

Article

Passive Hydrocarbon Sampling in a Shale Oil and Gas Production Area Shows Spatially Heterogeneous Air Toxics Exposure Based on Type and Proximity to Emission Sources

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Abstract: Shale oil and gas production areas are especially active in Texas. The Eagle Ford Shale in south central Texas contributes substantially to US oil and gas production; it has repeatedly been the focus of air quality studies due to its associated emissions. Among these emissions are hazardous air pollutants such as benzene, a known carcinogen. To monitor exposure to such compounds, we teamed up with local citizens in 2019 to begin a passive sampling study for hydrocarbons. The study tracked selected non-methane hydrocarbons at six locations throughout a busy central production area of the shale. A state air quality monitoring station allowed for a comparison exercise, and we report both the results of that exercise and the observations from various properties affected by the surrounding oil and gas exploration activities. The passive samplers accurately reflected mean to median ambient hydrocarbon levels despite high variability and skewness in the hourly measurements. Field sites either right next to oil and gas production pads, surrounded by more surface pads than other sites, or affected by an additional emission source showed higher exposure to selected hydrocarbons. Passive sampling shows promise to bridge the gap between centralized air monitoring and campaign-style mobile monitoring to evaluate hydrocarbon emissions and abundances. It is a cost-effective way to provide both spatial and temporal information on exposure levels.

Keywords: passive sampling; non-methane hydrocarbons; oil and gas production; shale; air toxics exposure



Citation: Schade, G.W.; Heienickle, E.N. Passive Hydrocarbon Sampling in a Shale Oil and Gas Production Area Shows Spatially Heterogeneous Air Toxics Exposure Based on Type and Proximity to Emission Sources. *Atmosphere* **2023**, *14*, 744. <https://doi.org/10.3390/atmos14040744>

Academic Editors: Chinmoy Sarkar and Roger Seco

Received: 1 March 2023

Revised: 4 April 2023

Accepted: 12 April 2023

Published: 19 April 2023



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1. Introduction

The renewed domestic oil and gas production boom in the United States has caused a substantial increase in hydrocarbon emissions to the atmosphere [1]. Known as unconventional oil and gas (UOG) production, the associated “fracking” wells, typically several horizontals per vertical borehole, produce hydrocarbons for several years following an exponential decay from an initial maximum rate [2,3]. This requires continuous drilling operations accessing different sections of the shale rock to maintain overall field production rates [4,5], leading to many hundreds of sites in shale production areas [6–8] that require gas and liquids handling hardware and infrastructure, including gas flares, which act as sources of the hydrocarbons emitted into the atmosphere [1,9–14]. Methane and non-methane hydrocarbons (NMHCs) can escape into the atmosphere via leaks in gas handling infrastructure (fugitive emissions) or through accidental or purposeful venting (e.g., a pressure relief valve) [14–18]. They also partially dissolve in liquid hydrocarbons containing five or more carbon atoms and then outgas from the liquids routed to and stored in local tank batteries. Tanks holding condensate or raw oil products are significant sources of NMHCs based on high vapor pressures and direct vapor displacement upon tank filling (flushing), liquid transfers offsite, or evaporation and fugitive emission during storage [12,17,19].

Once in the lower atmosphere, NMHCs can contribute to near-surface ozone formation upon their oxidation and based on their reactivity with the OH radical as well

as the regional NO_x abundance [15,20–23]. Although most emissions from oil and gas production activities consist of saturated NMHCs, such as alkanes, which have relatively low atmospheric reactivity, high abundances can compensate in environments where more reactive hydrocarbons such as isoprene have low emission rates [24]. This also includes the simplest aromatic hydrocarbon, benzene, which has an average tropospheric lifetime of 7–10 days [25]. Such NMHCs with a comparatively long lifetime can therefore accumulate in the regional atmospheric boundary layer, causing higher exposures for the local population and environment. This has caused additional concerns based on the toxicity of selected NMHCs, particularly from the group of aromatic hydrocarbons called BTEX (benzene, toluene, ethylbenzene, and xylenes) [26–38].

As the most toxic among the BTEX compounds, benzene has been recognized as a major toxic air pollutant for several decades [39]. EPA lists a non-cancer toxicity threshold of approximately 9 ppb (reference concentration for chronic inhalation exposure, RfC [39]), the lowest among atmospheric NMHCs. Benzene is also a cancer-causing agent; however, there is no widely agreed upon threshold or reference concentration corresponding to, e.g., a 1:10⁵ likelihood of contracting cancer upon life-long exposure [40]. While the World Health Organization (WHO) set a lower guideline of approximately 0.5 ppb benzene [41], several US states have set thresholds triggering state agency action (such as more detailed monitoring) if exceeded, varying from values as low as 0.2 ppb (24-h average) in Maine to as high as 1.4 ppb (annual average) in the State of Texas.

Ambient air benzene abundances dropped significantly in response to the introduction of reformulated gasoline, improving combustion efficiency, and the catalytic conversion of vehicle exhaust, addressing its former main emission source: on-road car traffic [42–47]. However, direct evaporative benzene emissions from the oil and gas industry, such as at refineries, remain a significant source [46,48]. This source was previously very small in rural areas but has now become the dominant source in UOG production areas, exposing rural populations to significant amounts of a subset of toxic NMHCs, including benzene [49].

Areas in Texas where such exposures have developed with the “shale boom” include the Eagle Ford Shale in south central Texas and the Permian Basin in northwest Texas. However, few air quality monitoring stations exist across these large rural regions. While a single, even central station can characterize local exposure over time, mobile monitoring can characterize spatial exposures over short periods. In both cases, though, significant investments must be made into the measurement platforms and their maintenance. A cost-effective alternative increasingly employed instead is passive sampling [50]. Monitoring for NMHCs, particularly BTEX compounds, using passive samplers has been employed for at least two decades [51,52]. It was recently made mandatory for fenceline monitoring at oil refineries by the US EPA, known as Method 325 [48,53–55]. The EPA methodology, as well as recently described methodologies derived from it [56–59], have relatively low NMHC uptake rates based on the geometry of collection. In contrast, cartridges using the Radiello[®] system have more than ten times higher uptake rates. The Radiello[®] system has been described and used by numerous authors [51,60–73] but is not widely used in the US. Our group began using Radiello[®] metal mesh cartridges with Carbograph 4 filling, deployed inside yellow diffusion tubes, in 2018 [74]. Here, we report results from a long-term study in the central production area of the Eagle Ford Shale, around Karnes and neighboring counties. Our objectives were (i) to evaluate the passive sampling methodology against data recorded at an hourly frequency by a Texas state-operated local air monitoring station, and (ii) to determine whether these central, but localized monitoring data are representative of NMHC exposures across a larger region, especially when compared with data from locations closer to known emissions sources. We review the analytical methods in Section 2, present validation data from the local state air monitoring station in Karnes City in Section 3, describe the field observations in Section 4, discuss our findings in Section 5, and offer some conclusions in Section 6.

2. Methods

The air sampling methods and sample analysis were described in more detail in Sablan et al. [74]. We used Radiello® cartridge passive air sampling (RAD145, 350 mg carbograph 4 filling, purchased from Restek Inc., Bellefonte, PA, USA) to determine ambient hydrocarbon concentrations via a diffusion and adsorption process. The samplers were exposed to ambient air inside yellow diffusive bodies (RAD1202, also purchased from Restek), suspended underneath a protective plastic dome to keep out rainwater, and installed approximately 1–1.5 m above ground using commercial shepherd hooks. During transport to and from a deployment site, or during necessary storage times, the sampling cartridges were kept inside glass tubes sealed with tight polyethylene caps (RAD1991, 2.8 mL volume) [67]. Although this methodology has been evaluated for selected hydrocarbons [55,61–63,67], only the similar EPA Method 325 has previously been used in shale oil production areas [75]. Hence, we decided to carry out a comparison with the State of Texas’ validated, hourly hydrocarbon measurements to verify our data’s compatibility with legally accepted observations in Texas.

As our field study was in a rural area distant from the laboratory and intended to be long-term, we established a volunteer community to deploy the samplers with the assistance of a local nun traveling the area frequently for social work. Sampler deployment, turnaround, and analysis were structured as shown in Figure 1. Each location’s property owner (“host”) accommodating a sampling setup was provided with three sets of samplers, one deployed, one currently in analysis or circulation, and one to install at the next desired switchover time. A protocol sheet was completed at switchover time recording site location, cartridge sampler codes, and installment and de-installment times. As in our pilot study [74], two replicates were deployed at each monitoring site, and one blank (unopened glass container with cartridge) was kept at each site. The volunteers, typically the local landowners themselves, were trained to exchange the cartridges approximately once weekly, replace them with the spare set, and fill out the protocol sheet. The exposed sets were collected during a 24 h period and express-shipped to our laboratory at Texas A&M University in College Station (Figure 1). Analyses were typically completed within another 24–48 h, after which all desorbed cartridges were additionally cleaned (heating for 20 min at 240 °C under high-purity H₂ flow) and return-shipped for redistribution to the landowners (Figure 1).

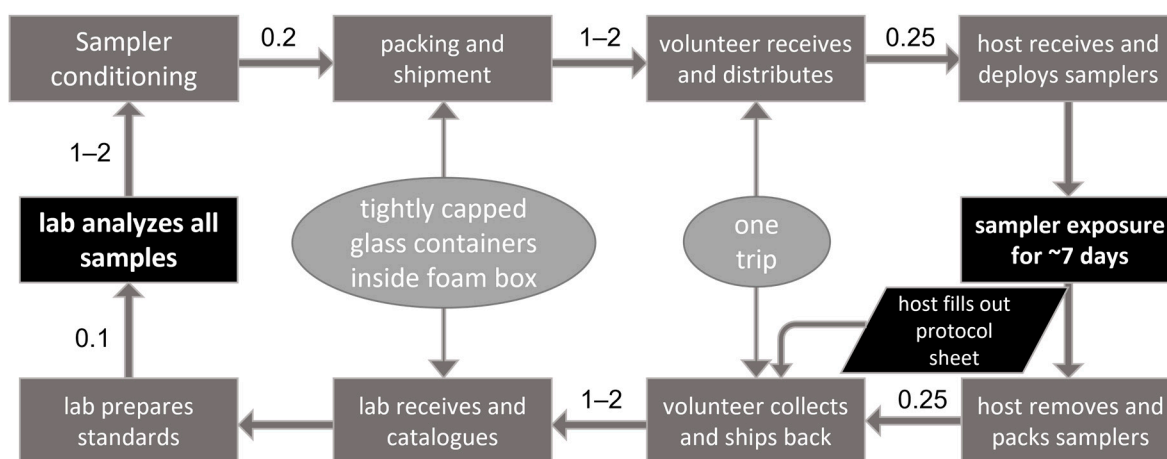


Figure 1. Flowchart of Radiello® hydrocarbon passive sampler turnaround. Individual process steps are outlined inside grey rectangles, critical steps inside black rectangles. Oval connectors provide background information on two intermediate steps each. A data input step provided in the field is outlined by a black rhombus. Numbers alongside the progress arrows provide the approximate times in days between the process steps.

