

# EXECUTIVE SUMMARY

## HARC Project H-114 Executive Summary

The OH radical, considered as atmospheric vacuum cleaner, plays a key role in atmospheric processes, including ozone generation. Many metropolitan areas including Houston, DFW, etc. have morning ozone excursions that are difficult to explain. HONO provides a reservoir for a photolytic morning OH release, but measured values of HONO are not enough to account for the observed excursions. Nitrophenols can potentially generate HONO and hence an assessment of atmospheric nitrophenols is of importance. Also, several nitrophenols are phytotoxic, estrogenic and act as vasodilators, raising direct concerns about adverse health effects. Nitrophenols could easily be scavenged by rain (they are highly water soluble) and hence measurement of nitrophenols in both air and rain are relevant. That vehicular exhaust contains nitrophenols is well documented but there is no significant data in the US on nitrophenol concentrations either in air or in precipitation. This project was a pilot to determine if nitrophenols exist as measurable concentrations in the air and rainfall in Houston.

The original plan was to develop and deploy a continuous analyzer. Funds were available two weeks before the field study was to begin and the project was funded at \$45,000 instead of the requested \$150,000. We opted to make a discrete sorbent-based sampling with subsequent analysis in the laboratory. It was not known what specific nitrophenols may exist in Houston air. An initial library of ten nitrophenols was acquired. They varied in their pKa, water solubility, Henry's law constant etc. In order to study gas phase nitrophenols and to perform quantitative analysis, standard gas phase nitrophenols were generated by fabricating gravimetrically calibrated nitrophenol-filled permeation tubes made from low density polyethylene tubing maintained at 30 ° C. A significant amount of effort was spent on developing and optimizing the separation of a mixture of *o*-nitrophenols by liquid chromatography (LC). The final method used was unique in that it used the ionizability of nitrophenols to preconcentrate them on an ion exchange column and using their lipophilic nature separating them on a high efficiency small particle size (2 μm) reverse-phase column. The detection of nitrophenols was achieved by coupling the LC effluent to a state-of-the-art heated electrospray ionization triple quadrupole tandem mass spectrometer with high mass resolution. Several nitrophenols were thus identified, initially in rain samples.

We examined various solid sorbents and chose silica gel. Sampling and capture of several NPs and tolerance to humidity was checked in the laboratory. We developed and built a PC-controlled 24-channel sampler for use in Houston at the Moody Tower Sampling site on the UH campus during the 2009 SHARP study from April 15 through May 31. University of Houston (UH)

personnel were trained and kindly changed sorbent cartridges for us every day and stored capped sample cartridges at -20 C until we brought them back for analysis. An elution protocol was developed that produced a sample compatible with the analysis protocol.

While we analyzed some initial samples by IC-LC-MS/MS it would have been impossible to analyze the 1000+ samples by MS/MS technique within the available time and cost. In addition, while mass spectrometry is a wonderful identification technique, in the absence of isotope dilution, it is not a reliable quantitation technique in a complex sample due to variation in the sample matrix and varying degrees of ionization suppression.

We successfully fabricated a highly sensitive LED-liquid-core-waveguide based long path absorbance detector. The Teflon AF tube used as the LCW was itself gas permeable and the entire detection cell was thus immersed in concentrated ammonia and the ammonia permeating into the LC effluent turned it alkaline, rendering the elute nitrophenols yellow (they behave as acid base indicators – colorless in acid, yellow in base) and allowing an inexpensive LED and a \$2 light to voltage converter (also from Texas, Texas Advanced Optical Systems) to permit an ultrasensitive detector (with a path length as long as 142 cm).

The dominant nitrophenols found in air were, not surprisingly, the same as those primarily seen in precipitation. The four prevalent nitrophenols were found to be present in the air samples collected at University of Houston. These are 2,4-Dinitrophenol ( $2.03 \pm 0.69 \text{ ng/m}^3$ ), 4-nitrophenol ( $6.04 \pm 1.11 \text{ ng/m}^3$ ), 2-nitrophenol ( $2.30 \pm 0.92 \text{ ng/m}^3$ ) and 2-Methyl-4-nitrophenol ( $2.61 \pm 0.79 \text{ ng/m}^3$ ).

While we have full faith in sample analysis and there is no doubt that various nitrophenols are indeed present, we believe that these concentrations are far smaller than what actually exists in air and the sample has either not been quantitatively collected or degraded after collection or both. We base this conclusion on the fact that that very little diurnal variation was observed in the samples. Further rain data strongly suggest that the air concentrations are likely 1.5 -2 orders of magnitude greater than what we report above. Few Houston rain samples have yet been analyzed because we had some concerns about the integrity of the rain samples collected by the UH group. But rain concentrations have been measured here in UTA. Analysis of the most recent sample on 09/10/2009 (total rainfall 5.46 cm) indicated for example  $0.86 \pm 0.00$ ,  $4.68 \pm 0.03$ , and  $2.26 \pm 0.03 \text{ } \mu\text{g/L}$  aqueous concentrations of 2,4-Dinitrophenol, 4-nitrophenol and 2-Methyl-4-nitrophenol. Assuming a boundary layer height of 500m, the corresponding concentrations in the air column would be in the order of 100-500  $\text{ng/m}^3$ . These values are only likely to be higher in Houston.

We tested the humidity effect in the laboratory at 80% RH and found it to be negligible. But it was decided to make the sampling volume substantially higher in Houston because of low concentrations anticipated. Higher humidity than tested and greater sampling volumes may have resulted in collected nitrophenols being displaced by moisture. There may also have been partial or near complete degradation of nitrophenols after sampling during storage despite low temperature storage. Finally nitrophenols may have migrated from the silica to the polymeric cartridge body.

The rain samples to be investigated for the presence of nitrophenols, were collected at UTA and UH campuses (as indicated before, these have not been analyzed yet due to integrity concerns. An automated rain sampler was used at UTA; the measured concentrations were 2,4-Dinitrophenol (0.04-3.31  $\mu\text{g/L}$ ), 2-nitrophenol (0.29-0.69  $\mu\text{g/L}$ ), 4-nitrophenol (0.20-4.89  $\mu\text{g/L}$ ) and 2-Methyl-4-nitrophenol (0.11-2.26  $\mu\text{g/L}$ ).

The irony is that this has only intensified the need for the development of a continuous analyzer that can be deployed in the field and that will provide reliable nitrophenol concentrations in Houston air.