Report on Arsenal data for USACAMP

The Isaacman-VanWertz group conducted two generally sampling strategies for identifying potential emissions of concern downwind of the Radford Arsenal. Sampling was conducted in the Prices Fork neighborhood approximately 2 kilometers away from the Arsenal in the predominant wind direction, on a commercial site in an open field. Some local emissions are expected from commercial activities on the site, but site selection sought to maximize distance from local activities.

Sampling was conducted through the collection of sorbent tubes and the continuous operation of a photoionization detector for approximately one year.

Sorbent tube sampling

Samples were collected on commercially available gas sampling cartridges consisting of passivated stainless-steel tubes packed with Carbotrap 202, a combination of Carbopack B and Carbopack C sorbents. Sampling was conducted opportunistically, with samples collected for a 2-hour duration with two replicate samples and a field blank collected at all times. Four periods of sampling were conducted. Samples were analyzed by thermal desorption gas chromatography mass spectrometry, with target compounds — benzene, toluene, ethylbenzene, and xylenes - quantified through the introduction of multi-point calibrations. No samples were observed to have concentrations of target compounds above thresholds of concern.

Real-time sampling

A Sensit SPOD real-time total VOC monitor was deployed for approximately one year. This sensor uses a photoionization detector to measure a sum of all VOCs, though detector sensitivity can vary across compounds, so it represents only an approximate or relative concentration. A sample of data is shown in Figure 1, which is representative of what is observed. Generally, a background is observed that has a strong diurnal cycle, with occasional brief spikes in concentration.

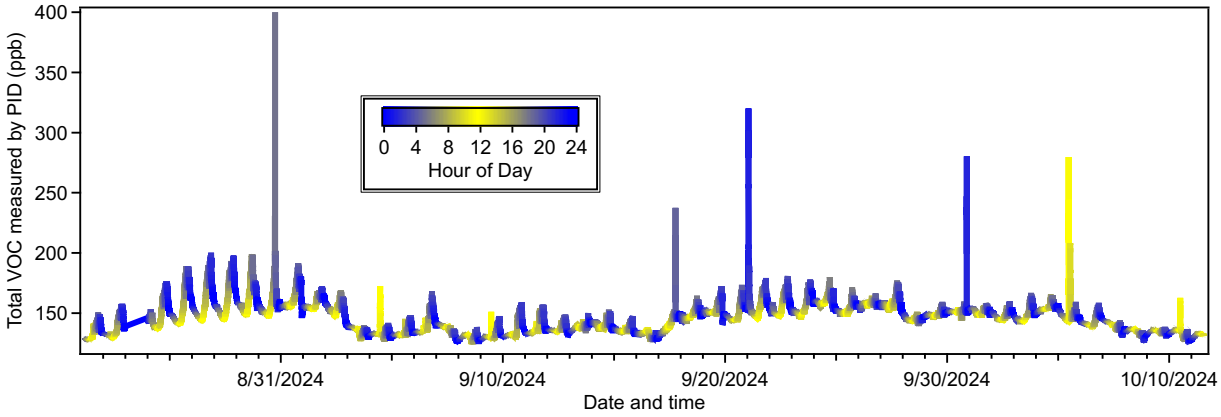


Figure 1. Representative data from the Sensit SPOD showing a diurnal pattern with a peak in late afternoon/early evening and intermittent peaks at varying times of day.

The observed diurnal patterns are common for compounds emitted from natural systems, which are ubiquitous in the Southeastern U.S. To explore the role of natural emissions in the system, diurnal profiles are shown across different seasons in Figure 2. In the spring and summer, when natural emissions are expected to be strongest, there is a stronger diurnal profile. This profile is opposite in the winter, with lower concentrations and nighttime peaks in concentration, a pattern commonly observed for emissions from anthropogenic sources may be due to the nearby road that sees relatively heavy rush hour traffic. Together, these profiles and the overall patterns shown in Figure 1 suggest a combination of regional anthropogenic and biogenic emissions generally influence the site, with potential transient plumes from some specific source that may or may not be the Arsenal.

