-particle-counter (FALCON)

6.1 Abstract

We present the development and calibration of a Forward-scattering Autonomous Low-cost Compact Optical-particle-counter (FALCON). Building upon existing designs for a forward scattering optical particle counter, the FALCON features an updated laser diode, a custom laser diode driver, and a modified laser beam shape and quality achieved with custom focusing optics. The improvements featured in the FALCON permit the theoretical detection of ammonium sulfate particles as small as 80 nm and we report the calibration of the FALCON to ammonium sulfate particles as small as 101 nm in diameter. In addition we assess the ability of the FALCON to accurately size particles of various refractive indexes and present a comparison of the size dependent pulse heights for 101 nm ammonium sulfate and 104 nm sodium chloride particles. We also present designs for a second generation of the FALCON that will incorporate the same optics, geometries, and fundamental operating parameters of the original FALCON into a smaller, more compact instrument body that will minimize weight and afford longer term autonomy.

6.2 Introduction

Aerosol particles, generated from both natural and anthropogenic sources, are ubiquitous in Earth’s atmosphere. Aerosol particles present a significant health hazard in urban environments [Lave & Seskin, 1973; Bernstein et al., 2004, Turócsi et al., 2012], play a central role in Earth’s radiation budget [IPCC, 2007] and act to limit visibility
through the scattering and absorption of radiation [Seinfeld & Pandis, 1998]. The effects of aerosol particles on human health in urban environments are of particular concern; epidemiological studies have demonstrated strong correlation between particulate matter loadings and adverse effects on human health [Pope, 2007; Pope et al., 2002]. Enhanced rates of allergies [Ring et al., 2001a; Ring et al., 2001b; Brunekreef & Sunyer, 2003], cardiovascular disease [Pope & Dockery, 2006; Berger et al., 2006; Samet et al., 2000], lung cancer [Tie et al., 2009] and premature death [Lave & Seskin, 1973] have all been linked to increased exposure levels of fine mode particle concentration (dry diameter ($d_p$) < 2.5 μm). Accurate measurements of aerosol particle number and mass distributions are required to properly assess the extent to which ambient aerosol particles impact human health and alter Earth’s radiation budget. In the following manuscript we report on the development of a low-cost miniature optical particle counter designed to addresses the critical gap in fine spatial and temporal scale measurements of particle number and mass concentrations that are necessary to advance our understanding of the connections between ambient particle loadings and human health effects.

### 6.2.1 Impact of Aerosol Particles on Human Health

The extent to which particles impact human health is complex function of particle size and chemical composition. Particulate matter with high water-soluble fractions, e.g. transition metals with redox potential, play critical roles in the initiation of oxidative DNA damage. Similarly, select organic compounds found in aerosol particles, can have mutagenic and cytotoxic properties and have been shown to contribute to cytotoxicity mechanisms within the body [Valavanidis et al., 2008]. Research has shown that the
chemical composition of particulate matter, can result in adverse cellular effects through several mechanisms with the associations between chemical compositions and particle toxicity stronger for the fine and ultrafine PM size fractions [Valavanidis et al., 2008].

The extent to which aerosol particle impact health is weighted by their size, as large particles \((d_p > 2.5 \mu m)\) are efficiently removed via deposition in the nasal, pharyngeal, or laryngeal passages and rarely reach the lungs [ICRP, 1994]. Similarly, very small particles \((d_p < 2 \text{ nm})\) are removed via diffusion loss to the nasal, pharyngeal, or laryngeal passages. As a result, accurate measurement of particles with diameters in the 2 nm to 2 \(\mu m\) size range are most critical to impact human health. Recent analyses have suggested that particles with diameters less than 100 nm can pass through the alveoli and be transmitted to other organs [Pope et al., 2002], resulting in higher plaque deposits in arteries and increased risk of cancer when particulates are laden with carcinogenic components. In a recent analysis, Peng et al. [2008] showed that PM\(_{10}\) was not statistically correlated with increased respiratory disease when the fine mode \((d_p < 2.5 \mu m)\) particles were removed from the analysis. These results, when coupled to the typical size distribution for aerosol particles (Figure 6.1) highlight that ambient measurements of both particle size and number concentrations are required for evaluating the linkage between particulate matter and respiratory health hazards. It follows that additional information on ambient particle size distributions, beyond PM\(_{2.5}\), would greatly enhance the application of air quality data in large scale public health studies.
Figure 6.1: Top Average ambient particle size distribution in Pacific Beach, CA. Bottom Modeled fractional deposition of inhaled particles as a function of particle diameter in the nasopharyngeal and laryngeal, the tracheobronchial and the alveolar regions of the human respiratory tract during nasal breathing. Data from: ICRP 1994.

