

# Geographic Characterization of Benzene Plumes in California

Andrew R. Murray<sup>1,2</sup> Diego Riveros-Iregui<sup>1</sup> Alexander Hall<sup>3</sup>

<sup>1</sup>The University of North Carolina - Chapel Hill

<sup>2</sup>Oak Ridge Associated Universities

<sup>3</sup>U.S. Environmental Protection Agency Office of Research and Development

## Key Points:

- Spatial extents of benzene plumes are still poorly understood.
- Most plumes are not spatially captured by groundwater testing.
- Better models are needed to inform monitoring well selection for leaking sites.

---

Corresponding author: Andrew Murray, [Murray.AndrewR@epa.gov](mailto:Murray.AndrewR@epa.gov)

## Abstract

Underground storage tanks are tanks buried underground for the purpose of storing and dispensing a wide range of hazardous products, primarily fuel products such as gasoline and diesel. In the United States there are currently 540,000 open (in operation) tanks. Since 2000, there have been more than 118,000 reported releases. When fuel products release into the ground or onto the surface they can contaminate local soil and groundwater resources, as well as pollute the air by means of vapor intrusion. Petroleum hydrocarbons, which are known carcinogens, pose a threat to human and environmental health. They can persist in the environment for decades, and can contaminate drinking water to unsafe levels which are less than the human threshold for smell or taste. Benzene is a carcinogenic petroleum hydrocarbon found in fuel products and several studies have been conducted on its potential for mobilization in the environment, however these studies generally contain a limited number of sites within a limited geographic area and much remains to be understood related to environmental drivers.

## 1 Introduction

Benzene, a carcinogenic component of petroleum products such as gasoline is known to be released into the environment as the result of leaking underground storage tanks (LUST). There are currently about 540,000 active petroleum underground storage tank (UST) systems and a backlog of 62,000 LUST sites in the United States (US EPA, 2021). The definition of a LUST or a release can vary depending on which state or federal regulations you consider. The federal government considers reportable quantities of petroleum products to be anything over 25 gallons, or a spill that cannot be cleaned up within 24 hours (National Archives, 2022). Nationally, for about every 7 active USTs, one will report a release in its lifetime (US EPA, 2021). Many studies have been done on benzene plume length and attenuation (e.g., Connor, Kamath, Walker, & McHugh, 2015; Kamath et al., 2012; Shih, Rong, Harmon, & Suffet, 2004). However, much is still unknown about the behavior and extent of benzene plumes. For example, while most papers focus on distance (one-dimensional), fewer characterize total impacted area (two-dimensional), and those that do, typically focus on only a small number of contaminated sites. A review paper on studies of benzene plume length showed that research in this area included between 22 to 289 LUST sites per study (Connor et al., 2015). McHugh, Kulkarni, Newell, Connor, and Garg (2014) included over 4,000 LUST sites, however this was not focused

on distance or area but rather trends in concentration over time. A key reason for the limited number of sites included in these studies is data availability. Although states are required to test and characterize sites contaminated or suspected to be contaminated by LUSTs, very limited amounts of these data are made public. In prior studies, authors accumulated limited amounts of field data from multiple agencies and sources. An exception to this limited data availability is California’s Geotracker database, the largest publicly available database of its kind, which includes field data for LUST cleanup sites dating back to 2000.

There has yet to be a study done on benzene plume areas that sufficiently considers a large number of field studies, geographic diversity of sites, and two-dimensional plume shape. Further, no study has been able to offer insight into how well plume areas are being captured by monitoring wells, which could help to make future testing campaigns more efficient and accurate. In this paper, we consider the largest number of field studies to date in a two-dimensional study and use publicly available data obtained from California’s GeoTracker database to compare our findings with those of Connor et al. (2015) to determine how a larger and more diverse sample size supports or disagrees with the findings of other studies. We then spatially normalize plumes by determining the mean linear direction of benzene flow and rotate them so as to artificially overlay them and determine the two-dimensional areas that are most commonly impacted relative to the LOP. Finally, we characterize two-dimensional benzene plume areas to determine how effective monitoring wells are at completely capturing benzene plumes in California and discuss the implications of our results. We find that in the vast majority of LUST cleanup sites, it is likely that plume areas are larger than previously thought. These essential investigations will help to determine if plumes are being effectively measured and inform future efforts to estimate plume extents.