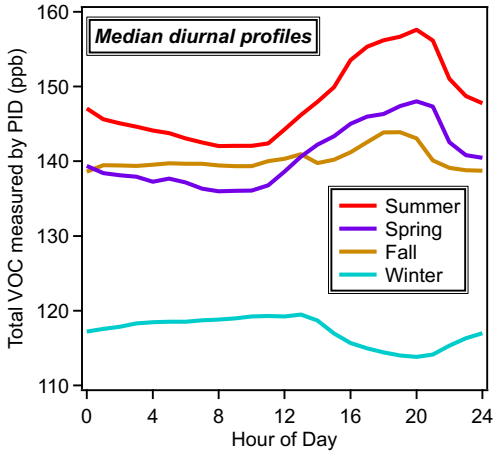


Figure 2. Diurnal profiles of total VOC data showing a daytime peak in the summer, common for natural emissions, and a nighttime peak in the winter, common for regional emissions from human activities.

By separating background signals from intermittent spikes in concentration, the influence of potential local sources can be extracted. Biogenic signals are expected to have temperature-dependent emissions with a relatively predictable relationship, which is observed in these data. The dashed line in Figure 3 represents the approximate shape of the relationship based on published temperature dependence in biogenic emissions supporting the conclusion from the diurnal patterns that a substantial fraction of the total VOCs in this region are naturally emitted. However, clear spikes in data are also observed and represent the same types of peaks shown in Figure 1.

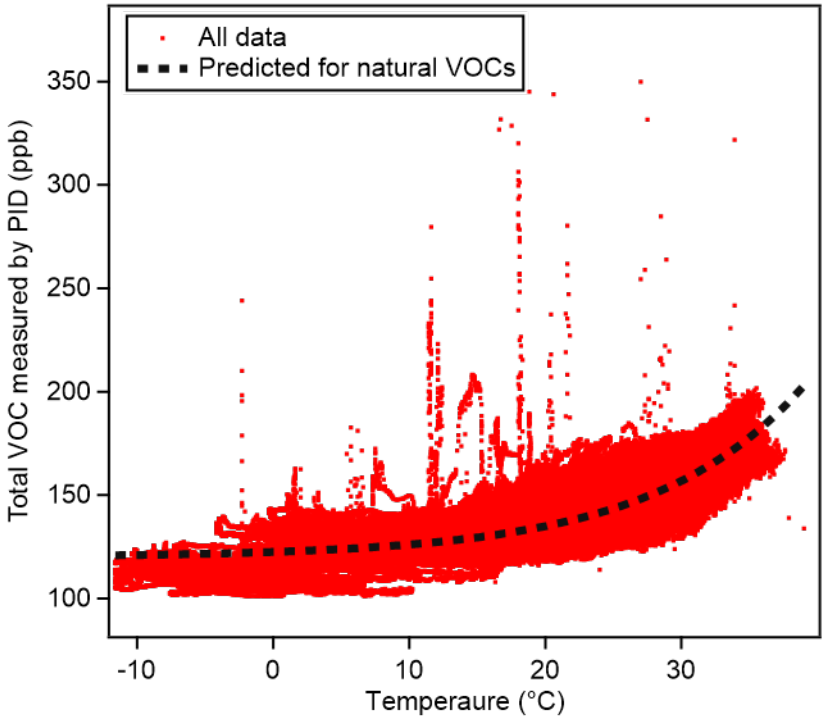


Figure 3. Measured concentrations of total VOCs as a function of temperature showing a strong background consistent with natural sources, alongside intermittent spikes