2.1. Study Sites

Field sites within the Eagle Ford were selected after a meeting and discussion with locally interested citizens from in and around Nordheim, TX, a small community located immediately north of a recently established oil waste landfill facility operated by Petro Waste Environmental LP (hereinafter called the “Hohn Rd. facility”). Citizens were interested in evaluating potential air quality impacts from the surrounding oil and gas exploration and the related new oil waste dump. Two sites were initially selected (summer 2019), one in Nordheim and one next to a large oil production pad site with a near-constant flare. Three additional sites were added later, and the Nordheim site was moved closer to the waste dump after approximately half a year of monitoring. All sites are shown on a map of the area in Figure 2 alongside the density of active oil and gas production sites. The site Panna (P), along TX-123, was located 300–400 m west (W) of a larger oil and gas production site with a gas flare. Fifteen additional, active pad-sites were found within 2 km of the residence. An “odor log” was kept by the landowner volunteer at this site, describing visual and olfactometric observations from the volunteer’s residence weekly. The site Karnes East (KE) was surrounded by four oil and gas production pad sites to its immediate northeast (NE), southeast (SE), and southwest (SW), all within 500 m distance; 17 more pad sites within a 2 km distance, mostly to its NW and SW; and a large midstream facility 1 km to its SW. The site Osterloh (O) had fewer active pad sites surrounding it, with only one to its ENE within 500 m, and an additional 12 within 2 km in all directions. The initial town of Nordheim site (Nh) had two pad sites within 500 m located to its E, but an additional 11 within a 2 km distance (mostly within its NW sector), plus the Hohn Rd. facility 1.5 km to its SE. The 2nd Nordheim site was directly north (<400 m) of the Hohn Rd. facility, 1.5 km east of the town center, but had only four oil and gas production pad sites within a 2 km distance. Lastly, the Texas Commission on Environmental Quality (TCEQ) Karnes City air monitor (site KC) is located at the SE end of the small city. It has one active pad site within 500 m, but an additional ten pad sites within a 2 km distance, mostly in its southern and eastern sectors. There is also a midstream facility located 2.2 km to its SW. The Karnes City center is located 1.5 km to its WNW. Our sampling was carried out approximately 50 m to the SW of the monitor.

We note that this rural area overall has a low car traffic density, a factor commonly important as a major source of NMHC emissions. However, as we have shown previously [50], NMHC data from the Karnes City air monitor were not dominantly influenced by car traffic in the area even when it was located in the center of town. Rather, NMHC emission sources from the industrial oil and gas exploration in the region dominate ambient abundances.

2.2. Sample Analysis

All Radiello cartridges were analyzed for selected NMHCs using thermal desorption (Perkin-Elmer ATD400 autosampler) followed by gas chromatography with flame ionization detection (TD-GC-FID) [74]. Quantification was achieved by producing 3-point calibration curves via the dilution of a standard mixture containing ppm-level toluene and n-hexane produced in 2014. The standard was recently re-evaluated against a new gas standard containing the same hydrocarbons and found not to deviate. All field samples and standards were desorbed at 220 °C for 15 min under high-purity hydrogen flow from a generator (Matheson TriGas, Montgomeryville, PA, USA); pre-concentrated onto a cooled microtrap (−5 °C) filled with Carbotrap X inside the ATD400; then rapidly thermally desorbed on-column. The previously used 60 m, 0.25 mm ID Rtx-624 separation column was replaced with a wide-bore, 60 m non-polar Rtx-1 column in fall 2019, the same column used by TCEQ for NMHC measurements at its air quality monitors.

High-purity hydrogen was used as a carrier and FID fuel gas. Analytical precision at the ppb level was 2% or better (from replicates of standards), while accuracy was 5% or better based on the standard’s accuracy as provided by the manufacturer. Quality control using blanks and field replicates revealed (i) background levels were present for several hydrocarbons analyzed, but typically did not exceed 5% or less of the ambient levels except

for the xylenes; and (ii) median replicate differences were typically within 10–20% of each other depending on the compound, but occasionally exceeded 50–100%, especially for small-abundance compounds such as n-octane or the xylenes. Cartridges were flagged when replicate differences exceeded 50% and replaced when the large difference persisted (three cartridges over one year). Data are reported as averages between the two replicates, as a single value if one replicate was lost, or as NA if both replicates were lost or it was unclear which replicate represented the outlier in a comparison with differences exceeding 100%.

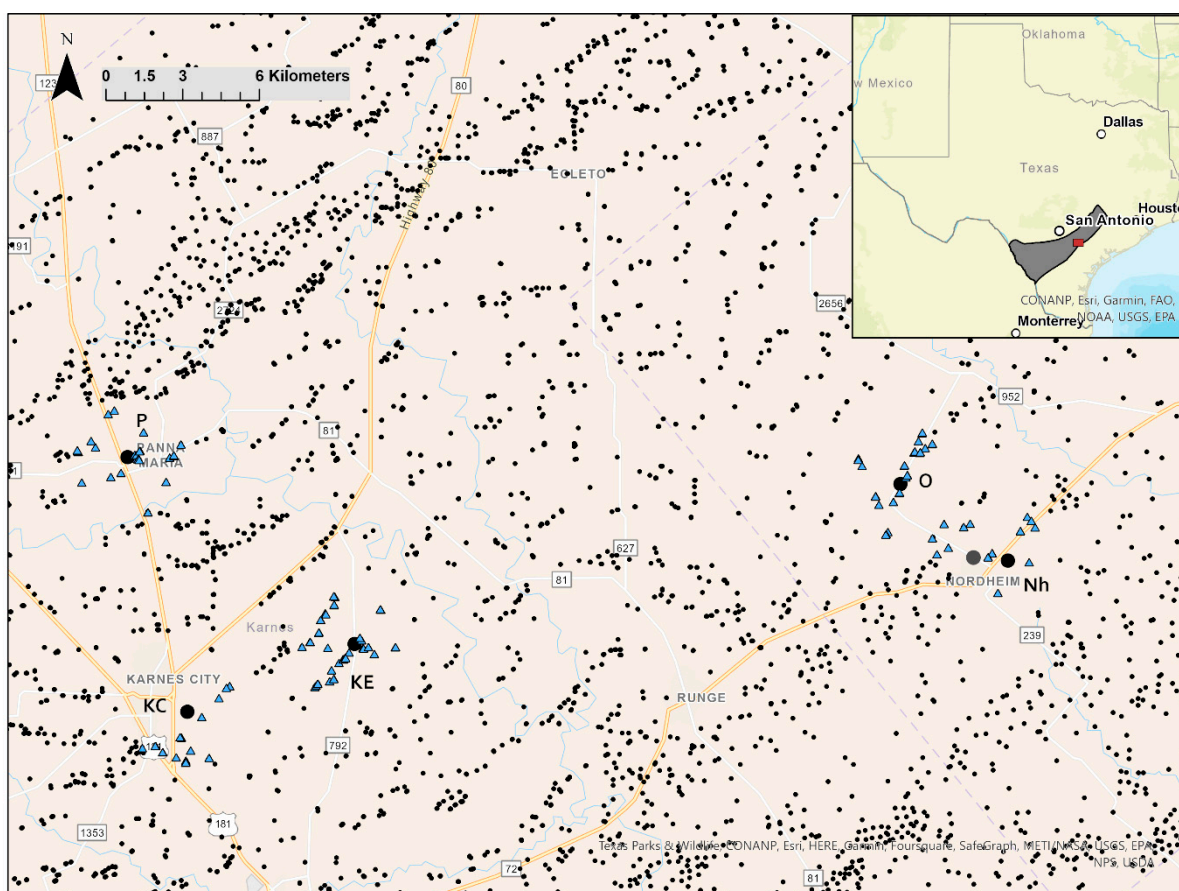


Figure 2. Map of the investigation area in the Eagle Ford shale. Deployment sites (east to west: Nordheim—Nh, Osterloh—O, Karnes East—KE, Karnes City—KC, Panna Maria—P) are depicted as larger black dots; actively producing wells as small black dots; and wells linked to surface pads within 2 km of each sampling site as blue triangles. The old Nordheim site is depicted as a grey dot. The inset shows a map of Texas with an outline of the Eagle Ford Shale area (in grey) and the study region highlighted by a red rectangle southeast of San Antonio. Figure created in ArcGIS using “World Navigation Map” with inputs from Esri, HERE, Garmin, FAO, NOAA, USGS, © OpenStreetMap contributors, and the GIS User Community. Well data used in the map are freely available from the Railroad Commission of Texas (RRC) at <https://www.rrc.texas.gov> (accessed on 11 April 2023).

Independent of precision, the accuracy of Radiello[®] passive sampling measurements against higher-time-resolution data in the field has only been evaluated once in detail [68]. Based on our own laboratory and field testing, we previously estimated that the accuracy of passively sampled hydrocarbon concentrations using Radiello[®] samplers is in the order of 25% or better. By comparing our field data to nearby, validated hourly measurements we could make a better classification and estimate of the field-based accuracy for those NMHCs quantified using either methodology, and we report on this comparison in Section 3 for several relevant compounds, including benzene and toluene.

