Statement of Work

Wasatch Front Ammonia and Chloride Observations (WaFACOs 2018/19)

Randal S. Martin (PI), Utah State University
Kerry Kelly (Co-PI), University of Utah
Jaron Hansen (Co-PI), Brigham Young University

Project Duration: July 1, 2018 – December 31, 2019

This Statement of Work (SOW) summarizes planned ambient measurements centered around gaseous ammonia (NH_3) and hydrochloride acid (HCl) during the winter of 2018/2019 and the summer of 2019. As discussed below, additional supporting measurements of $PM_{2.5}$ distribution and composition and mobile measurements of temporally-refined NH_3 and other parameters will also be conducted.

Background:

Numerous previous studies, most recently the 2017 multi-agency Utah Winter Fine Particulate Study (UWFPS, https://documents.deq.utah.gov/air-quality/planning/technical-analysis/research/northern-utah-airpollution/utah-winter-fine-particulate-study/DAQ-2018-004037.pdf) have examined the composition and formation mechanisms of the local wintertime particulate. Consistent among all of these studies is the predominance of ammonium nitrate as the main component of the elevated $PM_{2.5}$ concentrations across the Wasatch Front. Indeed, within the summary of the 2017 UWFPS, it is pointed out that although the local airsheds appear to be slightly ammonia-rich in regards to NH_4NO_3 formation, there are times, especially during extended persistent cold pool capping events (inversions) in which the atmosphere switched to a more ammonia-limited regime. It should be noted that it was also found that the Cache Valley was more consistently ammonia-rich. Directly quoting the UWFPS report "*This may suggest that the system in Utah Valley and particularly the one in the Salt Lake Valley is close to the equivalence point between nitrate limited and ammonium limited regimes, and reductions in either reagent (nitrate and/or ammonia) may be effective in leading to reductions in ammonium nitrate aerosol*." The UWFPS report also pointed out the current NH_3 emissions inventory does not adequately replicate the observed NH_3 measurements, both in distribution and ambient concentration and concluded that the uncertainty in NH_3 data are a significant deficiency un the current state of knowledge.

Figure 1A shows the average ambient, ground level NH_3 measurements from 10 distributed sites taken during the 2017 study. As can be seen, there did appear to be somewhat of a gradient from north to south, with an average concentration of 31 ppb. A similar study in 2016 found an average concentration considerably less (8 ppb). Conversely, parallel studies, but with much more dense network, in the Cache Valley found concentrations very similar across both years: 78 and 65 ppb, respectively. Therefore, a more detailed, both spatially and temporally, understanding of the NH_3 behavior along the Wasatch Front needs to be a priority in order for appropriate remediation scenarios to be implemented.

In discussions with DAQ and EPA personnel, questions have also been raised about the influence of atmospheric chloride on both particulate formation chemistry and oxidant photochemistry during both the wintertime pollution events and summer time ozone episodes. A small study was conducted in the summer of 2015 using 15 passive samplers to assess the hydrochloric acid (HCl) distribution along the northern Wasatch Front and the southern and southwestern edge of the Great Salt Lake (https://documents.deq.utah.gov/air-quality/planning/technical-analysis/research/northern-utah-airpollution/gsl-HCl/DAQ-2018-000761.pdf). Figure 1B shows the average HCl concentration distributions fond during the study. The overall average summertime HCl concentration of 0.95 ppb, not significantly

different from other urban area values reported in the literature, but approximately 5x values reported for rural/remote areas. It is of interest to note that a notable gradient was found with higher values from west to east, likely owing to the large magnesium refinery on the western edge of the Great Salt Lake. These results were also observed in the 2017 UWFPS previously referenced. As with NH_3, a more complete understanding of the availability of gas-phase chloride, as represented by HCl, will aid in the development of more reliable data and models for the management of Wasatch Front air quality.

