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Technical Memorandum

March 29, 2022 STI-921031-7892

To: Belen Leon, Imperial County Air Pollution Control District (ICAPCD)

From: Josette E. Marrero, Ningxin Wang, Annie Anderson

Re: Data Summary of 12 Months of Air Quality Measurements along the New River in Calexico, CA

Summary

This memorandum summarizes air quality monitoring data collected at a monitoring site at the city of Calexico Water Treatment Plant, adjacent to the New River, between December 3, 2021, and December 5, 2022. The New River monitoring project was initially scheduled to operate for just the six-month period between December 2021 and June 2022, but was extended for an additional six months. Data from the first six months of monitoring was summarized in a technical memorandum submitted in September 2022.

Analysis of the data collected during the entirety of the 1-year monitoring period revealed the following key findings:

- High data completeness was achieved throughout the monitoring study for each of the pollutants measured. Each analyzer collected over 94% of possible measurements.
- Each pollutant showed a similar diurnal trend where the highest concentrations were observed during the evening or early morning hours, and the lowest concentrations were observed in the afternoon.
- The annual average concentrations of hydrogen sulfide (H_2S) exceeded the chronic reference exposure limit; no other pollutants exceeded this health threshold. However, the monitoring site was also situated close to a wastewater treatment plant, which may have contributed to elevated concentrations. Overall, the contribution from the wastewater plant to H_2S concentrations cannot be distinguished from the influence from the New River.
- A variety of volatile organic compounds (VOCs) were detected in the whole air canister samples, and a small number of polycyclic aromatic hydrocarbons (PAHs) were detected in poly-urethane foam (PUF) samples. The average concentrations of these species are typical of urban or industrial environments. No pesticides were detected in any of the PUF samples collected throughout the year.
- Concentrations of all species detected in the offline samples were below chronic health thresholds.

Background

Air quality measurements were conducted at a monitoring site located at the city of Calexico's Water Treatment Plant (**Figure 1**) in an effort to better understand the potential air quality impacts from the New River. The New River, which flows north from Mexico into the Imperial Valley, is one of the most important pollution sources in the region. The contamination of the river has been known for decades, as it contains bacteria and pesticides from municipal waste, undertreated industrial wastewater, and agricultural drainage. While the river water is tested monthly in the U.S., little is known about the river's impact on air quality within Calexico. The goal of this monitoring study was to develop a better understanding of the New River's air quality impacts as a critical step in working towards improving environmental quality and human health in the region.

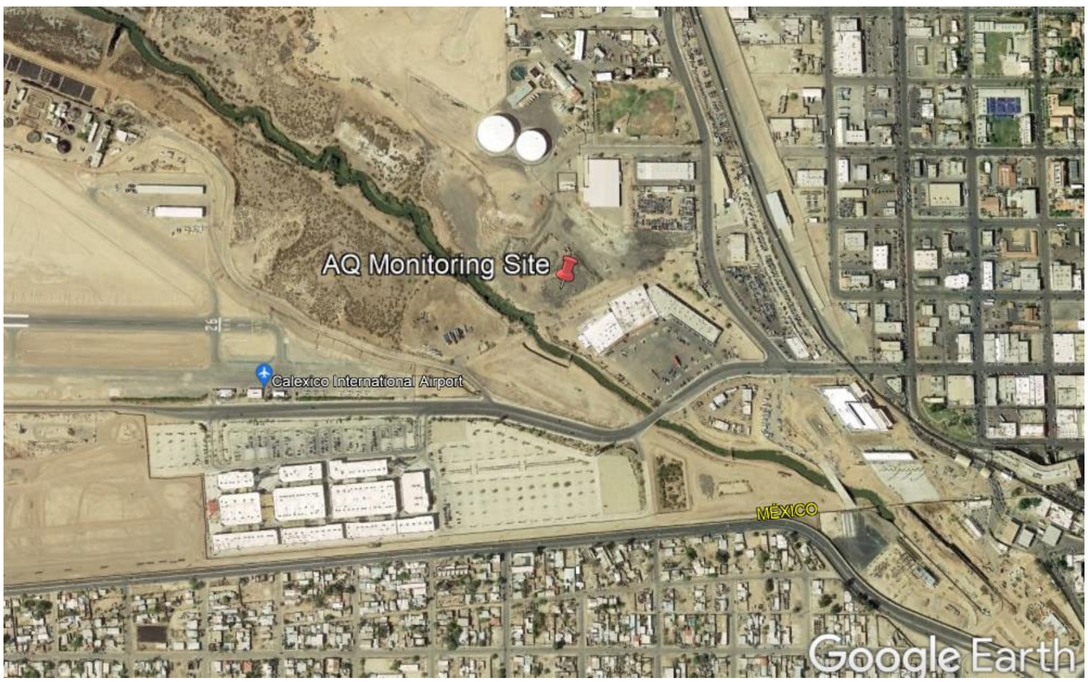

Figure 1. Location of the air quality monitoring site at the Calexico Water Treatment Plant, in relation to the New River and U.S.-Mexico border.

The air quality monitoring included continuous 5-minute measurements of H_2S, ammonia (NH_3), and meteorological parameters (wind speed, wind direction, temperature, and relative humidity), and 10-minute measurements of benzene, toluene, and o-xylene (referred to as BTX). In addition, whole air canisters and high-volume samples collected on PUF cartridges were used to identify a wide variety of VOCs, polychlorinated biphenyls (PCBs), and pesticides. The canisters were collected every four days and spanned a 24-hour period, while two samplers were used to collect PUF samples continuously on 6-and 12-day cycles.

Data Completeness

In the monitoring and data management plan, the data completeness objectives were 75% completeness for all parameters. Throughout the 12-month monitoring period, efforts were made to minimize gaps in measurements or data loss in order to meet those criteria. Routine preventative maintenance was conducted monthly to ensure all analyzers were in good working order. All data were ingested into our data management system and evaluated manually on a daily basis by a data analyst to ensure their validity. Data were invalidated when instrumental or operational conditions were the reason for suspicious data. Completeness statistics are defined as follows:

- **Possible:** The maximum number of data points that could have theoretically been logged based on the data output frequency for each analyzer.
- **Captured:** The number of data points that were logged in the data management system.
- **% Missing:** The percentage of data points not logged by the data management system.
- **% Invalid:** The percentage of data points flagged as invalid in the data management system. For this project, this equates to the percentage of time there was maintenance being performed on the analyzers.
- **% Suspect:** The percentage of data points flagged as questionable and in need of further review by an analyst.
- **% Valid:** The percentage of data points flagged as valid based on quality control checks.
- **% Complete:** The percentage of data points recorded relative to the number possible.