2.3. Auxiliary Data

Meteorological and air quality data were collected from the air quality monitoring station in Karnes City (CAMS 1070, EPA Site Number 482551070), operated by TCEQ. New observations were recorded by the station hourly, for both meteorology and air quality data. Data were downloaded in 2022 from TCEQ's online database at https://www.tceq.texas.gov/cgi-bin/compliance/monops/yearly_summary.pl?cams=1070, (last accessed 11 April 2023) and R software was used to analyze and calculate statistics for all data (R: A language and environment for statistical computing; R Foundation for Statistical Computing, Vienna, Austria, <https://www.R-project.org/>, last accessed 11 April 2023).

The meteorology in this part of Texas is strongly seasonal and regular. Winds are modest and blow steadily from the S to SE during summer (June to October). Spring and fall seasons (March to May, November) display slightly stronger winds and wind direction variability, while gustier winds generally shift between southerly and northerly directions during the cool season (December to February) as regular cold fronts pass into Texas. A wind rose for the 2-year 2019–2020 period is provided in Figure 3.

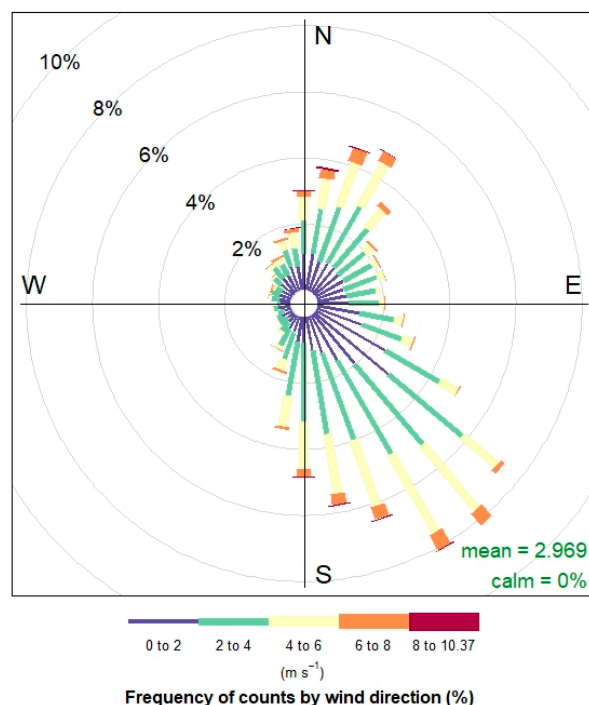


Figure 3. Wind rose based on meteorological measurements at the TCEQ Karnes City air quality monitor from combined 2019–2020 data.

3. NMHC Validation Measurements

Passive sample collection commenced near the Karnes City air quality monitoring station for several months supported by two different volunteers living in the area. Sampling at this site was identical to sampling at all other sites. Validated NMHC data from the monitor were downloaded in 2022, and all hourly measurements between the passive sampler deployment and removal dates and times were assigned to the passive sampling periods. This included numerous hourly measurements for which no ambient air data were available due to quality control checks, overwhelmingly occurring at night. As night-time NMHC abundances are often higher than daytime ones, leading to a stronger weighing of daytime data when calculating statistics, we used linear extrapolation to fill in all missing values. Furthermore, we replaced all hourly zero values with one half the respective detection limit, given by TCEQ as 0.4 ppbC [24]. Figure 4a,b show a linear regression between the calculated monitor averages and passive sampling data for benzene and toluene. To reflect the substantial NMHC variability and positive skewness during all

analyzed periods, interquartile ranges (IQRs) were included in the plot. Despite this large variability, the passive samplers reflected NMHC averages to within 20–30% in both cases. The same was true for most other NMHCs investigated. Most NMHCs discussed here and listed in Table 1 showed regression slopes deviating less than 30% and not statistically different from unity, and with no intercept biases (intercepts not statistically different from zero). In the case of the two minor-abundance NMHCs n-heptane and xylenes, a better comparison, i.e., a slope closer to one, was obtained when using the medians of the monitor data. For these compounds, the average bias (MNB, Table 1) was still moderate. In all cases, regression checks (such as leave-one-out statistics) revealed no major issues with the raw data, including no consistent trend related to the sampling period duration. Nevertheless, most compounds showed a small but consistent low bias compared to the monitor data, while benzene showed the opposite, and this needs to be evaluated further in future work with Radiello[®] samplers in comparisons to other independent measurements.

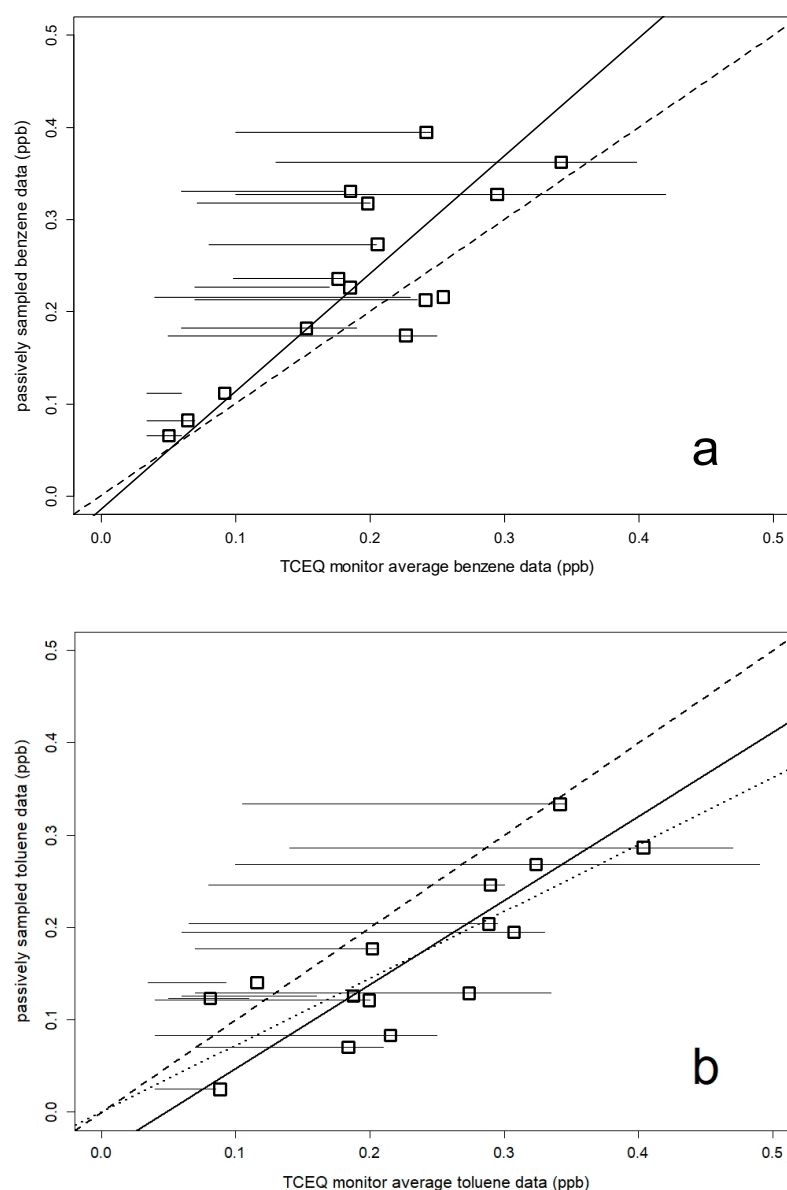


Figure 4. Regression plots of passively sampled benzene (a) and toluene (b) against average air quality monitoring data. Dashed lines represent the ideal 1:1 relation, and solid lines the major axis regression result. Horizontal bars represent the hourly air monitoring data interquartile ranges; the dotted line in (b) is the result of an OLS regression forced through the origin.

Table 1. Regression statistics for selected NMHCs comparing averaged hourly state monitor measurements to passively sampled data for 5–17-day deployment periods. OLS = ordinary least squares, RMA = ranged major axis, MNB = mean normalized bias [76].

NMHC Compound	r^2	OLS Intercept	OLS Slope	RMA Intercept	RMA Slope	MNB
n-hexane	0.832	0.129	0.742	0.061	0.801	−12.8%
benzene	0.630	0.042	0.989	−0.014	1.279	23.7%
toluene	0.665	−0.005	0.743	−0.042	0.900	−26.1%
methylcyclohexane	0.823	0.001	0.783	−0.014	0.845	−22.2%
cyclohexane	0.494	0.044	0.842	−0.029	1.141	4.3%
n-heptane	0.703	−0.009	0.463	−0.036	0.552	−57.1%
mp-xylene	0.022	0.034	0.109	−0.068	1.233	−42.9%

4. Ambient Exposure Observations

4.1. General Features

We depict the observed ambient levels of two different NMHCs in Figures 5 and 6. Each measurement period is shown as a colored horizontal bar spanning the deployment period at the different locations investigated. The main period of missing data fell into the spring 2020 onset of the global COVID-19 pandemic, during which sampling was paused for approximately two months in response to stay-at-home orders in Texas. Other missing periods were typically caused by sample loss during processing due to large water loads on the cartridges or damage to cartridges in the field. The longest overall record existed for the Nordheim (Nh) site, albeit accompanied by a move within the town closer to the local Hohn Rd. waste facility, as indicated. We observed both seasonal and weekly variations among and between sites. Seasonally, higher concentrations were generally observed during the cooler months (Dec, Jan) than in the other seasons. This is typically caused by seasonal average planetary boundary layer (PBL) depth dynamics [24], with deeper PBLs in the hot Texas summers and shallower PBLs during the cooler months. Week-to-week differences tended to be small at some sites (KC, O) and larger at others (e.g., P). Abundances varied between sites and showed at times large variability at individual sites (P, KE). The latter is discussed below. Since all measured NMHCs were generally well-correlated, we focus our discussion on n-hexane to represent n-alkanes, methylcyclohexane to represent naphthenes (cycloalkanes), and benzene or toluene to represent aromatic compounds.