In response to the measured effect that increased exposure to aerosol particle loadings has on human health, the Environmental Protection Agency (EPA) established primary and secondary standards for particle pollution as part of the Clean Air Act of 1970. The National Ambient Air Quality Standards (NAAQS) classify particle pollution as a
criteria pollutant considered harmful to the public and the environment and regulate inhalable particles smaller than 10 μm in diameter (PM₁₀). Since 2012, the EPA has refocused the NAAQS for particulate matter, concentrating on particles with diameters \( d_p \) less than 2.5 μm (PM₂.₅). The current PM₂.₅ NAAQS is set at 35 μg m⁻³ (24-hour average) and 12 μg m⁻³ (annual average) \[EPA, 2012\]. The current government standards for monitoring and regulating particulate matter are solely based on PM₂.₅ and do not account for particle size, number concentration, or particle chemical composition.

The cubic dependence of an aerosol particle’s mass on particle radius results in the majority of the total particulate mass for a typical urban region residing in particles with diameters greater than 500 nm. A typical urban aerosol number and mass distribution is depicted in Figure 6.2, demonstrating that while the number distribution of aerosols is weighted toward the sub-micron region, the mass distribution is weighted toward the larger super-micron particles. For example, the mass of just one 10 μm particle is equivalent to the mass of \(10^9\) 10 nm particles. As a result, regulations that target aerosol particle mass loadings can have little to no impact on particle number concentrations, and regulations that target aerosol particle number concentrations, can have little to no impact on particle mass loadings. The current monitoring of aerosol particle mass loadings provides an incomplete picture of the atmospheric aerosol distribution in a given urban air shed and regulations that target aerosol particle mass loadings may have little to no impact on total particle number concentrations.
Figure 6.2: Average aerosol number distribution (Figure 4.2A) collected with a DMT UHSAS during the 2013 SARP campaign during multiple missed approaches at Los Angeles International Airport. The corresponding mass distribution was calculated using an average density for urban aerosol of 1.5 g cm\(^{-3}\) [Geller et al., 2006].
6.2.2 Scales of Variability

Further, it is not currently clear what the required spatial and temporal scales with which particle number and mass need to be sampled in order to provide meaningful data for health studies. Within an urban environment, it has been shown that particle number and size distributions will display large spatial and temporal variability [e.g., Pirjola et al., 2012], a result of heterogeneity in primary emissions and the short, size-dependent lifetime of particulate matter. To assess local and regional air quality, monitoring agencies are required to maintain a network of gaseous and particle pollutant monitors which are either federal reference methods (FRM) or federal equivalent methods (FEM). The measurements are systematically obtained with the intent of routine comparison against the ambient air quality standards for regulatory purposes.

San Diego County is required by the code of federal regulations (40CFR 58.10a) to have a minimum of 9 PM\textsubscript{2.5} samplers within the sampling network. At present there are a total of 12 PM\textsubscript{2.5} measurements, of which five are FRM samplers. The FRM samplers used in San Diego County are Thermo (R&P) FRM Partisol-Plus 2025 samplers. To be used in regulatory efforts, the PM\textsubscript{2.5} sensor must be either an FRM or FEM sampler located at the neighborhood scale [SDAPCD, 2010: http://www.sdapcd.org/air/reports/2009_network_plan.pdf]. These measurements are the sole continuous source of observation-based constraints for the current generation of regional scale air quality models. As a result there are only five monitors of PM\textsubscript{2.5}, with hourly time resolution, that are used to assess air quality for the over 3 million residents of San Diego County. Given the strong heterogeneity in particulate matter on the city-scale, a network of 5 samplers is insufficient for capturing either the mean state or providing a
representative measurement of other locations within the city (Figure 6.3). This limits the application of these data to studies linking particle loadings to health effects. As a consequence, regulatory agencies and the general community lack access to real-time air quality data at the spatial scales required to make informed decisions regarding personal exposure to outdoor air pollutants.

Figure 6.3: Location of existing FRM PM$_{2.5}$ measurements in San Diego County. The five R&P Partisol-Plus 2025 samplers (red star) are utilized for regulatory monitoring, measuring PM$_{2.5}$ at hourly time resolution at a minimum of once every three days. The two BAM samplers are non-regulatory, have an hourly time resolution, and measure PM$_{2.5}$ daily.