The percentage of data completeness for each parameter monitored is summarized in Table 1. For each of the pollutants measured, there was high data completeness throughout the monitoring study, with each analyzer collecting over 94% of possible measurements. The majority of data collected were flagged as valid (greater than 87% for each pollutant). Each analyzer had at least 3% of data reported as missing during the 12-month monitoring period, with the analyzer monitoring the eGC species (benzene, toluene, o-xylene) reporting 5.6% of data for each species as missing. This was largely due to site issues following a large storm in October 2022. The storm caused a power outage to all sensors that lasted several days and required the local utility company to repair. In addition, rainwater damaged internal components on the eGC analyzer, which needed several days to procure and install replacement parts.

Meteorological sensors were in working order and provided wind speed and wind direction measurements over 97% of the time. During February 2022, all meteorological sensors were audited against U.S. Environmental Protection Agency (EPA) guidelines by an external group to verify measurements, and all sensors passed the audit within specifications.

Table 1. Summary of data completeness for each pollutant measured along the New River.

Pollutant	# Possible	# Captured	% Missing	% Invalid	% Suspect	% Valid	% Complete
H_2S	105,792	102,313	3.29	5.05	0.17	91.48	94.41
NH_3	105,792	102,620	3.00	6.81	2.80	87.39	94.89
Benzene	52,896	49,922	5.62	2.78	0.00	91.59	94.06
Toluene	52,896	49,933	5.60	2.78	0.00	91.61	94.08
o-Xylene	52,896	49,938	5.59	2.78	0.00	91.62	94.09
Wind Direction	105,792	102,622	3.00	0.02	0.00	96.99	97.00
Wind Speed	105,792	102,622	3.00	0.02	0.00	96.99	97.00

In addition to the continuous monitors, a total of 79 whole air canisters were collected between December and November and were analyzed by the laboratory for over 100 common VOCs. A total of 40 PUF samples were collected on the 6-day schedule, and another 21 were collected on a 12-day cycle. Laboratory analysis has been completed on these samples to quantify more than 40 common pesticides and PCBs. As with the online samples, the data completeness target for all canister and PUF offline samples was 75%. This target was met for all canister samples and all 6-day and 12-day PUF samples.

General Data Trends

Continuous monitoring data were analyzed to reveal typical patterns in each of the compounds measured, including the time of day or day of the week when concentrations are highest. A statistical summary of the continuous 5-minute and 10-minute measurements collected between December 2021 and December 2022 is listed in Table 2, including averages, standard deviation, and minimum and maximum values. The minimum detection limits (MDL) of the continuous analyzers are roughly 0.4 ppb for H_2S and 1 ppb for all other compounds. It should be noted that negative concentration values in ppb are not physically possible but reflect the signal noise of the analyzers; they have therefore been included in the statistical summary.

Table 2. Statistical summary of all H_2S, NH_3, and BTX concentrations reported during the New River monitoring study.

Pollutant	Mean (ppb)	Standard Deviation	Minimum (ppb)	Maximum (ppb)
H_2S	15.6	31.9	-1.2	791
NH_3	24.9	19.9	-2.9	495
Benzene	0.64	0.74	0	19.9
Toluene	1.10	1.35	0	51.9
o-Xylene	0.81	0.61	0	29.5

During the twelve-month monitoring period, average concentrations of benzene and o-xylene were lower than the analyzer can detect, while toluene was just above the MDL. However, NH_3 and H_2S concentrations ranged from barely detectable to several hundred parts per billion.

Wind speed and direction measurements can be used to relate observed gas concentrations to potential sources. Figure 2 (top) shows wind roses displaying the most common wind directions and wind speeds observed at the monitoring site each season using hourly averaged data. The wedges are broken up in 30-degree increments and highlight the direction from which the wind is blowing. During most seasons at this site, winds were most commonly from the west or northwest (combined 50% of the time), meaning the monitoring shelter was appropriately situated downwind of the New River for most of this study. Winds began to come more frequently from the southeast during the summer months (June, July, and August).

Winds ranged from calm (less than 2 mph) to a maximum speed of 32 mph during the study period. Overall, winds over 10 mph were observed less than 20% of the time, and occurred most often during the months of March through May. Calm winds were observed approximately 32% of the time.

Wind measurements were compared to other meteorological sensors in the region during the same time frame, including California Air Resources Board (CARB) monitoring sites in Calexico, El Centro, and the Imperial Airport, as well as the California Irrigation Management Information System’s (CIMIS) Meloland site. Wind speeds were generally well aligned across these other sites. Figure 2 (bottom) illustrates the similarities in wind measurements between the New River monitoring site and the nearest meteorological site in Calexico.