## 2 Materials and Methods

### 2.1 California release definitions

The definition of a release varies from state to state, however all states must report releases that meet or exceed the criteria of the federal reporting requirements. Many releases do not meet this threshold but may still appear in California’s geotracker database. California defines a release as “any spilling, leaking, emitting, discharging, escaping, leach-

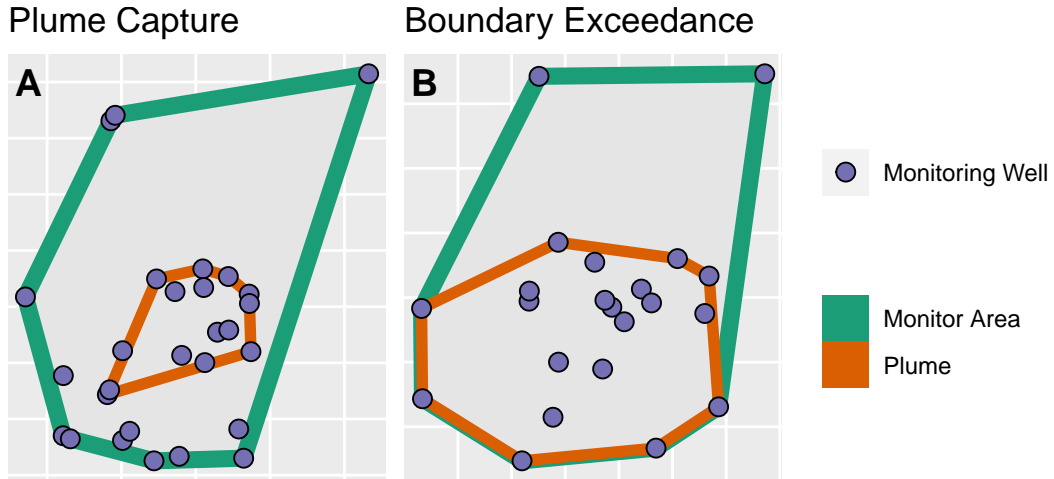
ing, or disposing from an underground storage tank into or on the waters of the state, the land, or the subsurface soils” (California Legislature, 2003). In California, operators are not required to report a release or spill if they are “able to clean up within eight hours after the release was detected or should reasonably have been detected, and which does not escape from the secondary containment, does not increase the hazard of fire or explosion, and does not cause any deterioration of the secondary containment of the underground storage tank.” However the operator must record the incident in monitoring reports (California Legislature, 1984). If these thresholds are exceeded, the operator must report the spill to the appropriate state agency (California Legislature, 2013).

## 2.2 Determining Plume Length

The data obtained from GeoTracker contains groundwater samples from 42,045 unique LUST sites, however the majority of these sites do not have multiple geolocated monitoring wells with groundwater samples in excess of the federal MCL (5 ug/L). All data was downloaded from the Geotracker public data portal (CA Water Board, 2022) by county, merged together and filtered to only sites defined as a ‘LUST Cleanup Site’. There is no specific way of determining origin point of a release. This is common as most releases are discovered as a result of tank removal and it is often unclear from exactly where a release occurred. While the geotracker database does provide xy locations for both ‘UST / UST pit’ and ‘former UST’ locations, these data only exist at less than 200 of LUST cleanup sites. Therefore, we define the leak origin point (LOP) as the point where benzene concentration was the highest at a given site. If there were multiple measurements of the maximum concentration at different points, the earliest measurement was used. As in Connor et al. (2015), the plume is defined as the distance between the LOP and the farthest monitoring well which had a sample above two separate thresholds, 5 ug/L and 10 ug/L to match with methods used by previous studies. To be clear, the current federal MCL for benzene is 5 ug/L. We only use the 10 ug/L threshold for comparison of benzene distance. To delineate two-dimensional areas of plumes, we use the EPA 5 ug/L MCL. Geolocations of wells were projected to the California Albers projection and measured in meters using the sf package (Pebesma, 2018). All analysis in this paper was done with R statistical software (R Core Team, 2021) and RStudio (RStudio Team, 2020).