6.2.3 Instrumental requirements for the next generation of air quality monitoring

Particle number and size distributions have been shown to demonstrate large spatial and temporal variability within an urban environment [Orru et al., 2009; Pirjola et al., 2012; Zhu et al., 2002; Virtanen et al., 2006]. To demonstrate this further, we show in Figure 6.4 results from our own mobile laboratory study in the Pacific Beach area of San Diego, CA. In this study, a commercial UHSAS (DMT) was used to create high resolution maps of particle number and mass concentrations. As a marker for the variability in particle number concentration within the study region, we calculate the number of standard deviations each individual grid cell is away from the sample area mean (Fig. 6.1A). The dataset collected in Pacific Beach from the mobile samplers is at very high resolution for a distributed network (>100 sensors km$^{-2}$). Even at this resolution, the variability in total particle number spans 2 standard deviations on spatial scales of less than 1 km. Capturing this spatial and temporal variability is currently limited by the availability of dense sample networks consisting of reliable, yet inexpensive particle sizing instruments. In addition, sampling platforms that can measure between the surface and 500 m, while translating horizontally and vertically within the complex and evolving nature of urban environments are also in need. Advancements in quadrotor unmanned aerial vehicles (UAVs) present an attractive solution to urban aerosol sampling; providing a sampling platform that is mobile, maneuverable, and able to sample vertical profiles within urban settings (discussed previously in chapter 5). In addition to requiring a high sensitivity and low size range to accurately size and count the aerosol population, payload restrictions of the quadrotor UAVs require an instrument that is light weight (< 2.5 kg), with a small footprint. Here,
we report the development of a new, low-cost, miniature optical particle counter that is capable of measuring particles between 80 – 1000 nm.

Figure 6.4: Number of standard deviations either above or below the mean total particle concentration for the sample region for grid cells of ca. 100m x 100m. Data shown is calculated from the mobile measurements in Pacific Beach (shown in Fig. 6.1). This equates to 113 sensors km⁻².

6.3 Instrument Design

6.3.1 Existing Miniature Optical Particle Counters

Currently a variety of small scale, inexpensive optical particle counters (OPCs) are commercially available that utilize scattered light to measure particle size. The current commercially available miniature-OPCs are limited in both the size range and resolution with which they are able to size and count aerosol particles (Table 6.1). In addition to the commercially available counters, modifications of these commercial systems with improved counting efficiencies have also been presented in the literature [Clarke et al.,
2002; Hill et al., 2008]. The first modifications were presented by Clarke et al. [2002], in which the MetOne 237A optical sensor was modified to accept custom electronics providing a higher resolution of 256 size bins over the 0.3-14 μm diameter range. Following Clarke et al., the Compact Lightweight Aerosol Spectrometer Probe (CLASP) builds upon the MetOne scattering cavity improving the resolution of the original cavity to 16 size bins over the diameter range of 0.24-18.5 μm at a rate of 10 Hz [Hill et al., 2008]. These systems are all limited in regards to their lowest detectable size range. Gao et al. [2013] presented a miniature optical particle counter that utilizes forward scattering, building off of a similar design presented by Kiselev et al. [2007], using a modified forward scattering lens instead of a pair of custom designed off-axis elliptical mirrors and incorporating a 405 nm laser diode which was demonstrated to have a lower detectable size limit of 125 nm; the resolution was not presented.

Table 6.1: Currently available inexpensive, miniature instruments and sensors available for particle counting and the particle diameter based size range and resolution for each.

<table>
<thead>
<tr>
<th>Instrument/Sensor</th>
<th>Size Range (μm)</th>
<th>Resolution</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MetOne GT-521S/GT-526S</td>
<td>0.3-10</td>
<td>2-6 Size Bins</td>
<td>[MetOne Instruments]</td>
</tr>
<tr>
<td>Dylos DC1100</td>
<td>0.5-10</td>
<td>2 Size Bins</td>
<td>[Dylos Corporation]</td>
</tr>
<tr>
<td>Shinyei ppd42ns</td>
<td>&gt;1</td>
<td>2 Size Characterizations</td>
<td>[Holstius et al., 2014]</td>
</tr>
<tr>
<td>Clarke et al.</td>
<td>0.3-14</td>
<td>256 Size Bins</td>
<td>[Clarke et al., 2002]</td>
</tr>
<tr>
<td>CLASP</td>
<td>0.24-18.5</td>
<td>16 Size Bins</td>
<td>[Hill et al., 2008]</td>
</tr>
<tr>
<td>Gao et al.</td>
<td>&gt;0.125</td>
<td>Not Available</td>
<td>[Gao et al., 2013]</td>
</tr>
</tbody>
</table>
6.3.2 Theoretical Basis for an Improved mini-OPC