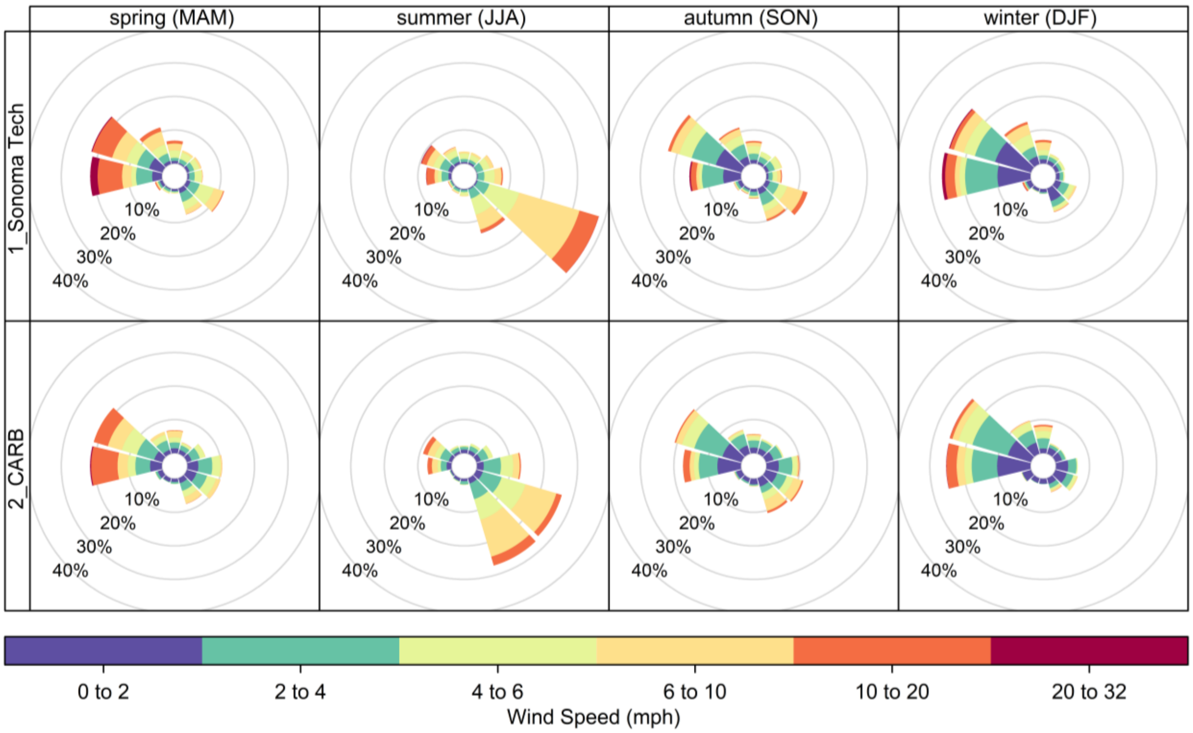

Figure 2. Agreement between wind conditions observed at the New River monitoring site (top) and the CARB regulatory site in Calexico (bottom) during the 12-month monitoring period.

To illustrate the diurnal trends in concentration data, Figure 3 shows the hourly averages of each species plotted as a function of the hour of the day. Each of the plots in Figure 3 includes the 95th confidence interval of the mean, which shows the range of values in which we can be 95% confident contains the true mean of the data set. For most of the pollutants measured, concentrations were highest during the evening or early morning hours, while the lowest concentrations are observed in the afternoon. Similarly, the variability in each of the measurements was highest during the early morning or late evening hours. While a diurnal pattern was observed for each of these gas species, day-to-day trends were less pronounced, other than slightly reduced concentrations of benzene on the weekends (not pictured). H_2S concentrations were similar regardless of the day of the week.

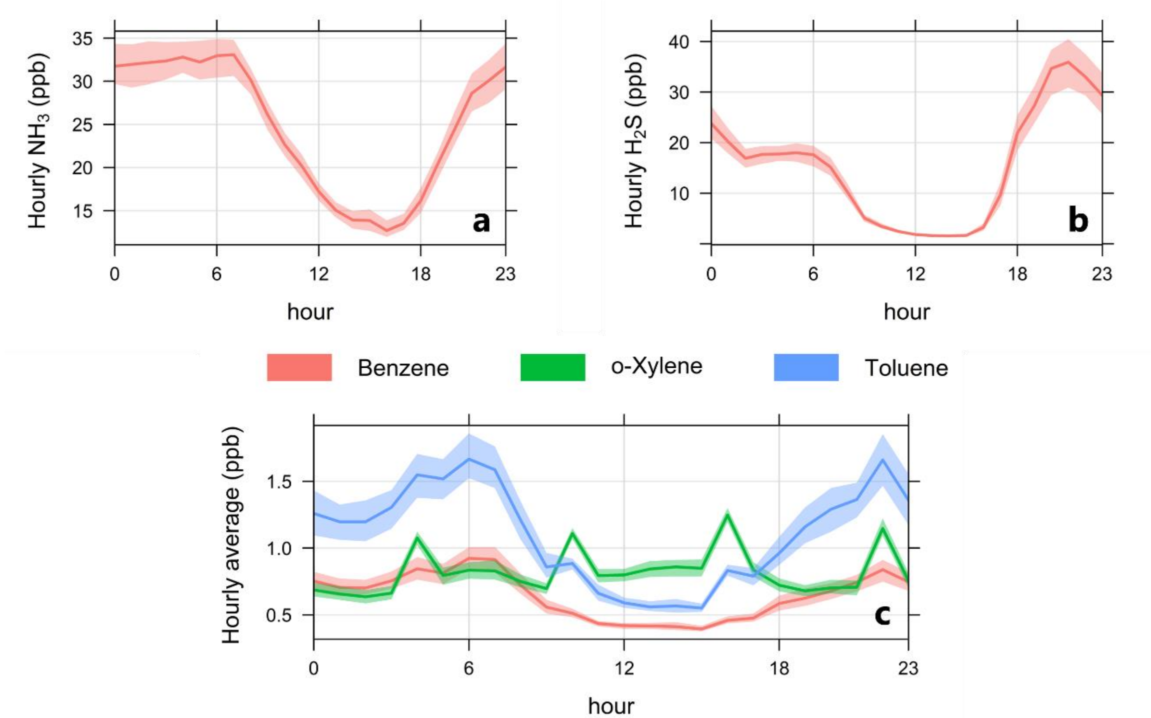

Figure 3. Diurnal trends of NH_3 (a), H_2S (b), and BTX compounds (c) observed during this study period, showing highest concentrations in the morning or evening hours for all species except o-xylene. Data are averaged to hourly concentrations.

Monthly trends are presented in Figure 4. Panel A shows trends for NH_3, which had its highest concentrations in September and October and lowest observed values in late spring and early summer. H_2S (panel B) showed summertime lows and December and January highs. The same trend was observed for benzene and toluene concentrations (panel C). These monthly variations in concentrations were consistent with the seasonal patterns of benzene and toluene, as observed in a previous analysis characterizing air toxics in the U.S.[1] Wintertime highs are often not necessarily due to an increase in emissions, but may in part be due to a lower planetary boundary layer during the winter months, which results in less dilution of pollutant concentrations. Conversely, the heat of the summer months meant higher mixing heights, more dilution and transport, and lowered concentrations. In contrast, o-xylene showed the opposite trend, with summertime highs and lowest concentrations observed in the winter. However, because concentrations of benzene, toluene, and o-xylene each remained below the analyzer's detection limits for much of this study period, the observed trends have high uncertainty and should not be considered definitive.

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[1] McCarthy M.C., Hafner H.R., Chinkin L.R., and Charrier J.G. (2007) Temporal variability of selected air toxics in the United States. *Atmos. Environ.*, doi:10.1016/j.atmosenv.2007.1005.1037.