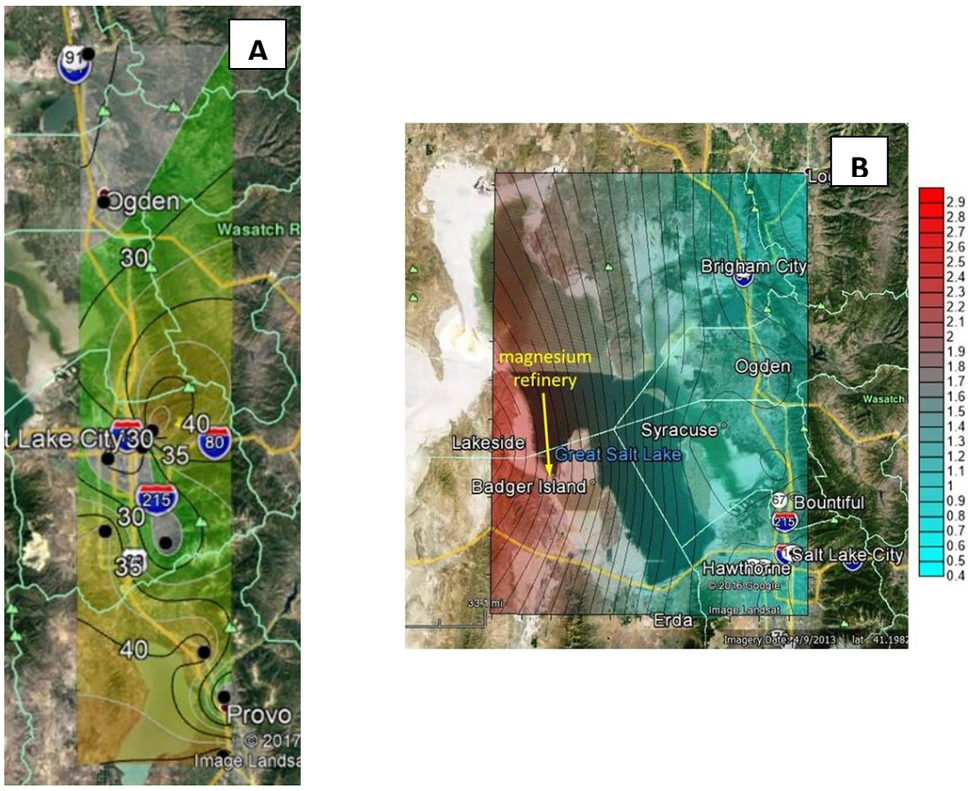

Figure 1. (A) Average Wasatch Front NH_3 concentration distribution during the 2017 UWFPS, and (B) average Wasatch Front HCl concentration distribution during the summer of 2015.

Project Objective

The simplified objective of the proposed study is to define the spatial and temporal behavior of atmospheric ammonia and hydrochloric acid along the Wasatch Front across both summer and winter seasons. This objective will be accomplished through three tasks developed in consultation with the Utah Division of Air Quality and the U.S. Environmental Protection Agency. These tasks, as describe separately below, are: (1) Networked NH_3 and HCl Studies, (2) $PM_{2.5}$ Ionic and Other Selected Constituents Spatial Distributions, and (3) Mobile and Temporary Stationary Real-time NH_3 Assessments. Project planning meetings will be conducted in late summer of 2018, protocol development and site identifications/visits will be conducted in the fall of 2018, and four week sampling campaigns will be conducted in the winter and summers of 2019.

Dr. Randal S. Martin from Utah State University (USU) will serve as the overall project PI, while Dr. Kerry Kelly from the University of Utah (UoU) and Dr. Jaron Hansen from Brigham Young University (BYU) will serve as Co-PIs. Drs. Kelly and Hansen will primarily oversee undergraduate student technicians in the deployment and recovery of passive and particulate samples, but also aid in the development of sample locations and subsequent data analysis.

Task 1: Networked NH_3 and HCl Studies

The main focus of the proposed project is to spatially and temporally quantify the ambient distributions of gas-phase ammonia (NH_3) and hydrochloric acid (HCl). Gas-phase NH_3 concentrations will be assessed using single-stage Ogawa passive samplers equipped with commercially-purchased sorbent pads. The concentrations of gas-phase HCl will be captured using Radiello passive samplers with mesh-caged, silica gel cartridges. At each field location, the samplers will be housed under and appropriate wind/rain screen, as suggested by the manufacturers. The PI has extensive experience with both of these sample systems.