![Figure 6.5: Dependence of Mie scattering efficiency on particle diameter, calculated at both 405 nm (purple) and 780 nm (red) for a spherical particle with a refractive index \(m = 1.5 - 0i\).](image)

One of the limitations of the commercial MetOne OPC is that the minimum detectable particle size is 300 nm (S/N = 2), much larger than the median particle diameter in an urban air mass (Figure 6.2). Mie scattering calculations suggest that replacing the 780 nm diode laser and silicon photodiode with a higher power (200 mW) 405 nm laser and a matching GaP (or GaN) photodiode would enable the detection of smaller particles. The success of the modification relies on the fact that in the Mie scattering regime, the scattering efficiency for small particles (e.g., \(d_p < 500 \text{ nm}\)) is inversely proportional to the wavelength of light. As a result, it is expected that using a higher power, blue-shifted light source will result in a lowering of the minimum detectable aerosol particle size. This is shown theoretically in Figure 6.5, where the scattering efficiency as a function of particle
diameter is calculated from Mie theory for a spherical particle (index of refraction \( m = 1.5 - 0i \)) for both 405 nm and 780 nm light sources. It is possible that the increase in laser power may be negated by a decrease in the response \( (A/W) \) of the GaP photodiode, however the largest gain will be achieved by lowering the wavelength of radiation. Assuming detection of a particle with scattering efficiency of 0.32 (that calculated for a 300 nm particle at 780 nm), we conservatively estimate that incorporation of a 405 nm laser will reduce the minimum detectable particle size to approximately 100 nm.

![Figure 6.6: Dependence of Mie scattering efficiency on particle diameter, calculated at 405 nm for spherical particles with refractive indices of: 1) \((\text{NH}_4\text{)}_2\text{SO}_4 \ [m = 1.52 - 0i]\), 2) carbon \([m = 1.39 - 0i]\) and 3) organic carbon \([m = 1.96 - 0.66i]\).](image_url)

It is well known that non-spherical particles are not well characterized by Mie theory and that the degree to which the sampled particles are non-spherical will impact the peak area-size calibration [Whitby & Liu., 1967]. Further, it is also well known that the scattering efficiency is sensitive to the refractive index of the particle (Figure 6.6), further
complicating the application of the calibration to ambient particles [Quenzel, 1969]. For example, the refractive index for (NH₄)₂SO₄ is 1.521 - 0i [CRC, 1999], while that of organic matter is variable, for example in the recent analysis of Schmid et al. [2009], a value of 1.39 (± 0.13) was calculated for organic matter found in biomass burning aerosol [Schmid et al., 2009]. Relative humidity (RH) will also directly affect the refractive index and thus scattering efficiency for a given particle type [Wang & Rood, 2008] and can be accounted for with simultaneous measurements of RH. The current commercially available miniature-OPCs are designed with the detector centered 90° to the aerosol stream, utilizing a mirror to direct the 100° solid angle fraction in addition to the direct 15° solid angle fraction scattered light to the detector. Based off the calculated scattering patterns for a 405-nm-wavelength light source incident on various sized spheres (index of refraction 1.5), shown in Figure 6.7, it is evident that the concentration of scattered light is most concentrated at forward angles [Prahl, 2002; Bohren & Huffman, 1983]. Gao et al. [2013] demonstrated that forward scattered light could be detected while separating out the laser beam. Here, we expand upon this initial work, focusing on advancements in cavity design, laser diode stability, and inlet characterization.
Figure 6.7: Simple polar graphs of the scattering patterns for a 100 nm (A) and 250 nm (B) sphere with a refractive index of 1.521 - 0i. The sphere is located at the center of the polar plot and the light is incident from the left. Scattering patterns were reproduced from patterns calculated by Scott Prahl’s Mie Scattering Calculator at the Oregon Medical Laser Center using the Bohren and Huffman code [Prahl, 2002; Bohren & Huffman, 1998].
6.3.3 Overview of the FALCON