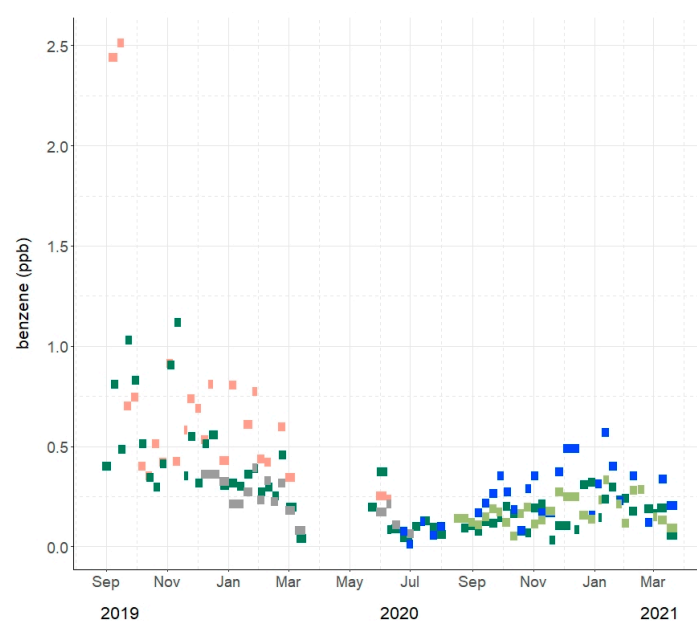


Figure 5. Benzene time series for all sites. Each segment's width represents the period of deployment.

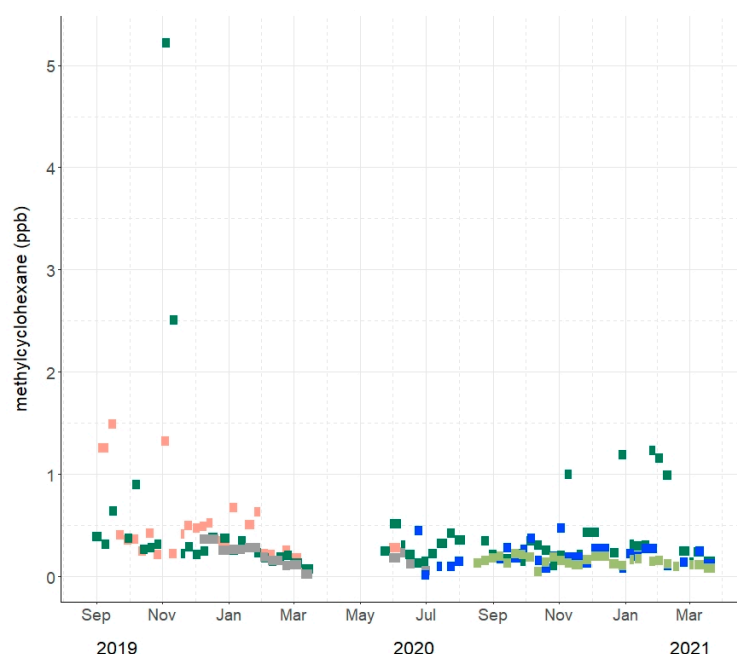


Figure 6. Methylcyclohexane time series for all sites, similar to Figure 5.

The highest concentrations of benzene were recorded early during the study (P site, fall 2019) and later at the KE field site. The P site's pre-pandemic benzene levels were not statistically significantly different from those of the Nh site ($p = 0.11$), due to higher than usual early variability at the Nh site, as discussed below. During the cool period from December to early March, the P site's benzene data, however, were statistically higher compared to both the Nh and especially the nearby KC site ($p = 0.011$, $p < 0.001$, respectively). Similar statistical differences were observed in the subsequent cool season from November 2020 to March 2021 between the higher levels at the KE site compared to the O site ($p = 0.019$) and the Nh site ($p = 0.014$). These distinct differences held for several other NMHCs measured, with the largest differences observed for the n-alkanes.

Data from the KC site were comparable in range to the other sites but showed less variability overall and smaller week-to-week differences during the period of operation.

4.2. Concentration Anomalies

Three periods with significant deviations occurred at two different field sites. First, high NMHC levels were recorded at the P site at the beginning of the project, September 2019 (Figures 5 and 6). Second, two weeks of high alkane and naphthene levels were recorded in November 2019 at the Nh site (Figure 5). Third, several individual weeks of elevated NMHC levels were encountered at the new Nh site mostly in late 2020 and early 2021 (Figure 6).

The first such anomalies, at the P site, were accompanied by odor complaints and an associated odor log kept by the landowner. During the two weeks of high benzene values at that location (P, Figure 5, 10–24 September), the owner repeatedly noted the same “petroleum smells” and a “very large flare” or “extremely/very high [flare] flames” at the adjacent pad site 300 m to his east. To relate the subjective odor log entries with our observations, we converted each daily odor log entry into a number from zero to four by qualifying smells as equal to four (“sickening”), three (“strong”), two (“medium”), one (“mild”), or zero (“no smell”). Each day's numbers during passive sampler deployments were then added together. In addition, observations of an at least “large” flare flame were given an additional score of one. The scatter plot between our subjective odor totals and measured n-hexane levels is shown in Figure 7. Despite our simple odor conversion, there was a statistically significant correlation between those measures. Similar correlations

held for other NMHCs. A similarly strong correlation ($r^2 = 0.31$, $p = 0.026$) at the P site existed between the odor estimate and the fraction of 1 h winds out of easterly directions. In combination, these observations suggested a discernible local impact from the pad site to the homeowner's east during the observational period in 2019/20.

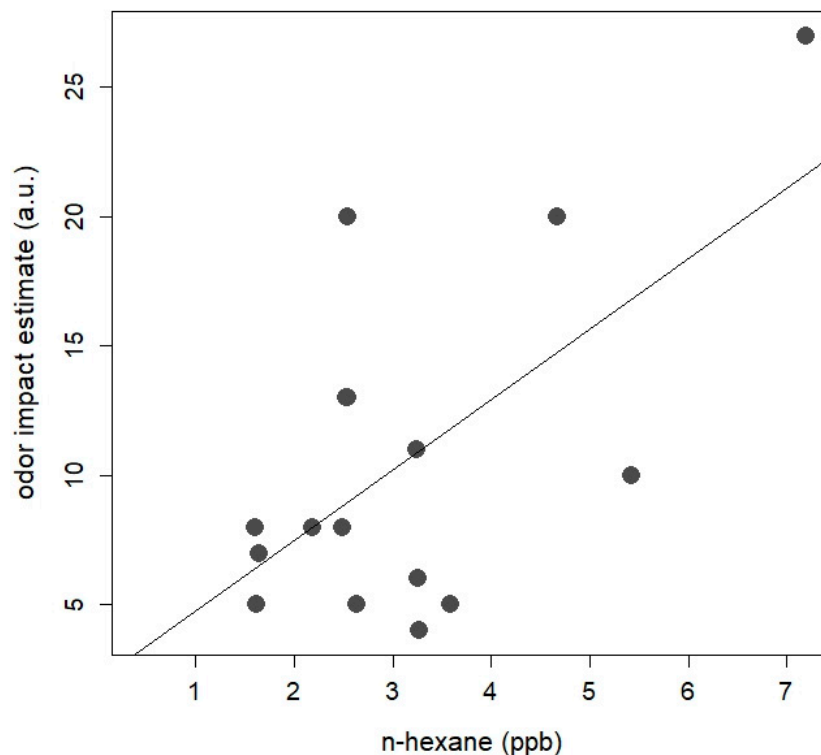


Figure 7. Correlation scatter plot between n-hexane observations and a derived odor impact estimate based on converting daily verbal odor descriptions into a weekly total number ($r^2 = 0.34$; $p = 0.01$).

The second set of anomalies occurred in early November 2019 and was related to a gas-well blowout just 7.5 km north of Nordheim [77]. The NMHC emissions plume from the blowout location was carried south over Nordheim twice at night in the first few days of the blowout, and again a week later after a cold-front passage (8 November), at which time, however, emissions from the blowout had dropped [77]. Both early November samples from Nordheim clearly reflected elevated ambient NMHC levels, mostly n-alkanes and naphthenes.

The third anomaly occurred multiple times at the new Nordheim site, when much higher-than-average concentrations of selected NMHCs were observed (Figure 6). The six anomalies were characterized by elevated levels of NMHCs with seven or more carbon atoms. For instance, the levels of methylcyclohexane, n-heptane, toluene, and the xylenes were elevated, but the levels of the hexanes or benzene were not. This is illustrated in the correlation plot in Figure 8, in which both the six weeks of elevated toluene levels and the two blowout impact weeks are highlighted. The six periods of elevated, low-vapor-pressure NMHCs were consistent with the nearby Hohn Rd. facility's air emissions permit, which listed mostly aromatic hydrocarbon emissions, though virtually no benzene, from an oil/water separator tank as the expected allowable emissions (<15 tons per year; [78]). Methylcyclohexane is not explicitly listed in the permit as it is not considered a hazardous air pollutant (HAP). However, it is often associated with emissions from oil and gas exploration [79–81]. Two of the highlighted periods coincided with official community odor complaints submitted to the TCEQ at the end of July 2020 and the end of January 2021, in both cases prompting an onsite visit by an environmental investigator, who filed a report. In both cases, the TCEQ agent observed brief “unpleasant” or “petrochemical” odors downwind of the waste facility but did not detect elevated VOC concentrations using

a hand-held meter (Multi-RAE Pro multi-gas analyzer, equipped with a PID for detecting unsaturated volatile organic compounds (VOCs), such as aromatics). During neither of the two investigations were any additional air samples taken. Notably, however, local residents filed 30 odor complaints, and TCEQ investigators traveled to Nordheim 14 times in response to these complaints between the summers of 2019 and 2021.