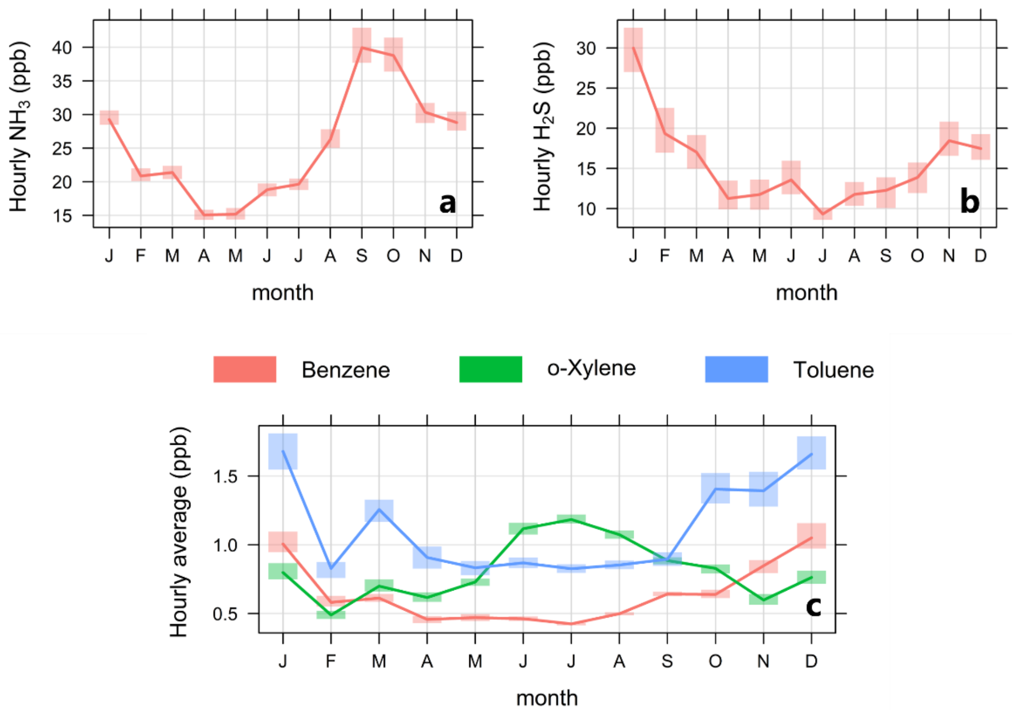

Figure 4. Monthly trends of NH_3 (a), H_2S (b), and BTX compounds (c) observed during this study period, showing highest concentrations in December or January for H_2S, benzene, and toluene. The highest concentrations were observed in July for o-xylene and September for NH_3. Data are averaged to monthly concentrations.

Hourly average concentrations of H_2S were consistently above 30 ppb between the hours of 6 p.m. and 12 a.m. (panel B in Figure 3). This threshold is the acute (1-hr) reference exposure level (REL) according to the California Office of Environmental Health Hazard Assessment (OEHHA). A time series of hourly H_2S concentrations for the entire 12-month period is shown in Figure 5. Data are colored by whether hourly values were above (red) or below (teal) the 1-hour REL. Hourly exceedances of the REL did occur throughout the 1-year monitoring period, although the frequency of REL exceedances was highest in January.

None of the other species exceeded the OEHHA 1-hr REL concentrations even once, as summarized in Table 3. Only benzene concentrations came within 90% of the hourly REL, and this occurred only once during the study.

OEHHA also sets RELs for chronic exposure, which are designed to address continuous exposures. The exposure metric used for chronic RELs is the annual average. For all species except H_2S, the average concentration over the whole year of sampling remained below the chronic REL, as seen in Table 3. While benzene was close to the chronic REL, recorded concentrations of benzene were close to the detection limit of the eGC analyzer and have greater uncertainty. The average H_2S concentration recorded throughout the year was 15.6 ppb, which is above the chronic REL threshold of 7.2 ppb. However, given the proximity of the New River monitoring site to the water treatment plant, a known source of H_2S, it is unclear if this trend is true for the wider region. Additional year-long studies along other sections of the New River could shed more light on the health impact of H_2S exposure in the region.

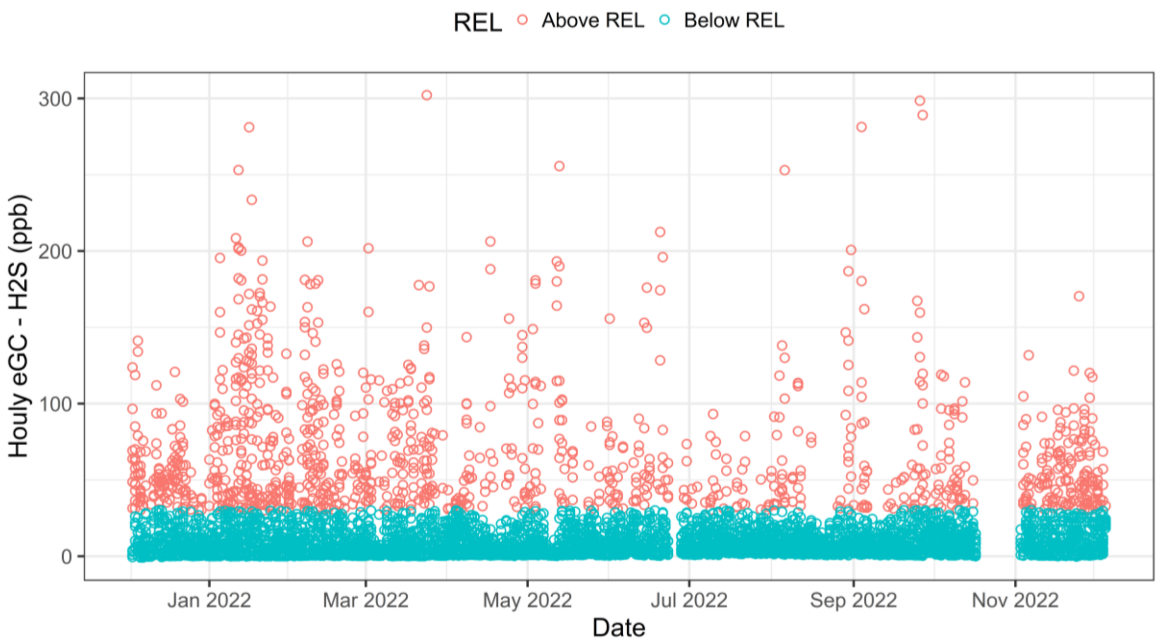

Figure 5. Hourly concentrations of H_2S recorded at the New River monitoring site. Highest concentrations were observed in the winter months (January to March).

Table 3. Hourly concentrations of each pollutant measured at the New River monitoring site and their comparison to the 1-hr (acute) REL and Chronic REL.

Pollutant	Hourly Mean (ppb)	Hourly Max (ppb)	1-hr REL (ppb)	Chronic REL (ppb)
H_2S	15.6	302.1	30	7.2
NH_3	24.9	248.7	4,594	287
Benzene	0.6	7.7	8.5	0.9
Toluene	1.1	13.2	1,327*	79.6
o-Xylene	0.8	7.7	5,066	161

*1-hr REL for Toluene previously reported as 9,818 ppb but was updated by OEHHA to 1,327 ppb.

Source Identification

For each of the species measured, concentrations can also be provided in context of wind conditions to help identify likely sources. **Figures 6 and 7** contain polar plots for each species, which show concentrations of each of the pollutants measured alongside wind directions and wind speeds.