The FALCON builds upon the framework presented by Gao et al. [2013] for a forward scattering optical particle counter employing a 405-nm laser diode light source. Several modifications and improvements were made to improve the overall performance of the instrument. The first generation of the FALCON incorporates modifications that include updates to the laser diode, development of a custom driver for the laser diode, and modification of the laser beam shape and quality achieved with new focusing optics. The second generation of the FALCON incorporates the same optics, geometries and fundamental operating parameters of the first generation cavity with a new, smaller and compact scattering cavity and instrument body. The second generation design is primarily a hardware modification to minimize weight and afford longer term autonomy. As such, we primarily present instrument metrics from the first generation instrument.

6.3.4 Laser Diode and Custom Diode Driver

The ability of an optical particle counter to accurately detect and size a particle is dependent on the signal to noise ratio (SNR) achieved for the respective particle size; the higher the SNR the higher the accuracy of the instrument. As particle size decreases toward the lower end of our size range of interest, 0.1 to 1 μm, the intensity of scattered light and subsequent signal decreases. To improve the counting efficiency at lower size ranges we need to lower the instrument background noise.

Gao et al. [2013] demonstrated that laser diode power stability is a major limiting factor in the detection of small particles in these types of devices. Power output fluctuations from the laser diode itself can drastically increase the background signal of the
instrument and result in wider pulse height distributions for particles of the same size interacting the beam at different periods of power output. As such, the more stable the power output of the laser diode the higher the signal to noise of the instrument and the lower the particle size that is capable of being detected.

In this system we utilize a 405-nm-wavelength 100 mW TO18 5.6 mm Sony Laser Diode Laser. In addition to the high power output (100 mW) and low cost (ca. $8 per unit), these laser diodes are also equipped with an internal photodiode. Incorporating this internal photodiode into our laser diode driver circuit we were able to build a simple yet effective constant power laser diode driver that is able to produce a laser beam with a very stable power output. The laser diode driver schematic is shown in Figure 6.8
Figure 6.8: Schematic of the laser diode driver circuit that incorporates the feedback of the laser diode’s internal photodiode to stabilize the power output of the laser diode producing a constant power output from a passively cooled laser diode.
6.3.5 Laser Diode Focusing Optics

The laser diode utilized in this instrument provides an efficient, high powered output beam at low cost. However, these commercially available diode lasers present a few challenges with respect to generating a tightly focused beam with minimal loss in beam quality. The laser diode utilized in this instrument is an edge-emitting laser diode that produces a highly divergent output beam with an elliptical cross section and some associated astigmatism. To correct for the highly divergent nature of the edge-emitting laser diode, we utilize a three layer lens system (L1, Figure 6.9) to collimate the beam into a circular beam with a diameter of ca. 3 mm.

Following collimation, we utilize a PCX cylinder lens (L2, Figure 6.9) to focus our collimated circular beam into a thin sheet approximately 0.2-0.3 mm thick and 5 mm wide, 100 mm down instrument. Utilizing the cylindrical lens to generate a thin sheet through which the aerosol jet transects, significantly improves consistent interaction between aerosol jet and laser beam as compared to systems focusing the laser beam to a nominal spot size \cite{Jonsson1995,Gao2013} The laser diode produces a beam with a radial intensity distribution close to a Gaussian distribution. Following the cylindrical lens, the scattering volume of the thin sheet has a wedged shaped power density, however the total energy scattered for a given size and velocity particle will remain constant \cite{Clarke2002}. By employing a cylindrical lens into the system, the resolution of the instrument will increase as the scattering signal pulses become more consistent.
Figure 6.9: Aerial view schematic the second generation FALCON depicting the laser diode mount, optics mounts, baffle tube, and scattering cavity. The cavity is designed such that two 405-nm V-Coat N-BK7 windows isolate the scattering cavity to improve aerosol stream through the laser beam path. The lenses, apertures, and windows are marked and correspond to the parts presented in Table 6.2.
To improve the laser beam shape, reduce background noise, and improve the counter sensitivity, two apertures were utilized at either end of the optics spacing tube. The first aperture (A1, Figure 6.9) is a 0.2 mm wide by 8 mm tall slit positioned ca. 2.7 mm from the cylindrical lens directly before the spacing tube. The second aperture (A2, Figure 6.9) is a 0.2 mm by 6 mm tall slit that acts to baffle the light that is refracted from the first aperture.