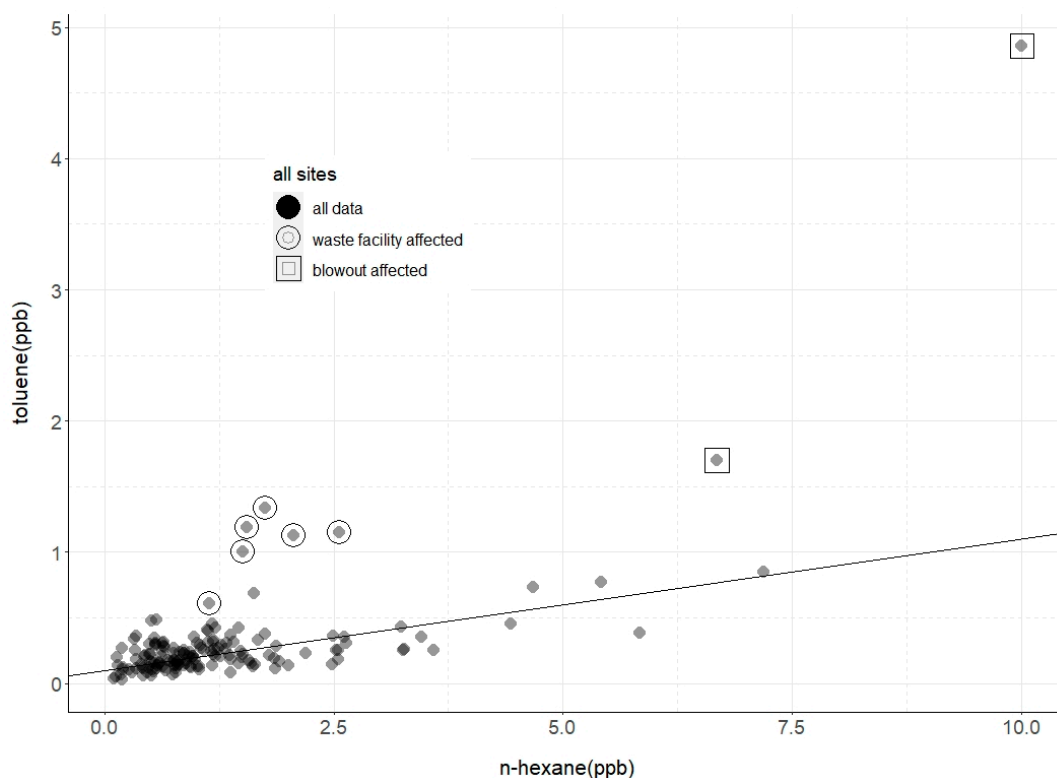


Figure 8. n-hexane vs. toluene scatterplot for the Nordheim sites. The tight correlation, illustrated by the solid regression line, was broken only during impacts from the nearby gas-well blowout (squared points) and impacts from oil waste deposited at the Hohn Rd. facility (circled points).

5. Discussion

We carried out a successful field campaign in the central Eagle Ford shale oil and gas production area from mid-2019 to early 2021. Our measurements occurred across six field sites and were carried out on private property with the assistance of landowners and volunteers, who collected and shipped samples to us and received and redistributed returned passive sampler sets. Our results, when compared to Texas State validated hourly measurements (Section 3), demonstrated that the passive hydrocarbon sampling technique used accurately reflected the average NMHC concentrations. In other words, in the context of rural Texas meteorological and geographical conditions, using Radiello® passive NMHC sampling accurately reflected the average weekly exposures for most of the compared NMHCs. Notably, the medians (and modes) of these NMHC data in the oil patch were significantly lower than the averages due to the right-skewed nature of this type of environmental data; additionally, for at least two of the minor NMHC compounds measured, passive sampling was closer to the medians observed at the air monitoring site. Furthermore, we note that while the hourly monitor data represent a legal standard, they are rarely compared against independent measurements, and TCEQ accepts 20% analytical precision over time.

While no obvious biases were encountered when we compared our data to hourly TCEQ air monitoring station NMHC data, benzene and toluene data showed small, opposite deviations from the averages of the air monitoring data. Though these were not statistically significant, they could lead to different benzene-to-toluene (B/T) ratios, and

this tendency needs to be explored in more detail in future work if the B/T ratio is used in data interpretation, e.g., [82,83].

Our field data showed significant and highly variable ambient levels of benzene in this environment. Pooling the data, we show a histogram of the benzene levels in Figure 9 alongside two health-based thresholds listed in Section 1. The TCEQ benzene long-term AMCV of 1.4 ppb was not exceeded except for twice early in the measurement campaign, with exceedances apparently related to non-standard operating conditions, including large flare emissions, at a nearby oil and gas production site. Much higher benzene levels have been observed in other shale oil and gas exploration areas [27,28]; however, these do not reflect integral exposure levels like the passive samplers do.

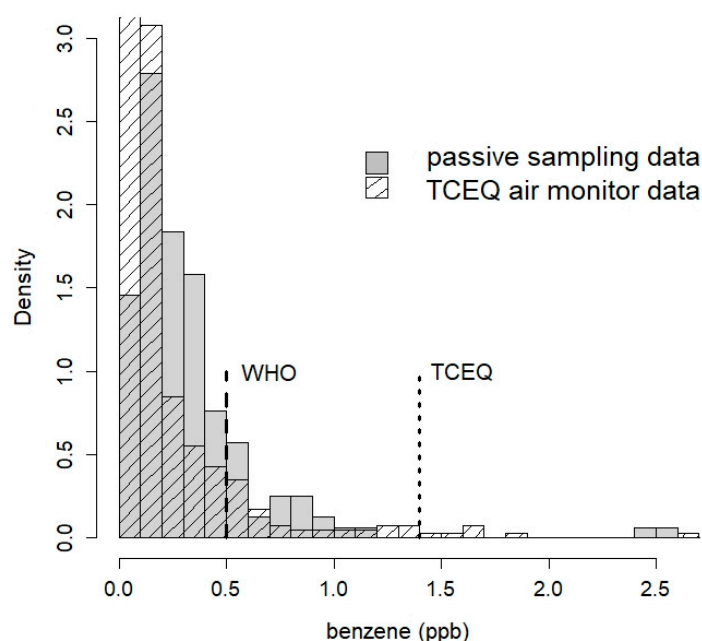


Figure 9. Histograms of our passive sampling data (grey bars) across all sites, compared to randomly selected hourly data of similar sample size and periods from the Karnes City air quality monitoring station (hashed bars). Indicated via a vertical dashed line is the WHO guidance value for benzene (0.5 ppb), and via a dotted line the TCEQ air monitoring comparison value (AMCV) for benzene (1.4 ppb).

Overall, the benzene levels in this area of the Eagle Ford remained mostly below 0.5 ppb, the WHO long-term reference concentration, across the sites. No other NMHC levels approached TCEQ's long-term AMCVs in this study. While this was encouraging from a public health perspective, the results may have been significantly affected by the COVID-19 pandemic, its shutdowns in spring 2020, and the associated reductions in regional oil and gas production. As we will show elsewhere, atmospheric NMHC abundances in air masses crossing the Eagle Ford Shale are correlated with oil and gas production amounts and dropped in 2020 alongside production. Thus, our results may be biased towards low values for some or all NMHCs monitored.

The averages, medians, and spread of our data were similar to the longer-term observations of benzene (and, by extension, the other NMHCs measured) at the regional TCEQ air monitor in Karnes City [49], included in Figure 9. However, the monitor showed a much higher fraction of data below 0.1 ppb and smaller fractions higher than 0.2 ppb benzene. Our results thus showed that individual exposures can be higher when a nearby emissions source contributes more to exposure than expected under standard operating conditions with limited NMHC emissions. This was demonstrated (i) via the observed time-series anomalies in combination with local visual and odor observations at the time of sampling, exemplified via the odor log comparison, and (ii) via higher average abun-

dances at sites very close to emissions sources (site P), or surrounded by a larger number of emissions sources within 2 km than other sites, in this case site KE vs. site O or KC. The latter difference was, however, not uniform across NMHCs. Alkanes such as n-hexane, which are emitted from virtually all oil and gas exploration sites, showed fewer statistically significant differences between sites than aromatic compounds such as benzene or toluene. While the former is known to be emitted from gas flares [9,49,84], the latter was apparently emitted in significant amounts from drilling muds and other solid and liquid oil (drilling) wastes delivered to the facility upwind of the Nh site.

The ability of passive sampling to reflect both short- and long-term exposure levels was illustrated by the impact a nearby gas-well blowout had on the observed concentrations. Two of the anomalous NMHC levels recorded at the Nh site were likely driven by only a few extreme values during 2, 3, and 8 November 2019. Based upon HYSPLIT modeling, the fraction of hours for which parts of the emissions plume may have been over Nordheim during those days was only 5–10%. We estimated that the NMHC levels in the plume must have been 10–50 times higher than outside the plume to cause the two anomalous weeks we observed. This was consistent with our earlier NMHC concentration estimates for the Nordheim location based on said HYSPLIT modeling [77]. Furthermore, we note that the blowout's emissions plume also passed over the P site during the first week of November, which can be seen as another anomalous methylcyclohexane value in Figure 6.

6. Conclusions

Overall, our data provide important observations that complement the still limited set of exposure estimates from extrapolated measurements or modeling [37,40,85]. The passive hydrocarbon sampling method is sensitive enough to observe low to sub-ppb abundances during relatively short sampling periods of 5–10 days. The monitored NMHCs were highly correlated to each other in this environment, where shale oil and gas production dominates NMHC emissions. Deviations from these correlations (Figure 8) show that independent emission sources can be discerned as they affect local exposure. Since the employed Radiello[®] system is comparatively affordable, sensitive, and time-integrating, it has advantages over stationary or mobile measurement systems when long-term exposure estimates are desired, such as for public health studies [40]. The potential health effects from exposure are caused by a mixture of acute and chronic exposures [40]. While the former is typically evaluated with high frequency, i.e., at least hourly measurements, the latter requires long-term monitoring. Our results demonstrated that passive sampling can provide information on both.