For two, four week periods, one during the winter of 2018/19 and one during the summer of 2019, up to forty (40) passive samplers for NH_3 and HCl will be distributed throughout the Wasatch Front. Although final locations will be decided in consultation with the PI's and the UDAQ investigators, approximately ten (10) sites will be identified from Bountiful north, including west towards Badger Island and likely Antelope Island, twenty (20) locations will be located throughout the Salt Lake City airshed, and ten (10) sites will be identified in the Utah County airshed. Each individual sample deployment will nominally be one week in duration. From historical experience, it has been found to adequately allow for sufficient, quantifiable sample collection for the chosen passive technologies. For comparison, the National Atmospheric Deposition program's passive Ammonia Monitoring Network (AMoN) mandates a two-week sample deployment for their nation-wide network of passive samplers. However, it should be noted that the AMoN samplers must assess a wider range of expected NH_3 concentrations, including much lower expected values. Dr. Kerry Kelly (UoU) will oversee undergraduate technicians in the deployment and recovery of the samplers from the SLC and northern airsheds, while Dr. Jaron Hansen (BYU) will serve in the same function for the Utah County airshed. Drs. Kelly and Hanson will also be responsible for associated sample storage and quality control until they can be transferred to Dr. Randy Martin (USU) for analysis.

The NH_3 and HCl passive samples will be quantified via ion chromatography following standard protocols at the USU's Utah Water Research Laboratory under the direction of Dr. Martin, an Environmental Engineering M.S. student, and one of UWRL's senior laboratory technicians. The ultimate products of this task will be weekly average gas-phase concentrations of ambient, gas-phase NH_3 and HCl for each of the airsheds. Additionally, spatially-resolved isopleth maps of the ambient, gas-phase NH_3 and HCl concentrations throughout the extent of the Wasatch Front will be produced – including the identification of high and low concentration areas for both the winter and summer seasons.

Task 2: $PM_{2.5}$ Ionic and Other Selected Constituents Spatial Distributions

In conjunction with Task 1's passive networks, at least 10 AirMetric $PM_{2.5}$ MiniVol sampling systems will be deployed to passive sampler locations to be selected after discussion among the investigators. The MiniVols will be programed to operate for a runtime between 24 hours and up to the full (passive sampler) weekly deployment. Gravimetric analysis of the collected filters at UWRL will determine the observed, integrated $PM_{2.5}$ concentrations. After mass analysis, the filters will be eluted with purified, distilled water at UWRL and analyzed for suite of low-molecular weight anions and cations, primarily looking at chloride (Cl^-) content and the possible importance of Cl^- in local and spatial $PM_{2.5}$ photochemistry, will also be examined. In addition to the 2018/19 winter and 2019 summer sampling campaigns, it is planned to test the extended (seven day) MiniVol deployments during the fall of 2018 for sufficient and/or overloaded sample collection.

In addition to the above ionic analysis, at least three (3) locations will be identified for the installation of parallel MiniVol samplers. At these locations, one or two additional MiniVols will be operated for the same time period. These secondary systems will be used for collection of

particulate matter to be separately analyzed for crustal elements and carbon content. Separate Teflon 47 mm filters will be collected and commercially-quantified using x-ray fluorescence (XRF) for the elemental analysis and pre-fired quartz filters will be collected and commercially-quantified for organic and elemental carbon (EC/OC) analysis.

Task 3: Mobile and Temporary Stationary Real-time NH_3 Assessments

The recent purchase of a Picarro G2103 real-time NH_3 analyzer through a cooperative efforts of UDAQ, Weber State's University's National Centers for Automotive Science and Technology (NCAST), and USU, allows parallel examination of finer spatial and temporal resolution of NH3 concentrations throughout the sample airsheds. As purchased, the Picarro is being vendor-modified to be able to directly measure not only ambient NH_3 concentrations, but also direct measurements of source-level (e.g. tailpipe) concentrations. The G2103 collects can quantify ambient sample from sub-ppb to greater than 10 ppm, with a time resolution approaching 1 second. As a part of this project, a commercial cylinder of certified NH3 calibration gas will be purchased at an approximate concentration range (e.g. 100-500 ppb) which can then be diluted down for a multiple point calibration of the sampling system.

The system is planned to be mounted either in an existing USU trailer or in a TBD mobile platform, and transects during the two seasonal passive field campaigns of the targeted airsheds will be conducted in order to more fully understand the temporal nature of the ambient NH3 behavior and locate potential "hot spots" of high NH_3 concentrations and possible source locations and relative strengths. With either platform, the system can also be temporarily stationed at areas of interest (high traffic areas, waste water treatment plants, fertilizer production facilities, etc.) for more detailed examinations. These activities will be finalized during preliminary investigator meetings, and with consultation with UDAQ and likely the EPA. Additionally, UDAQ personnel have secured an initial agreement with the NEIC Division of the EPA, to tentatively schedule their mobile NH_3 van for coincident sampling as well. These plans will also be finalized in early team planning meetings. It should be noted the Picarro instrument was not explicitly purchased for this, but for a range of UDAQ-related investigations and its scheduling will have to be carefully managed.