Observed spikes can be quantified and examined in terms of their "enhancement" calculated as the concentration observed above what would be expected from the regional background signals (i.e., the red dots in Figure 3 minus the black dashed lines). These enhancements are observed to occur at a range of times of day and are found to primarily come from the west and north (Figure 4a). However, these are also the dominant wind directions (Figure 4b), so most data are observed in these directions. It is not possible to full determine the source of these enhancements. Those that occur during the day could be due to local activity at the commercial site or could reflect transport from a farther location. Nighttime peaks are more likely to represent a less local site, as the commercial activities were not usually conducted outside of daytime business hours, but the precise source of these spikes cannot be unambiguously determined. In general, such

enhancements are observed roughly once per week and tend to persist for between 5 minutes and one hour. Enhancements observed at night are in particular predominantly observed from the north.

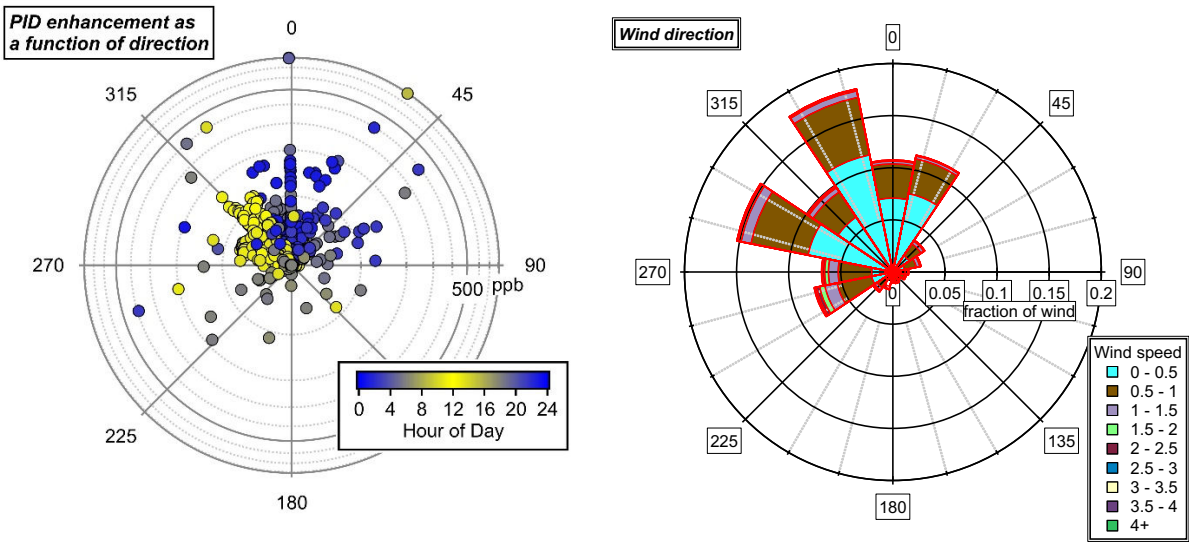


Figure 4. Measurements as a function of wind direction including (a) enhancements in total VOC, on a log-scaled radial axis, and (b) windspeed as a wind rose.

Conclusions

From the SPOD photoionization detector, it appears that a substantial fraction of total VOCs is from natural emissions, which is expected given the high vegetative cover in the region. However, there are occasional plumes coming from some source likely to the north or west that has intermittent impacts on the neighborhood. It cannot be ruled out that these spikes are from the Arsenal, but there is also not clear evidence that that is the case. At least some fraction of these spikes is probably from highly local or on-site activities. Given the observations of total VOCs, it is not unexpected that concentrations of target compounds of concern were not observed in the chemically resolved sorbent samples. The short duration of these plumes is likely to make them difficult to capture and thus difficult to apportion to a source, but the total VOC measurements suggest that such plumes are not particularly common or long lived. Capturing the content of these plumes would require longer-term real-time compound-resolved measurements, a capability that is possible but labor intensive and thus relatively expensive. Overall, these data cannot definitively demonstrate that the Arsenal is not having a downwind influence but do suggest it is not likely that any such influence is strong or frequent in this neighborhood.