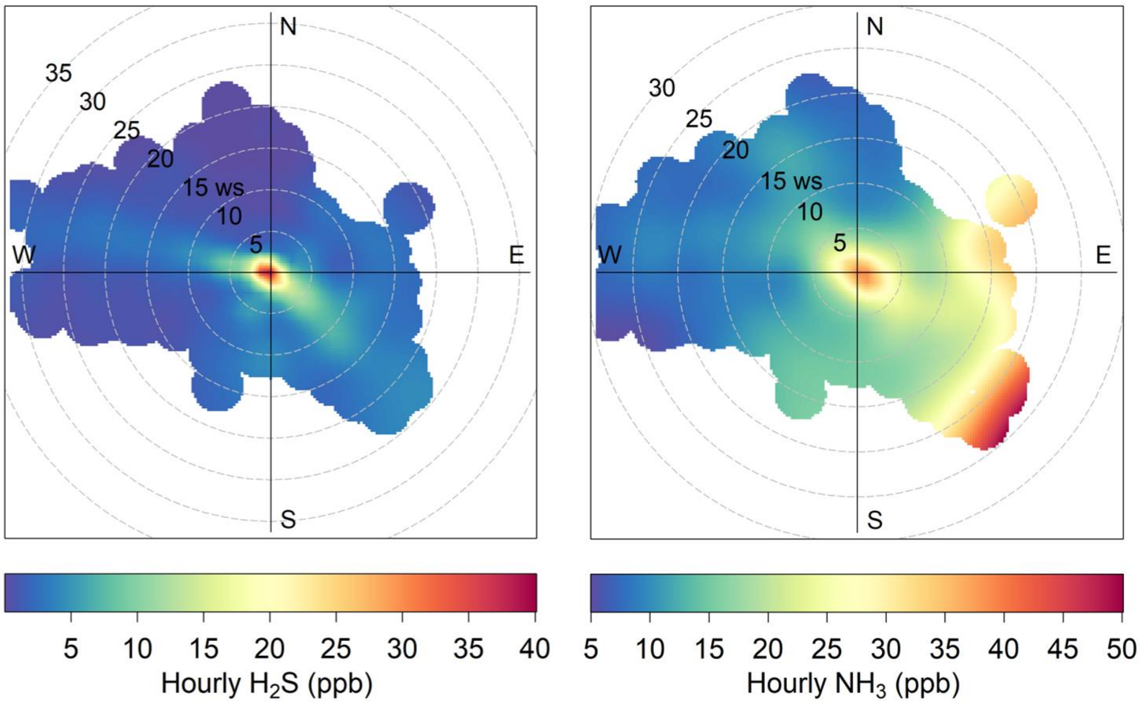

Figure 6. Polar plots showing hourly concentrations of NH_3 (right) and H_2S (left) during various wind conditions.

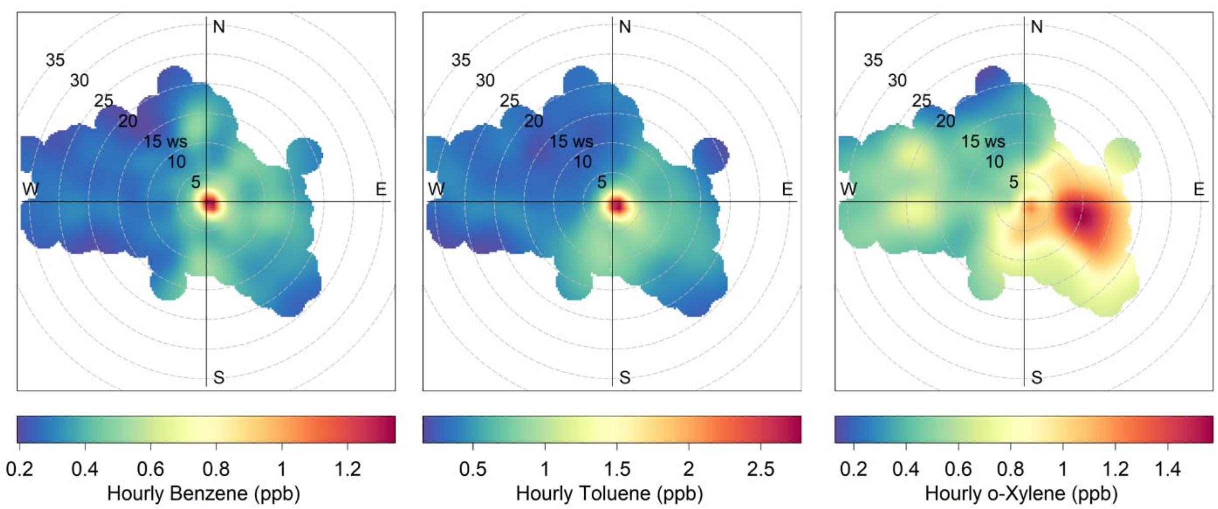

Figure 7. Polar plots for benzene (a), toluene (b), and o-xylene (c), illustrating concentrations observed during all wind conditions.

The left panel in Figure 6 illustrates that higher H_2S concentrations (warm colors) were observed under predominantly low wind speeds, typically less than 5 mph, and corresponded to winds blowing from the southeast and west-northwest. This suggests a local source as opposed to transport of H_2S. While the New River could be one of the sources, particularly under the more westerly wind conditions, it is possible that other local sources may have contributed to the elevated concentrations. Other nearby sources include the city's wastewater treatment plant to the northwest, and the city of Mexicali and entry point of the New River into Calexico to the southeast. The air quality monitors are situated on water treatment plant property (separate from the wastewater facility), about 70 meters (200 feet) from the New River, about 800-1000 meters (2,600 – 3,000 feet) from the wastewater treatment processing equipment, and about 600 meters (2,000 feet) from where the New River enters Calexico at the international border. Unfortunately, a source apportionment of the H_2S concentrations cannot be achieved with the data collected. Further, measured H_2S concentrations followed a similar pattern regardless of the day of the week, which does not indicate just one of the nearby sources as being the more dominant source. The contribution of each source to measured H_2S concentrations cannot be discerned from the data collected during this study.