While stationary 24/7 monitoring systems can be expensive to operate and maintain, and may not be representative for larger areas (as shown here), mobile measurements may cover larger areas, but typically only for limited periods such as during measurement campaigns. Passive sampling can bridge these methodologies, providing speciated spatial information at an adequate time resolution. A potential disadvantage is the requirement for manual sample exchanges across a larger deployment area. While EPA Method 325 was designed for refinery monitoring at the fenceline [48,55], which represents a limited sampling area, our deployment scheme to a shale oil and gas production area covered a substantially larger area, thus requiring a longer period of accessing and changing samplers on an approximately weekly basis. This was accomplished in our case through a regional volunteer network, and we will present results from a similar study in the Permian basin of Texas elsewhere.

Studies such as that described herein can be used to evaluate air toxics exposures currently estimated using proxies—here, specifically, the “well activity proxy” [86]. This proxy assumes well-site emissions that scale with production volumes such that exposure is driven by emission sites and their proximity to the location in question [37]. Calculating exposure thus uses site-specific production inverse-weighted by distances, possibly adjusted for activity measures or (seasonally changing) meteorology. Our study provides some evidence that the well activity proxy may be appropriate. However, it also highlights

that such a proxy is inadequate under abnormal operating conditions, when winds are consistently arriving from a certain direction, or when specific sources are unaccounted for. We conclude, therefore, that a particular proxy may need regional validation via measurements and site-specific meteorological data. Passive sampling seems an appropriate way to provide such data.

Author Contributions: Data curation, G.W.S. and E.N.H.; resources, G.W.S.; supervision, G.W.S.; visualization, G.W.S. and E.N.H.; writing—original draft, G.W.S.; writing—review and editing, G.W.S. and E.N.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was not directly funded. E.N.H. was supported in 2022 via an independent grant to Texas A&M University from the Health Effects Institute (HEI Energy, grant No. 4993-RFA E20-1/21-16).

Data Availability Statement: Data from this project is available through the Texas Data Repository at <https://dataverse.tdl.org/dataset.xhtml?persistentId=doi:10.18738/T8/7GYMBH> (accessed on 11 April 2023).

Acknowledgments: We are indebted to the landowners and volunteers in the Eagle Ford’s central counties of Dewitt and Karnes, without whose cooperation this study would not have been possible. We are especially grateful to lead volunteer and organizer Sister Elizabeth Riebschlaeger from Sisters of Charity of the Incarnate Word (CCVI), whose community engagement efforts and weekly efforts of collecting, distributing, and sending samplers back to College Station via Express Mail enabled and sustained this study. We are grateful for her and the other volunteers’ time, as well their contributions via travel and sample shipments, which ultimately made this study a success. Furthermore, we thank the former Texas A&M College of Geosciences for an undergraduate research support grant to Joel Holliman, who processed many of the samples that arrived in College Station on a weekly basis. Lastly, the author acknowledges partial financial support via a small crowdfund on Experiment.com, which sustained the GC operating gas supplies.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Allen, D.T. Emissions from oil and gas operations in the United States and their air quality implications. *J. Air Waste Manag. Assoc.* **2016**, *66*, 549–575. [CrossRef] [PubMed]
2. Kanfar, M.S. Comparison of Empirical Decline Curve Analysis for Shale Wells. Master’s Thesis, Texas A&M University, College Station, TX, USA, 2013.
3. Wachtmeister, H.; Lund, L.; Aleklett, K.; Höök, M. Production Decline Curves of Tight Oil Wells in Eagle Ford Shale. *Nat. Resour. Res.* **2017**, *26*, 365–377. [CrossRef]
4. Braun, B. Fracking. In *Keywords in Radical Geography: Antipode at 50*; Wiley: Hoboken, NJ, USA, 2019; pp. 128–133.
5. Murray, J.W. Limitations of Oil Production to the IPCC Scenarios: The New Realities of US and Global Oil Production. *Biophys. Econ. Resour. Qual.* **2016**, *1*, 13. [CrossRef]
6. Caretta, M.A.; Carlson, E.B.; Hood, R.; Turley, B. From a rural idyll to an industrial site: An analysis of hydraulic fracturing energy sprawl in Central Appalachia. *J. Land Use Sci.* **2021**, *16*, 382–397. [CrossRef]
7. da Costa, D.M.B.; Jesus, J.; Branco, D.C.; Danko, A.; Fiúza, A. Extensive review of shale gas environmental impacts from scientific literature (2010–2015). *Environ. Sci. Pollut. Res.* **2017**, *24*, 14579–14594. [CrossRef]
8. Jones, N.F.; Pejchar, L.; Kiesecker, J.M. The Energy Footprint: How Oil, Natural Gas, and Wind Energy Affect Land for Biodiversity and the Flow of Ecosystem Services. *Bioscience* **2015**, *65*, 290–301. [CrossRef]
9. Knighton, W.B.; Herndon, S.C.; Franklin, J.F.; Wood, E.C.; Wormhoudt, J.; Brooks, W.; Fortner, E.C.; Allen, D.T. Direct measurement of volatile organic compound emissions from industrial flares using real-time online techniques: Proton Transfer Reaction Mass Spectrometry and Tunable Infrared Laser Differential Absorption Spectroscopy. *Ind. Eng. Chem. Res.* **2012**, *51*, 12674–12684. [CrossRef]
10. Marrero, J.E.; Townsend-Small, A.; Lyon, D.R.; Tsai, T.R.; Meinardi, S.; Blake, D.R. Estimating Emissions of Toxic Hydrocarbons from Natural Gas Production Sites in the Barnett Shale Region of Northern Texas. *Environ. Sci. Technol.* **2016**, *50*, 10756–10764. [CrossRef]
11. Pétron, G.; Karion, A.; Sweeney, C.; Miller, B.; Montzka, S.; Frost, G.J.; Trainer, M.; Tans, P.P.; Andrews, A.; Kofler, J.; et al. A new look at methane and nonmethane hydrocarbon emissions from oil and natural gas operations in the Colorado Denver-Julesburg Basin. *J. Geophys. Res. Atmos.* **2014**, *119*, 6836–6852. [CrossRef]
12. Lyon, D.R.; Alvarez, R.A.; Zavala-Araiza, D.; Brandt, A.R.; Jackson, R.B.; Hamburg, S.P. Aerial Surveys of Elevated Hydrocarbon Emissions from Oil and Gas Production Sites. *Environ. Sci. Technol.* **2016**, *50*, 4877–4886. [CrossRef]