Table 6.2: Specific part descriptions and cost for complete build of the second generation FALCON (Figure 6.8).

<table>
<thead>
<tr>
<th>Description</th>
<th>Seller</th>
<th>Part No.</th>
<th>Cost ($)</th>
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<td>8</td>
</tr>
<tr>
<td>3 Layer Glass Collimation Lens (L1)</td>
<td>Emma Technology</td>
<td>712012254509</td>
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<td>Edmund</td>
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<td>Focusing aspheric (L3)</td>
<td>Edmund</td>
<td>#66-013</td>
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</tr>
<tr>
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<td>#64-038</td>
<td>53</td>
</tr>
<tr>
<td>Window (W2)</td>
<td>Edmund</td>
<td>#64-042</td>
<td>63</td>
</tr>
<tr>
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<td>#83-900</td>
<td>750</td>
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<tr>
<td>Mini-Pumps</td>
<td>Sensidyne</td>
<td>A120INSNF63VN1</td>
<td>105</td>
</tr>
<tr>
<td>3D Printing Material Cost</td>
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</tr>
<tr>
<td>Electronics</td>
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<td>~300</td>
</tr>
<tr>
<td>Estimated Total</td>
<td></td>
<td></td>
<td>1500</td>
</tr>
</tbody>
</table>
6.3.6 Scattering Cavity Design for the Second Generation Sensor

The scattering cavity of the second generation instrument, as shown in Figure 6.9, incorporates two Laser V-Coated N-BK7 windows to isolate the scattering cavity from the rest of the instrument, reducing the volume of air on which the pump must pull to 5 cm$^3$. The inlet for the aerosol jet stream has an inner diameter of 1 mm and is positioned 1 mm away from the laser beam which is offset 3 mm from the center of the scattering cavity. The outlet has an inner diameter of 4.8 mm and is positioned ca. 5 mm from the laser beam. At a flow rate of 1.8 slpm through the cavity, the particles spend between 25-32 microseconds within the laser beam, dependent on the width of the laser beam (0.25-0.30 mm). By isolating the scattering cavity the efficiency with which we are able to generate a stable and consistent aerosol jet stream through the laser beam path will increase, ensuring more consistent pulse heights for a given size and type of particle.

6.3.7 Focusing Aspheric Lens, Scattered Light Detection

The focusing aspheric lens is mounted in the center of the scattering cavity offset from the aerosol stream by 14.67 mm ensuring an object distance of 21 mm between the lens and scattering aerosol. The object distance between the aerosol jet stream and the focusing aspheric lens is set based on parameters presented by Gao et al. [2013] to ensure adequate light collection while maintaining a reasonably small instrument size. This object distance results in the scattered light focusing at ca. 106 mm with an image separation of 18.22 mm. To allow the laser beam to pass cleanly through the lens, the focusing aspheric lens has a 2 mm by 8 mm slot drilled out of it 3 mm off center. The size of this slot was optimized to allow the entire laser beam to pass through the lens while minimizing the
amount of forward scattered light lost. The instrument utilizes a beam dump to absorb the incident laser beam to ensure that the instrument’s background is not extensively influenced by any incident light from the beam.

6.4 Results and Discussion

6.4.1 Laser Diode Baseline Stability

Since the amplitude of the scattered light intensity is directly proportional to the incident light intensity, any significant fluctuations in the optical output power of the laser diode light source can be detrimental to accurate particle sizing. Ensuring a stable laser diode baseline is critical to increasing our SNR and improving instrument performance. Incorporating the laser diode’s internal photodiode feedback into the laser diode driver resulted in significant improvements in baseline stability. When operating our system at a comparable background to that of Gao et al., we observe a mean background of -4.15 ± 0.09 V with a maximum possible fluctuation of 0.36 V. The Gao et al. system demonstrates a mean background of -3.97 ± 0.12 V with a maximum possible fluctuation of 0.59 V based off of the figures presented. By improving our background stability we have significantly increased our lower detection limit.

6.4.2 Detection Efficiency

The detection efficiency of the FALCON is assessed through a series of size dependent calibrations. Utilizing a constant output atomizer and differential mobility analyzer (DMA, TSI 3071A) ammonium sulfate particles were size selected and detected.
All detection efficiencies are in reference to a condensation particle counter, (CPC, TSI 3787). A brief schematic of this experimental setup is shown in Figure 6.10.