Many of the highest hourly NH_3 concentrations (over 25 ppb) also occurred at wind speeds below 5 miles per hour, indicating a source near the monitoring site. However, elevated NH_3 concentrations were also recorded when winds were between 5-15 mph. Unlike H_2S, concentrations of NH_3 were also elevated under all wind directions, especially from the southeast and southwest. The hot spot in the southeast quadrant of this figure is due to two highly elevated measurements (greater than 40 ppb) in early August. These observations were made during elevated wind speeds (20-22 mph). The combination of the infrequency of these measurements and the elevated wind speeds suggests an NH_3 source in the southeast direction that is either further away than what typically influences the site, or an infrequent but high-impact emitter. Typical NH_3 sources include livestock waste, fertilizer production, and manufacturing of solvents, all of which can be found in Imperial County and in neighboring Mexicali (southeast of the monitoring site). These patterns indicate that other NH_3 sources in the region are likely being transported to and impacting the monitoring site.

Like the diurnal plots, the polar plots for the BTX compounds in Figure 7 show similar patterns for benzene and toluene: the highest recorded concentrations were under calm wind conditions. Both compounds also reported elevated concentrations during moderate wind speeds (5-10 mph) from the southeast, northeast, and southwest. Hourly average concentrations did not typically increase when the winds were from the direction of the New River. This suggests that typical urban sources of benzene and toluene (vehicle exhaust, industrial solvents, and wood burning) had more of an impact on observed concentrations. This trend was mostly the same for o-xylene, with concentrations surpassing 1 ppb only when winds were from the southeast, representing more urban/industrial sources. Under all other wind conditions, o-xylene remained below 0.8 ppb and were thus not well detected by the eGC analyzer.

Offline Sample Analyses

Laboratory analyses for over 200 different species were conducted on whole air sample canisters and PUF cartridges. The analyses were reviewed to identify the most prevalent VOCs, pesticides, and PCBs impacting local air quality. **Figure 8** shows the frequency of detection of the 200 different chemical species, with most species being observed in less than 3% of samples. Several compounds from the PAHs and VOCs groups were detected in 100% of samples, and are discussed in detail below.

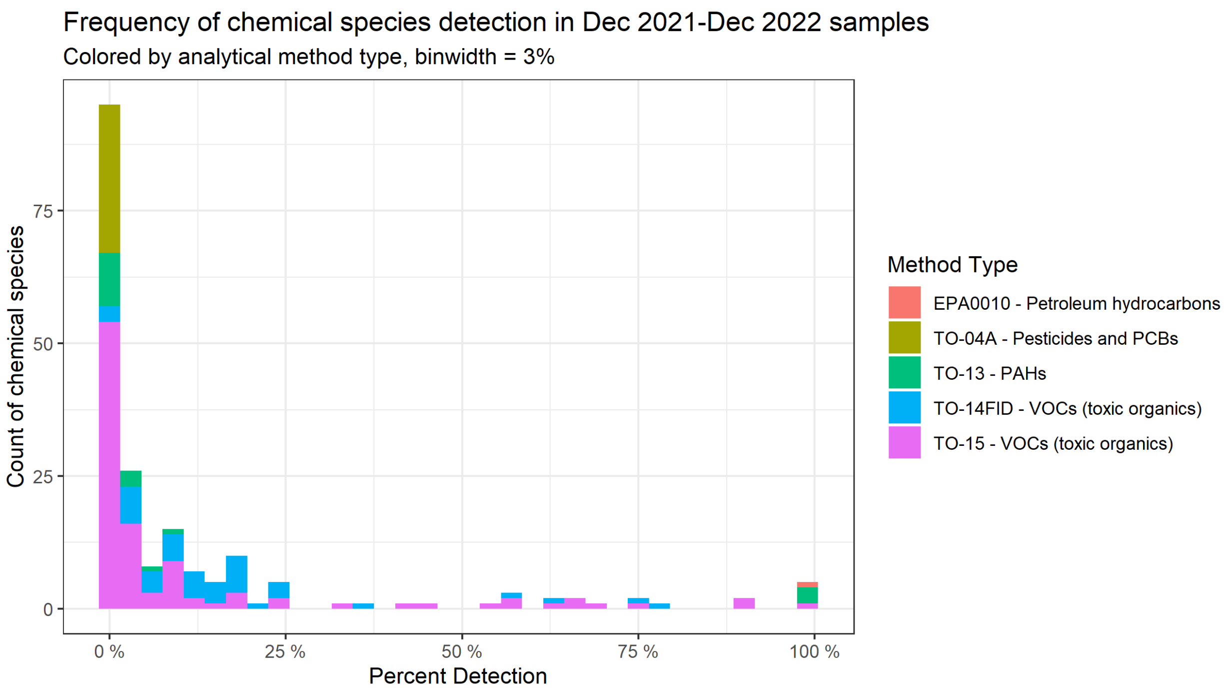

Figure 8. Percent detection histogram for all chemical species across five analytical methods.

PUF samples were analyzed with EPA TO-13 and TO-04A regulatory methods to quantify 46 different compounds, including pesticides, PCBs, and PAHs. Four of the 61 PUF samples collected were not able to be analyzed by the laboratory due to errors with the high-volume sampler. A summary of concentrations of each compound reported in the laboratory analysis is provided in Table 4.

Table 4. List of compounds detected in PUF samples collected at the New River monitoring site, and a statistical summary of the results.

Compound	# Samples Detected	% Detection	Mean (µg/m^3)	SD	Max (µg/m^3)	Min (µg/m^3)
Petroleum Hydrocarbons (C_{10}-C_{34})	1*	100	21.78	--	--	--
	58	100	4.17	3.54	23.3	0.603
1-Methylnaphthalene	60	100	0.26	0.17	0.927	0.025
2-Methylnaphthalene	60	100	0.15	0.1	0.520	0.014
Acenaphthylene	5	8.3	0.01	0.01	0.023	0.006
Fluorene	3	5	0.01	0	0.016	0.008
Anthracene	1	1.7	0.001	--	--	--
Fluoranthene	1	1.7	0.011	--	--	--
Pyrene	1	1.7	0.003	--	--	--

*Analyzed using method EPA0010.

Only three compounds were detected in all PUF samples: 1-methylnaphthalene, 2-methylnaphthalene, and petroleum hydrocarbons (which is a mixture of many chemicals containing 10-34 carbon atoms). Each of the three detected compounds is toxic and can be emitted from combustion of organic matter or fossil fuels; industrial waste; or from application of insect repellents. However, they do not have an associated REL (acute or chronic), so a comparison to those health standards could not be made.

Five additional compounds were detected infrequently in the PUF samples, including acenaphthylene, fluorene, anthracene, fluoranthene, and pyrene. Like 1- and 2-methylnaphthalene, these species are PAHs, a group of compounds emitted from multiple burning sources, including motor vehicle exhaust, wood smoke, fumes from asphalt roads, cigarette smoke, and grilling or charring food. The remaining compounds in the TO-13 and TO-04 lists were flagged as below the detection limit of the analysis method. Although the area is expected to be impacted by agricultural practices in the region, no pesticides were detected in any of the samples throughout the year. It is possible that any pesticides applied may have low volatility or are water soluble, and therefore would not have been able to be detected in the air samples.