13. Allen, D.T.; Cardoso-Saldaña, F.J.; Kimura, Y. Variability in Spatially and Temporally Resolved Emissions and Hydrocarbon Source Fingerprints for Oil and Gas Sources in Shale Gas Production Regions. *Environ. Sci. Technol.* **2017**, *51*, 12016–12026. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Roest, G.; Schade, G. Quantifying alkane emissions in the Eagle Ford Shale using boundary layer enhancement. *Atmos. Meas. Tech.* **2017**, *17*, 11163–11176. [\[CrossRef\]](#)
15. Rossabi, S.; Hueber, J.; Wang, W.; Milmoie, P.; Helmig, D. Spatial distribution of atmospheric oil and natural gas volatile organic compounds in the Northern Colorado Front Range. *Elem. Sci. Anthr.* **2021**, *9*, 36. [\[CrossRef\]](#)
16. Dalsøren, S.B.; Myhre, G.; Hodnebrog, Ø.; Myhre, C.L.; Stohl, A.; Pisso, I.; Schwietzke, S.; Höglund-Isaksson, L.; Helmig, D.; Reimann, S.; et al. Discrepancy between simulated and observed ethane and propane levels explained by underestimated fossil emissions. *Nat. Geosci.* **2018**, *11*, 178–184. [\[CrossRef\]](#)
17. Ghosh, B. Impact of Changes in Oil and Gas Production Activities on Air Quality in Northeastern Oklahoma: Ambient Air Studies in 2015–2017. *Environ. Sci. Technol.* **2018**, *52*, 3285–3294. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Tzompa-Sosa, Z.A.; Henderson, B.H.; Keller, C.A.; Travis, K.; Mahieu, E.; Franco, B.; Estes, M.; Helmig, D.; Fried, A.; Richter, D.; et al. Atmospheric Implications of Large C₂–C₅ Alkane Emissions from the U.S. Oil and Gas Industry. *J. Geophys. Res. Atmos.* **2019**, *124*, 1148–1169. [\[CrossRef\]](#)
19. Chen, H.; Carter, K.E. Hazardous substances as the dominant non-methane volatile organic compounds with potential emissions from liquid storage tanks during well fracturing: A modeling approach. *J. Environ. Manag.* **2020**, *268*, 110715. [\[CrossRef\]](#)
20. Helmig, D. Air quality impacts from oil and natural gas development in Colorado. *Elem. Sci. Anthr.* **2020**, *8*, 398. [\[CrossRef\]](#)
21. Pozzer, A.; Schultz, M.G.; Helmig, D. Impact of U.S. Oil and Natural Gas Emission Increases on Surface Ozone Is Most Pronounced in the Central United States. *Environ. Sci. Technol.* **2020**, *54*, 12423–12433. [\[CrossRef\]](#)
22. McDuffie, E.E.; Edwards, P.M.; Gilman, J.B.; Lerner, B.M.; Dubé, W.P.; Trainer, M.; Wolfe, D.E.; Angevine, W.M.; Degouw, J.; Williams, E.J.; et al. Influence of oil and gas emissions on summertime ozone in the Colorado Northern Front Range. *J. Geophys. Res. Atmos.* **2016**, *121*, 8712–8729. [\[CrossRef\]](#)
23. Cheadle, L.C.; Oltmans, S.J.; Pétron, G.; Schnell, R.C.; Mattson, E.J.; Herndon, S.C.; Thompson, A.M.; Blake, D.R.; McClure-Begley, A. Surface ozone in the Colorado northern Front Range and the influence of oil and gas development during FRAPPE/DISCOVER-AQ in summer 2014. *Elem. Sci. Anthr.* **2017**, *5*, 254. [\[CrossRef\]](#)
24. Schade, G.W.; Roest, G. Analysis of non-methane hydrocarbon data from a monitoring station affected by oil and gas development in the Eagle Ford shale, Texas. *Elem. Sci. Anthr.* **2016**, *4*, 96. [\[CrossRef\]](#)
25. Atkinson, R. Atmospheric chemistry of VOCs and NO_x. *Atmos. Environ.* **2000**, *34*, 2063–2101. [\[CrossRef\]](#)
26. Bolden, A.L.; Kwiatkowski, C.F.; Colborn, T. New Look at BTEX: Are Ambient Levels a Problem? *Environ. Sci. Technol.* **2015**, *49*, 5261–5276. [\[CrossRef\]](#)
27. Halliday, H.S.; Thompson, A.M.; Wisthaler, A.; Blake, D.R.; Hornbrook, R.S.; Mikoviny, T.; Müller, M.; Eichler, P.; Apel, E.C.; Hills, A.J. Atmospheric benzene observations from oil and gas production in the Denver-Julesburg Basin in July and August 2014. *J. Geophys. Res. Atmos.* **2016**, *121*, 25327. [\[CrossRef\]](#)
28. Helmig, D.; Thompson, C.R.; Evans, J.; Boylan, P.; Hueber, J.; Park, J.-H. Highly Elevated Atmospheric Levels of Volatile Organic Compounds in the Uintah Basin, Utah. *Environ. Sci. Technol.* **2014**, *48*, 4707–4715. [\[CrossRef\]](#)
29. Hu, L.; Millet, D.B.; Baasandorj, M.; Griffis, T.J.; Travis, K.R.; Tessum, C.W.; Marshall, J.D.; Reinhardt, W.F.; Mikoviny, T.; Müller, M.; et al. Emissions of C₆–C₈ aromatic compounds in the United States: Constraints from tall tower and aircraft measurements. *J. Geophys. Res. Atmos.* **2015**, *120*, 826–842. [\[CrossRef\]](#)
30. Macey, G.P.; Breech, R.; Chernaik, M.; Cox, C.; Larson, D.; Thomas, D.; Carpenter, D.O. Air concentrations of volatile compounds near oil and gas production: A community-based exploratory study. *Environ. Health* **2014**, *13*, 82. [\[CrossRef\]](#)
31. McKenzie, L.M.; Allshouse, W.B.; Byers, T.E.; Bedrick, E.J.; Serdar, B.; Adgate, J.L. Childhood hematologic cancer and residential proximity to oil and gas development. *PLoS ONE* **2017**, *12*, e0170423. [\[CrossRef\]](#)
32. McKenzie, L.M.; Blair, B.; Hughes, J.; Allshouse, W.B.; Blake, N.J.; Helmig, D.; Milmoie, P.; Halliday, H.; Blake, D.R.; Adgate, J. Ambient Nonmethane Hydrocarbon Levels Along Colorado's Northern Front Range: Acute and Chronic Health Risks. *Environ. Sci. Technol.* **2018**, *52*, 4514–4525. [\[CrossRef\]](#)
33. McKenzie, L.M.; Witter, R.Z.; Newman, L.S.; Adgate, J.L. Human health risk assessment of air emissions from development of unconventional natural gas resources. *Sci. Total. Environ.* **2012**, *424*, 79–87. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Thompson, C.; Hueber, J.; Helmig, D. Influence of oil and gas emissions on ambient atmospheric non-methane hydrocarbons in residential areas of Northern Colorado. *Elem. Sci. Anthr.* **2014**, *2*, 000035. [\[CrossRef\]](#)
35. Wollin, K.-M.; Damm, G.; Foth, H.; Freyberger, A.; Gebel, T.; Mangerich, A.; Gundert-Remy, U.; Partosch, F.; Röhl, C.; Schupp, T.; et al. Critical evaluation of human health risks due to hydraulic fracturing in natural gas and petroleum production. *Arch. Toxicol.* **2020**, *94*, 967–1016. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Elliott, E.; Trinh, P.; Ma, X.; Leaderer, B.P.; Ward, M.H.; Deziel, N.C. Unconventional oil and gas development and risk of childhood leukemia: Assessing the evidence. *Sci. Total. Environ.* **2016**, *576*, 138–147. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Khalaj, F.; Sattler, M. Modeling of VOCs and criteria pollutants from multiple natural gas well pads in close proximity, for different terrain conditions: A Barnett Shale case study. *Atmos. Pollut. Res.* **2019**, *10*, 1239–1249. [\[CrossRef\]](#)
38. Cushing, L.J.; Chau, K.; Franklin, M.; Johnston, J.E. Up in smoke: Characterizing the population exposed to flaring from unconventional oil and gas development in the contiguous US. *Environ. Res. Lett.* **2021**, *16*, 034032. [\[CrossRef\]](#)

39. EPA. *Integrated Risk Information System (IRIS). Chemical Assessment Summary: Benzene*; CASRN 71-43-2; EPA: Washington, DC, USA, 2003.
40. Holder, C.; Hader, J.; Avanas, R.; Hong, T.; Carr, E.; Mendez, B.; Wignall, J.; Glen, G.; Guelden, B.; Wei, Y. Evaluating potential human health risks from modeled inhalation exposures to volatile organic compounds emitted from oil and gas operations. *J. Air Waste Manag. Assoc.* **2019**, *69*, 1503–1524. [\[CrossRef\]](#)
41. World Health Organization. *Exposure to Benzene: A Major Public Health Concern*; WHO: Geneva, Switzerland, 2010.
42. Harley, R.A.; Hooper, D.S.; Kean, A.J.; Kirchstetter, T.W.; Hesson, J.M.; Balberan, N.T.; Stevenson, E.D.; Kendall, G.R. Effects of Reformulated Gasoline and Motor Vehicle Fleet Turnover on Emissions and Ambient Concentrations of Benzene. *Environ. Sci. Technol.* **2006**, *40*, 5084–5088. [\[CrossRef\]](#)
43. Russo, R.S.; Zhou, Y.; White, M.L.; Mao, H.; Talbot, R.; Sive, B.C. Multi-year (2004–2008) record of nonmethane hydrocarbons and halocarbons in New England: Seasonal variations and regional sources. *Atmos. Meas. Tech.* **2010**, *10*, 4909–4929. [\[CrossRef\]](#)
44. Lioy, P.J.; Georgopoulos, P.G. New Jersey: A Case Study of the Reduction in Urban and Suburban Air Pollution from the 1950s to 2010. *Environ. Health Perspect.* **2011**, *119*, 1351–1355. [\[CrossRef\]](#)
45. Yano, Y.; Morris, S.S.; Salerno, C.; Schlapia, A.M.; Stichick, M. Impact of a new gasoline benzene regulation on ambient air pollutants in Anchorage, Alaska. *Atmos. Environ.* **2016**, *132*, 276–282. [\[CrossRef\]](#)
46. Hsu, C.-Y.; Chiang, H.-C.; Shie, R.-H.; Ku, C.-H.; Lin, T.-Y.; Chen, M.-J.; Chen, N.-T.; Chen, Y.-C. Ambient VOCs in residential areas near a large-scale petrochemical complex: Spatiotemporal variation, source apportionment and health risk. *Environ. Pollut.* **2018**, *240*, 95–104. [\[CrossRef\]](#) [\[PubMed\]](#)
47. Sakizadeh, M. Spatiotemporal variations and characterization of the chronic cancer risk associated with benzene exposure. *Ecotoxicol. Environ. Saf.* **2019**, *182*, 109387. [\[CrossRef\]](#) [\[PubMed\]](#)
48. Mukerjee, S.; Smith, L.A.; Thoma, E.D.; Oliver, K.D.; Whitaker, D.A.; Wu, T.; Colon, M.; Alston, L.; Cousett, T.A.; Stallings, C. Spatial analysis of volatile organic compounds in South Philadelphia using passive samplers. *J. Air Waste Manag. Assoc.* **2016**, *66*, 492–498. [\[CrossRef\]](#) [\[PubMed\]](#)
49. Schade, G.W.; Roest, G. Source apportionment of non-methane hydrocarbons, NO_x and H₂S data from a central monitoring station in the Eagle Ford shale, Texas. *Elem. Sci. Anthr.* **2018**, *6*, 289. [\[CrossRef\]](#)
50. Marć, M.; Tobiszewski, M.; Zabiegała, B.; de la Guardia, M.; Namieśnik, J. Current air quality analytics and monitoring: A review. *Anal. Chim. Acta* **2015**, *853*, 116–126. [\[CrossRef\]](#) [\[PubMed\]](#)
51. Pennequin-Cardinal, A.; Plaisance, H.; Locoge, N.; Ramalho, O.; Kirchner, S.; Galloo, J.-C. Performances of the Radiello® diffusive sampler for BTEX measurements: Influence of environmental conditions and determination of modelled sampling rates. *Atmos. Environ.* **2005**, *39*, 2535–2544. [\[CrossRef\]](#)
52. Oury, B.; Lhuillier, F.; Protois, J.-C.; Morele, Y. Behavior of the GABIE, 3M 3500, PerkinElmer Tenax TA, and RADIELLO 145 Diffusive Samplers Exposed Over a Long Time to a Low Concentration of VOCs. *J. Occup. Environ. Hyg.* **2006**, *3*, 547–557. [\[CrossRef\]](#)
53. Mukerjee, S.; Smith, L.; Caudill, M.P.; Oliver, K.D.; Whipple, W.; Whitaker, D.; Cousett, T. Application of passive sorbent tube and canister samplers for volatile organic compounds at refinery fenceline locations in Whiting, Indiana. *J. Air Waste Manag. Assoc.* **2018**, *68*, 170–175. [\[CrossRef\]](#)
54. U.S. Environmental Protection Agency. *Method 325A—Volatile Organic Compounds from Fugitive and Area Sources*; U.S. Environmental Protection Agency: Washington, DC, USA, 2019; Volume 18.
55. Thoma, E.D.; Brantley, H.L.; Oliver, K.D.; Whitaker, D.A.; Mukerjee, S.; Mitchell, B.; Wu, T.; Squier, B.; Escobar, E.; Cousett, T.A.; et al. South Philadelphia passive sampler and sensor study. *J. Air Waste Manag. Assoc.* **2016**, *66*, 959–970. [\[CrossRef\]](#)
56. Healy, R.M.; Wang, J.M.; Karellas, N.S.; Todd, A.; Sofowote, U.; Su, Y.; Munoz, A. Assessment of a passive sampling method and two on-line gas chromatographs for the measurement of benzene, toluene, ethylbenzene and xylenes in ambient air at a highway site. *Atmos. Pollut. Res.* **2019**, *10*, 1123–1127. [\[CrossRef\]](#)
57. Hamid, H.H.A.; Latif, M.T.; Uning, R.; Nadzir, M.S.M.; Khan, F.; Ta, G.C.; Kannan, N. Observations of BTEX in the ambient air of Kuala Lumpur by passive sampling. *Environ. Monit. Assess.* **2020**, *192*, 1–14. [\[CrossRef\]](#)
58. Miller, D.D.; Bajracharya, A.; Dickinson, G.N.; Durbin, T.A.; McGarry, J.K.; Moser, E.P.; Nuñez, L.A.; Pukkila, E.J.; Scott, P.S.; Sutton, P.J.; et al. Diffusive uptake rates for passive air sampling: Application to volatile organic compound exposure during FIREX-AQ campaign. *Chemosphere* **2021**, *287*, 131808. [\[CrossRef\]](#) [\[PubMed\]](#)
59. Helmig, D.; Fangmeyer, J.; Fuchs, J.; Hueber, J.; Smith, K. Evaluation of selected solid adsorbents for passive sampling of atmospheric oil and natural gas non-methane hydrocarbons. *J. Air Waste Manag. Assoc.* **2022**, *72*, 235–255. [\[CrossRef\]](#) [\[PubMed\]](#)
60. Pennequin-Cardinal, A.; Plaisance, H.; Locoge, N.; Ramalho, O.; Kirchner, S.; Galloo, J.C. Dependence on sampling rates of Radiello® diffusion sampler for BTEX measurements with the concentration level and exposure time. *Talanta* **2005**, *65*, 1233–1240. [\[CrossRef\]](#) [\[PubMed\]](#)
61. Zabiegała, B.; Urbanowicz, M.; Namieśnik, J.; Górecki, T. Spatial and Seasonal Patterns of Benzene, Toluene, Ethylbenzene, and Xylenes in the Gdańsk, Poland and Surrounding Areas Determined Using Radiello Passive Samplers. *J. Environ. Qual.* **2010**, *39*, 896–906. [\[CrossRef\]](#)
62. Zabiegała, B.; Urbanowicz, M.; Szymanska, K.; Namiesnik, J. Application of Passive Sampling Technique for Monitoring of BTEX Concentration in Urban Air: Field Comparison of Different Types of Passive Samplers. *J. Chromatogr. Sci.* **2010**, *48*, 167–175. [\[CrossRef\]](#)