Deliverables

- Quarterly reports in a format to be specified by the Division of Air Quality
- Final Report (Dec. 31, 2019)
- Compiled and verified digital datasets for each of the above listed tasks in a format to be compatible with DAQ specifications, for ultimate public dissemination

Budget

As shown, in the proposed budget below, the requested funds for the 18 month project totaled $210,000, where $165,969 will be allocated to Utah State University (USU) and $44,031 will be allocated to UDAQ. As shown, personnel and associated fringe benefits costs for USU totaled $60,909. As is standard proposal protocol, faculty and professional staff are billed in units of months or fraction of months. Similarly, graduate student assistantships, nominally taken to be half-time appoints, are also billed in monthly units at a current rate of $1775/mo. However, as is done for the purpose of assessing lab-related fees (below), the half-time graduate assistantship can be estimated at 90 hrs/mo. For this project, USU undergraduate laboratory technician help was estimated at a total of 15 hr/wk for 50 weeks or a total of 750 hrs to be paid at $10/hr. It should be noted that slight salary increases (3%) were included for the change to the 2020 fiscal year (July 2019-Dec 2019). Calculated fringe benefit rates are based on a pool of actual administrative costs and are adjusted every six months to reflect potential changes. This procedure has been reviewed and approved by federal auditors who monitor

these costs and the university's indirect costs. There are different pools for contract employees, like Dr. Martin and Mr. Stewart which is currently charged at a rate of 46.5% and another pool for students and hourly employees. Separately, employer-provided insurance ($1,794) is required for all graduate students and the USU administration has made it part of a rule that at least some graduate student tuition ($3000) is required to be included separate from standard fringe benefits on all proposals.

Materials, supplies and EQL fees totaled $41,253. A more detailed breakdown of these costs can be supplied as desired, but briefly $22,110 were budgeted for sorption pads and passive sampler parts, $3,930 were budgeted for filters, calibration standards, instrument specific parts, $3,668 were budgeted for commercial filter speciation analysis (elemental and carbon content), and $2,500 were set aside for unplanned/miscellaneous costs. The budgeted EQL fees represent personnel-prorated required fees for operation at USU/UWRL's Environmental Quality Laboratory. As previously discussed, collaborators from UoU and BYU will be key to the success of this project and will be funded via subcontracts at levels $32,500 and 10,000, respectively. These subcontract costs where determined by the Co-PIs and were budget to reflect the faculty participation, undergraduate technician time for sample preparation, deployment, sample recovery, and travel costs associated with driving around the sampling areas. Travel by USU is estimated to require numerous trips from Logan to and around the samples areas along the Wasatch Front and is estimated at 3,400 miles (or $2,380). The F&A (indirect overhead) have been assessed at the agreed rate of 10%.

The $44,030.86 that will be allocated to UDAQ will be used to cover personnel costs, associated fringe benefits as well as travel and indirect costs. Environmental scientists from UDAQ will participate in the sampling sites selection, study design and planning as well as data analysis. A detailed breakdown of these costs is shown below.

Personnel: Dr. Randy Martin, PI (1.5 months)	$ 14,698.33
Personnel: Joe Stewart, UWRL lab tech (2 months)	$ 6,795.44
Personnel: M.S. Student (12 months, 90 hrs/mo)	$ 21,301.10
Personnel: UG student techs (750 hrs)	$ 7,575.00
Fringe Benefits	$ 10,538.71
Materials, Supplies, & EQL fees	$ 41,253.00
Other Op. Exp. (student insurance & MS tuition)	$ 4,794.00
Subcontracts (U of U $32,500; BYU $10,000)	$ 42,500.00
Travel (numerous RTs to Wasatch Front and sample sites)	$ 2,380.00
Total Direct Costs	$ 151,835.58
F&A (Indirect) Costs (at 10%)	$ 14,133.56
TOTAL USU COSTS	**$ 165,969.14**
UDAQ	
Personnel: Two environmental Scientists IV (2.5 months)	$ 25,120
Fringe Benefits: Two environmental Scientists IV @ 55% rate	$ 13,816
Travel	$ 208.86
Total indirect costs @ 12.55% rate taken from personnel costs and fringe benefits	$ 4,886.5
TOTAL UDAQ COSTS	**$ 44,030.86**
TOTAL PROJECT COST	**$ 210,000**