Canister samples were analyzed using the EPA TO-14 (FID) and TO-15 regulatory methods to quantify over 100 different VOCs. Species that were detected in greater than 30% of the samples are shown in Table 5, along with a summary of the statistical information. Acetone, toluene, and m,p-xylenes were detected in at least 80% of the canister samples collected. These compounds are frequently used in industrial processes, are found in vehicle emissions, or are a primary component of natural gas or other fuels, so their presence near the urban and industrial setting of Mexicali can be expected.

Table 5. List of VOCs detected in greater than 30% of the whole air samples collected at the New River monitoring site, listed with the average concentration information and chronic reference exposure limits from the California OEHHA.

Compound	% Samples Detected	Mean (ppbV)	SD	Max (ppbV)	Min (ppbV)	Chronic REL (ppbV)
Toluene	98.7	1.56	1.88	9.39	1.56	111
Acetone	90.9	4.61	4.96	32.8	4.61	--
m,p-Xylenes	89.6	0.53	0.41	2.46	0.53	161
Ethane	77.8	7.11	12.4	92.9	7.11	--
Benzene	75.3	0.39	0.76	4.94	0.39	0.9
Propane	75.0	11.5	17.9	107.4	11.52	--
Methanol	68.1	2.39	1.63	7.65	2.39	3052
2-Butanone	66.7	1.52	2.06	8.65	1.52	--

Compound	% Samples Detected	Mean (ppbV)	SD	Max (ppbV)	Min (ppbV)	Chronic REL (ppbV)
Ethanol	64.9	6.53	15.2	80.7	6.53	--
2-Butanone (MEK)	61.7	1.00	1.76	9.73	1.00	--
Hexane	57.4	0.60	0.75	4.20	0.6	1986
Styrene	55.8	0.29	0.17	0.95	0.29	211
n-Pentane	55.6	2.75	3.05	18.6	2.75	--
o-Xylene	53.2	0.31	0.19	1.19	0.31	161
2,2,4-Trimethylpentane	44.7	0.23	0.21	0.94	0.23	--
Ethylbenzene	42.9	0.27	0.19	0.89	0.27	460
n-Butane	37.5	3.57	4.42	20.3	3.57	--
1,2,4-Trimethylbenzene	32.5	0.27	0.30	1.65	0.27	--

The average concentration of each of these species across all samples was compared to the OEHHA chronic REL, which is intended to address continuous exposure and typically uses a one-year averaging time. Compounds like alkanes (ethane, propane, and butane) are not considered air toxics and do not have corresponding RELs. For the rest of the compounds, their chronic RELs are listed in Table 5. None of the detected compounds exceeded the chronic REL throughout the 12 months of monitoring at the New River.

In general, canister and PUF samples are a strong tool for identifying a greater number of species that may be affecting an area, but correlation with meteorological, diurnal, and seasonal patterns is limited by the lower frequency of measurements. Time series for the most prevalent species are presented in Figure 9. Polar plots are presented in Figure 10, which show concentration variations with wind speeds (grey circles) and wind direction using a smoothing function. Due to the multi-day sampling period for these samples, the mean wind speed and the mode wind direction during the sampling period were used. The polar plot analysis suggested a possible trend of higher petroleum hydrocarbons originating from the southeast, and higher acetone concentrations originating from the northeast. Other pollutants showed no specific trend.

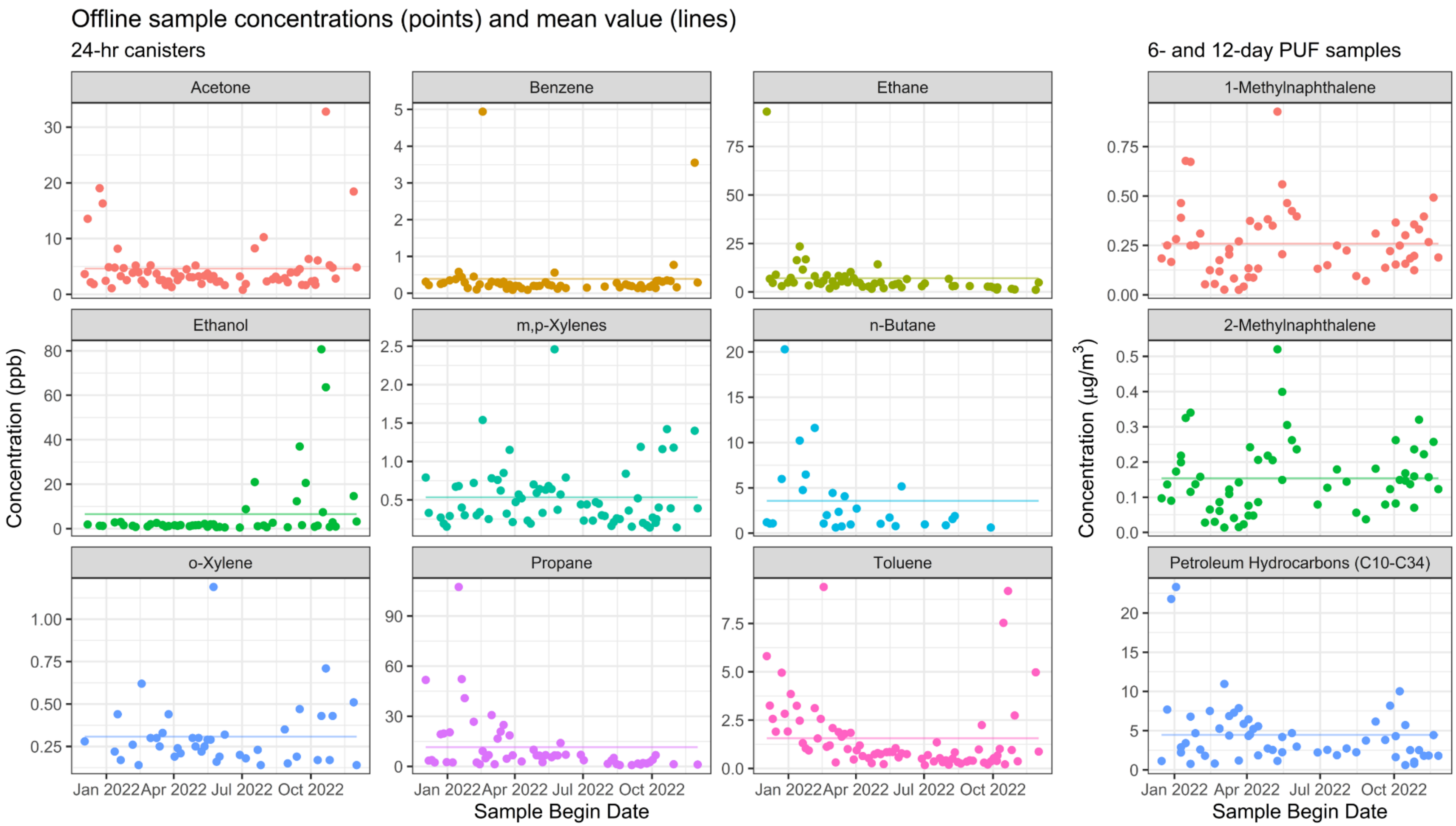

Figure 9. Time series of 24-hr canisters (left) and 6- and 12-day PUF samples (right) for the most commonly detected species.