63. Gallego, E.; Roca, F.J.; Perales, J.F.; Guardino, X. Evaluation of the effect of different sampling time periods and ambient air pollutant concentrations on the performance of the Radiello® diffusive sampler for the analysis of VOCs by TD-GC/MS. *J. Environ. Monit.* **2011**, *13*, 2612–2622. [\[CrossRef\]](#)
64. Mason, J.B.; Fujita, E.M.; Campbell, D.E.; Zielinska, B. Evaluation of Passive Samplers for Assessment of Community Exposure to Toxic Air Contaminants and Related Pollutants. *Environ. Sci. Technol.* **2011**, *45*, 2243–2249. [\[CrossRef\]](#)
65. Lan, T.T.N.; Binh, N.T.T. Daily roadside BTEX concentrations in East Asia measured by the Lanwatsu, Radiello and Ultra I SKS passive samplers. *Sci. Total Environ.* **2012**, *441*, 248–257. [\[CrossRef\]](#)
66. Kerchich, Y.; Kerbach, R. Measurement of BTEX (benzene, toluene, ethylbenzene, and xylene) levels at urban and semirural areas of Algiers City using passive air samplers. *J. Air Waste Manag. Assoc.* **2012**, *62*, 1370–1379. [\[CrossRef\]](#) [\[PubMed\]](#)
67. Król, S.; Zabiegała, B.; Namiesnik, J. Measurement of benzene concentration in urban air using passive sampling. *Anal. Bioanal. Chem.* **2011**, *403*, 1067–1082. [\[CrossRef\]](#) [\[PubMed\]](#)
68. Marć, M.; Namiesnik, J.; Zabiegała, B. BTEX concentration levels in urban air in the area of the Tri-City agglomeration (Gdansk, Gdynia, Sopot), Poland. *Air Qual. Atmos. Health* **2014**, *7*, 489–504. [\[CrossRef\]](#)
69. Marć, M.; Zabiegała, B.; Namiesnik, J. Application of passive sampling technique in monitoring research on quality of atmospheric air in the area of Tczew, Poland. *Int. J. Environ. Anal. Chem.* **2013**, *94*, 151–167. [\[CrossRef\]](#)
70. Marć, M.; Bielawska, M.; Wardencki, W.; Namiesnik, J.; Zabiegała, B. The influence of meteorological conditions and anthropogenic activities on the seasonal fluctuations of BTEX in the urban air of the Hanseatic city of Gdansk, Poland. *Environ. Sci. Pollut. Res.* **2015**, *22*, 11940–11954. [\[CrossRef\]](#)
71. Moolla, R.; Curtis, C.J.; Knight, J. Occupational Exposure of Diesel Station Workers to BTEX Compounds at a Bus Depot. *Int. J. Environ. Res. Public Health* **2015**, *12*, 4101–4115. [\[CrossRef\]](#)
72. Marć, M.; Śmiełowska, M.; Zabiegała, B. Concentrations of monoaromatic hydrocarbons in the air of the underground car park and individual garages attached to residential buildings. *Sci. Total. Environ.* **2016**, *573*, 767–777. [\[CrossRef\]](#)
73. Cruz, L.P.S.; Alve, L.P.; Santos, A.V.S.; Esteves, M.B.; Gomes, V.S.; Nunes, L.S.S. Assessment of BTEX Concentrations in Air Ambient of Gas Stations Using Passive Sampling and the Health Risks for Workers. *J. Environ. Prot.* **2017**, *08*, 12–25. [\[CrossRef\]](#)
74. Sablan, O.M.; Schade, G.W.; Holliman, J. Passively Sampled Ambient Hydrocarbon Abundances in a Texas Oil Patch. *Atmosphere* **2020**, *11*, 241. [\[CrossRef\]](#)
75. Eisele, A.P.; Mukerjee, S.; Smith, L.A.; Thoma, E.D.; Whitaker, D.A.; Oliver, K.D.; Wu, T.; Colon, M.; Alston, L.; Cousett, T.A.; et al. Volatile organic compounds at two oil and natural gas production well pads in Colorado and Texas using passive samplers. *J. Air Waste Manag. Assoc.* **2016**, *66*, 412–419. [\[CrossRef\]](#)
76. Emery, C.; Liu, Z.; Russell, A.G.; Odman, M.T.; Yarwood, G.; Kumar, N. Recommendations on statistics and benchmarks to assess photochemical model performance. *J. Air Waste Manag. Assoc.* **2017**, *67*, 582–598. [\[CrossRef\]](#) [\[PubMed\]](#)
77. Schade, G.W.; Gregg, M.L. Testing HYSPLIT Plume Dispersion Model Performance Using Regional Hydrocarbon Monitoring Data during a Gas Well Blowout. *Atmosphere* **2022**, *13*, 486. [\[CrossRef\]](#)
78. Texas Commission on Environmental Quality (TCEQ). *Permit by Rule Registration Number 155167*; TCEQ: Austin, TX, USA, 2019; 10p.
79. Hu, G.; Li, J.; Li, Z.; Luo, X.; Sun, Q.; Ma, C. Preliminary study on the origin identification of natural gas by the parameters of light hydrocarbon. *Sci. China Ser. D Earth Sci.* **2008**, *51*, 131–139. [\[CrossRef\]](#)
80. Yu, C.; Gong, D.; Huang, S.; Liao, F.; Sun, Q. Characteristics of Light Hydrocarbons of Tight Gases and its Application in the Sulige Gas Field, Ordos Basin, China. *Energy Explor. Exploit.* **2014**, *32*, 211–226. [\[CrossRef\]](#)
81. Warneke, C.; Geiger, F.; Edwards, P.M.; Dube, W.; Pétron, G.; Kofler, J.; Zahn, A.; Brown, S.S.; Graus, M.; Gilman, J.B.; et al. Volatile organic compound emissions from the oil and natural gas industry in the Uintah Basin, Utah: Oil and gas well pad emissions compared to ambient air composition. *Atmos. Meas. Tech.* **2014**, *14*, 10977–10988. [\[CrossRef\]](#)
82. Gelencsér, A.; Siszler, K.; Hlavay, J. Toluene–Benzene Concentration Ratio as a Tool for Characterizing the Distance from Vehicular Emission Sources. *Environ. Sci. Technol.* **1997**, *31*, 2869–2872. [\[CrossRef\]](#)
83. Heeb, N.V.; Forss, A.-M.; Bach, C.; Reimann, S.; Herzog, A.; Jäckle, H.W. A comparison of benzene, toluene and C2-benzenes mixing ratios in automotive exhaust and in the suburban atmosphere during the introduction of catalytic converter technology to the Swiss Car Fleet. *Atmos. Environ.* **2000**, *34*, 3103–3116. [\[CrossRef\]](#)
84. Stroscher, M.T. Characterization of Emissions from Diffusion Flare Systems. *J. Air Waste Manag. Assoc.* **2000**, *50*, 1723–1733. [\[CrossRef\]](#) [\[PubMed\]](#)
85. McMullin, T.S.; Bamber, A.M.; Bon, D.; Vigil, D.I.; Van Dyke, M. Exposures and Health Risks from Volatile Organic Compounds in Communities Located near Oil and Gas Exploration and Production Activities in Colorado (U.S.A.). *Int. J. Environ. Res. Public Health* **2018**, *15*, 1500. [\[CrossRef\]](#)
86. Konkell, L. Drilling into Critical Windows of Exposure: Trimester-Specific Associations between Gas Development and Preterm Birth. *Environ. Health Perspect.* **2018**, *126*, 104002. [\[CrossRef\]](#)

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