![Figure 6.10: A schematic detailing the experimental set-up utilized in the detection efficiency calibrations.](image)

In addition to the detection efficiencies for the FALCON we also present the detection efficiencies for three commercially available instruments, a modified MetOne red diode based OPC (redOPC) [Clarke et al., 2002], a Shinyei PPD42NS dust sensor, and a Droplet Measurement Technologies (DMT) Ultra High Sensitivity Aerosol Spectrometer (UHSAS) [Cai et al., 2008]. The instruments presented here cover a representative spectrum of various instrumentation cost levels, from the inexpensive (ca. $20) Shinyei PPD42NS to the high cost UHSAS (a $70k research instrument). It is important to note that the Shinyei PPD42NS is not a particle counting instrument and only carries a digital output related to light attenuation. Instead of a detection efficiency, we plot the percent time in the digital low state (a commonly used proxy for particle concentration) on the right
axis; this follows the work of Holstius et al. [2014]. The size dependent efficiencies are shown in Figure 6.11.

![Figure 6.11: Size dependent detection efficiency for the FALCON (blue), redOPC (red), and Shinyei PPD-60PV (green, right axis).](image)

The UHSAS performs as expected demonstrating a 100% counting efficiency for all particles size ranges tested here $60 \text{ nm} < d_p < 350 \text{ nm}$. The redOPC and the Shinyei PPD42NS demonstrate poor to nonexistent counting efficiencies for particles below 350 nm. The Shinyei PPD42NS is in the digital low state for 0% of the sampling time during the runs. The redOPC also performs as expected from the reported manufacturer operational size range, demonstrating a detection efficiency of 11% at 282 and sub-10% for any smaller particle size. The FALCON demonstrates a significant improvement in counting efficiency over the other small scale particle sensors. At 238 nm the FALCON
has a counting efficiency of ca. 100% and is capable of detecting all of the particles generated and passed through the sampling line. At 195 nm and 146 nm the counting efficiency of the FALCON begins to slightly decrease with the FALCON counting ca. 80% of the particles in the sample stream. At 88 nm, we are still able to detect particles, however we do so at an efficiency rate of ca. 30%. While the detection efficiency below 100 nm is not high enough to provide reliable counting statistics, the FALCON demonstrates the capability of counting particles >100 nm.

As is inherent in all light scattering based particle counters, the detection efficiency of the FALCON is limited by coincidence counting/loss at higher number concentrations. When high concentrations of particles are present in the sample stream, particles are much closer together and potentially overlap each other. This can result in several errors with respect to how the scattered light is processed; two smaller particles can be counted as one larger particle or particles can be hidden behind another particle, leading to a biased low total count in each case. To decrease the likelihood of coincidence counting during the detection efficiency calibrations, the calibrations were purposely run under low particle loading conditions (< 100 # cm⁻³). From the sample flow rate, inlet size, and the thickness of the laser beam, we calculate a theoretical coincidence counting threshold of ca. 1060 # cm⁻³. Sample measurements at particle concentrations above 1060 # cm⁻³ are expected to be biased by coincidence counting.
6.4.3 Size Dependent Scattering Efficiency

Figure 6.12: Time series of the inverted scattering signal produced by a 101-nm ammonium sulfate particle (Figure 6.12A) and that produced by a 238-nm ammonium sulfate particle (Figure 6.12B)