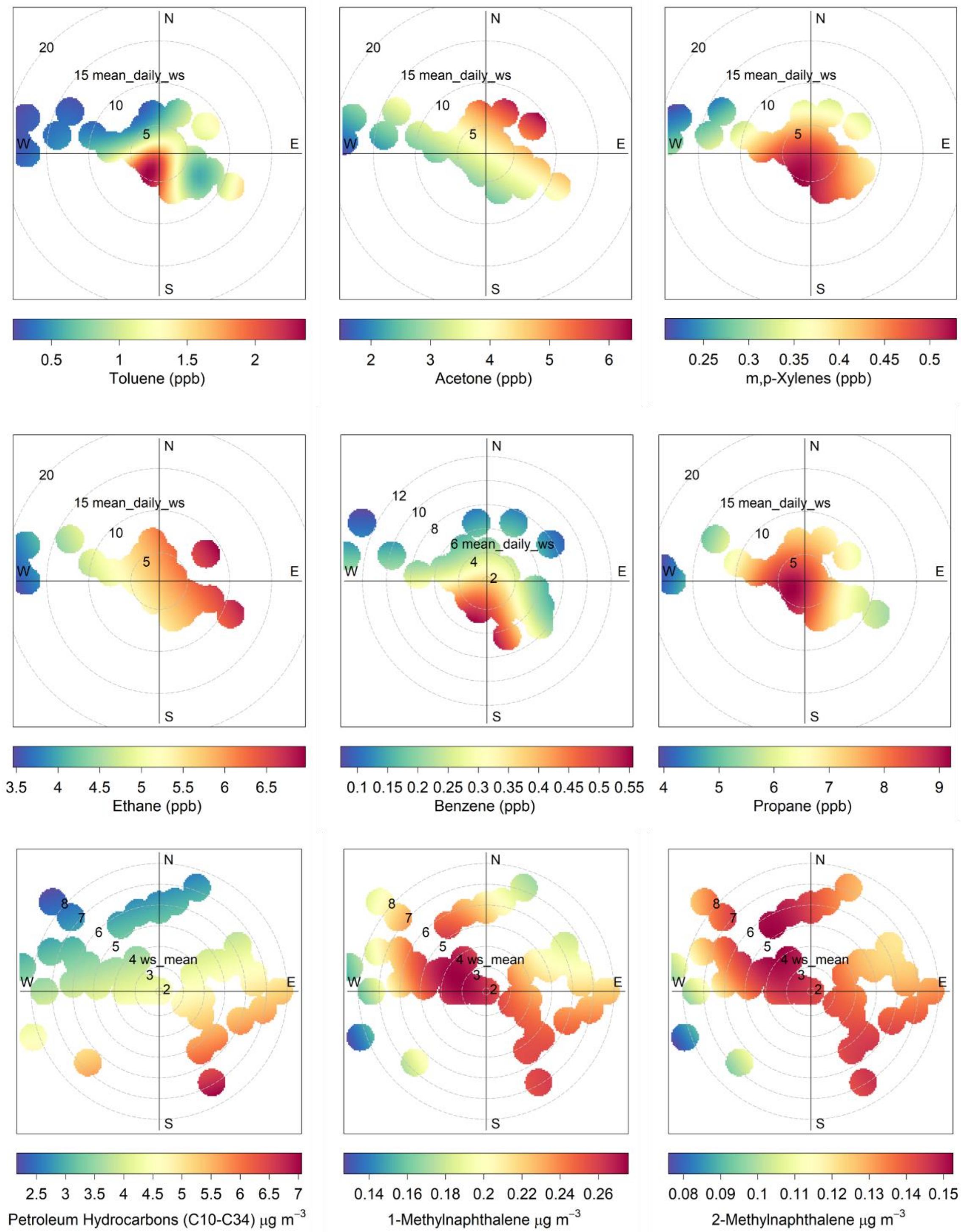

Figure 10. Pollution roses showing the concentrations of the most commonly detected species plotted against mean wind speed (grey circles) and mode wind direction on days when samples were being collected.

Conclusions

Air quality measurements at a monitoring site along the New River in Calexico were conducted between December 2021 and December 2022. During the twelve months, all continuous measurements of gaseous compounds and meteorological parameters were collected with high data completeness. Winds were recorded as being most often from the west or northwest during most of the year, except for the summer months, when winds became more southeasterly. This confirmed that the air monitoring shelter was well situated downwind of the New River.

Hourly concentrations of each of the continuously monitored pollutants were often highest during the evening and morning hours and showed a steady decline throughout the daytime hours. Seasonally, maximum concentrations were observed in September and October for NH_3, in July for o-Xylene, and in December and January for H_2S, benzene, and toluene. H_2S concentrations frequently exceeded the 1-hour acute REL threshold reported by the California OEHHA, most commonly in January.

A total of 79 whole air canisters were collected every four days for quantification of a long list of VOCs. About 15 different VOCs were detected in at least half of the samples, including compounds typically associated with industrial activities and fuels. An average of these compounds over the entire 12-month sampling period revealed that they were not being observed at levels above the chronic REL health thresholds. An analysis into wind conditions when canisters were filled revealed no strong correlations between reported concentrations and wind direction, meaning no individual likely sources could be identified. Similarly, 61 PUF samples were able to be analyzed for over 40 different pesticides and PCBs. Only three compounds of interest were detected and were present in every sample; however, these three compounds do not have a corresponding chronic REL for a health comparison.

Overall, identification of the primary source of these concentrations is complicated by the many local sources. High pollutant concentrations are not necessarily observed when winds are blowing from the direction of the New River. There is significant pollutant signal from the urban and industrial center of Mexicali, as well as the local agricultural sector. Furthermore, H_2S concentrations appear to have also been impacted by the wastewater treatment plant near the New River and monitoring shelter.