Generating size resolved particle distributions is based on the ability to differentiate different sized particles by their pulse heights. Representative pulses for 101 nm and 238 nm ammonium sulfate particles are shown in Figure 6.12. For any given size particle we expect to see a distribution of peak heights, the width of which directly determines the size resolution of the FALCON. The width of the peak height distributions is determined by several factors, including how consistent the aerosol flow through the laser beam is as well as small fluctuations in laser power and background. Pulse height distributions for 3
Figure 6.13: Size dependent relative pulse height distributions to the mean baseline (-2.14 V) for filtered room air and 101 nm, 180 nm and 238 nm ammonium sulfate.
sizes of ammonium sulfate particles with a $d_p < 250$ nm achieved with the FALCON are shown in Figure 6.13. The pulse height distributions demonstrate a clear ability of the FALCON to size 101 nm ammonium sulfate particles. The distributions also highlight the improved instrument performance achieved when using a cylindrical lens to focus the laser beam into a sheet instead of a point. Comparing back to the peak height distribution Gao et al. presented for 125 nm PSL spheres, the FALCON observes much smaller distribution widths for comparably sized particles. The FWHM for the pulse height distributions measured for 101 and 180 nm ammonium sulfate particles are ca. 0.29 V and 0.76 V, a significant improvement over the FWHM of ca. 1.4 V for the Gao et al. system for 125 nm PSLs. Figure 6.14 shows the average size dependent pulse height distributions $\pm 1\sigma$ for 101 nm, 180 nm, and 238 nm ammonium sulfate particles. The trend in increasing voltage with particle size follows that predicted by Mie theory, as represented by the increase in scattering efficiency with particle size. While fluctuations in laser beam power were mitigated in advance with the laser diode photodiode feedback driver, the FALCON was limited however in the consistency with which the aerosol stream interacted with the laser beam. This was the result of flow issues that stemmed from the physical nature of the 1st generation scattering cavity itself. Although we have demonstrated improvement in our pulse height distributions for a given size particle, the second generation sensor aims to improve the flow of aerosols through the scattering cavity to ensure a tighter aerosol jet and more consistent interaction between the laser beam and particles as previously discussed.
The ability to accurately size particles of various compositions is dependent on how the pulse heights of particles with the same size, but varying refractive index compare; as the particle’s composition changes, the refractive index may also change with larger refractive indexes corresponding to a greater intensity of scattered light and pulse height. In Figure 6.15 we present the pulse height distributions for 101 nm ammonium sulfate particles and 104 nm sodium chloride particles. According to Mie theory, the scattering signal of a 104 nm sodium chloride particle is ca. 41% larger than that of a 101 nm ammonium sulfate particle. Based on the pulse height distributions we calculate an average pulse heights (± 1σ) of 0.49 ± 0.12 V for the 101 nm ammonium sulfate particle and 0.73 ± 0.20 V for the 104 nm sodium chloride particle. We observe a 49% increase in the scattering signal for the sodium chloride particle vs. the ammonium sulfate particle, demonstrating a good agreement with Mie theory predictions. With a 2σ of 0.25 V for the
pulse height distribution of the 101 nm ammonium sulfate particle, the 49% increase in scattering signal as a result of the shift in refractive index could potentially introduce some sizing errors into the measurement as pulses on the larger side for the sodium chloride particle could fall out of the pulse range determined by the ammonium sulfate particles. This highlights the necessity of proper calibration of the sensor for the average refractive index of the sample being measured. While counting statistics may not be affected, sizing statistics are dependent on properly calibrating the instrument to a refractive index close to that of the sample.

Figure 6.15: Relative pulse height distributions to the mean baseline (~2.14 V) for 101 nm ammonium sulfate particles and 104 nm sodium chloride particles.
6.4.4 Future Directions

In addition to the scattering cavity and instrument body design changes that were highlighted earlier, we also plan to implement a few other modifications in the second generation of the FALCON that should improve the FALCON’s performance.

The 1st generation of the FALCON has a very basic electronics interface that the 2nd generation of the FALCON aims to improve upon to further increase our detection efficiency. The current 1st generation of the FALCON has the output of the PMT processed by a single stage gain amplifier before the signal is recorded. As such the pulses have an inherent long tail after the initial signal pulse as is characteristic of PMT signals displaying a fast rise time and a slow exponential decay (Figure 6.10). To correct for this, as well as filter out signal noise and improve the signal to noise ratio of the instrument we will plan to use a shaping amplifier, similar to the Cremat CR-200-X series, to re-shape the “tail pulse” into a fixed width Gaussian pulse. With the inclusion of a shaping amplifier, we aim to increase the signal to noise of the instrument while seeking to improve our counting efficiency. The shaping amplifier should decrease the likelihood that small pulses are buried under the noise from the first stage of amplification and should eliminate any issues with pulses riding on top of the long tail of a preceding pulse.

Future work will also investigate the potential of replacing the relatively expensive PMT detector with a less expensive, Si PIN photodiode with enhanced sensitivity in the emission wavelength range of violet-lasers. Looking at the expected total cost for 1 unit of the second generation FALCON (Table 6.2), 50% of the estimated total cost is attributed to the PMT detector. Although use of a photodiode will result in a significant decrease in the sensitivity the detector and will limit the lowest size we will be able to detect,
incorporating the photodiode instead of the PMT could lower the cost of the instrument by 42% and presents an attractive opportunity for a second less expensive, albeit less sensitive version of the FALCON.

6.5 Acknowledgements

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6.6 References


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