### 2.3 Evaluating Capture of Plumes by Monitoring Wells

Benzene plumes have been shown to spread over time and can persist for decades. Additionally, benzene plumes can disconnect over time and it is possible to have separation into two plumes (Molson, Barker, Frind, & Schirmer, 2002), which could lead to undetected plumes beyond testing boundaries, especially if the leak was detected years after a release began. We evaluate plume extents compared with monitoring well extents to determine if plumes are completely captured by monitoring wells or if concentrations greater than 5 ug/L are possibly extending beyond monitoring wells. To test this, we create convex hulls (Pebesma, 2018) of the monitoring wells which measured  $\geq 5\text{ug/L}$  for every site and also convex hulls for monitoring wells for every site. If a site has a sample that exceeds the federal MCL of 5 ug/L that is spatially coincident with the maximum testing boundary, we consider this ‘boundary exceedance’. If the testing boundary and the plume boundary do not intersect, and the plume is entirely within the testing boundary, we consider this ‘plume capture’ (Figure 1).



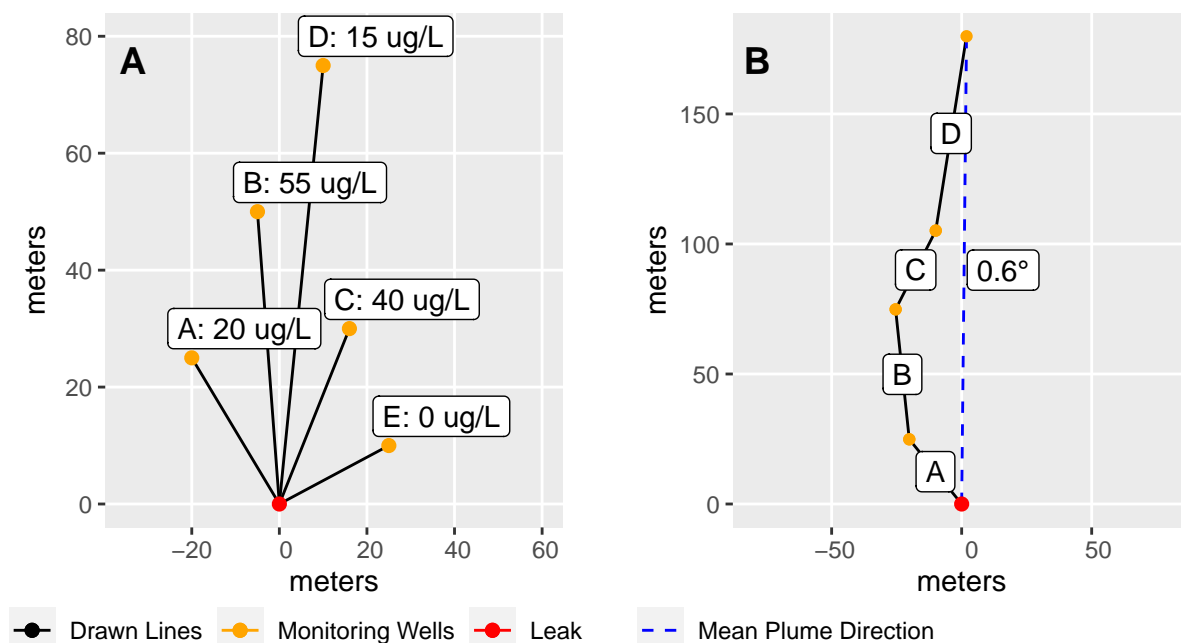
**Figure 1.** Example of Plumes that are completely captured by monitoring wells (A) and plumes which likely travel beyond the extent of monitoring wells (B).

### 2.4 Normalizing Plume Direction

We map the distribution of monitoring wells relative to the mean linear direction of a benzene plume. To determine the mean linear direction of benzene movement through the ground, we use weighted vector addition to determine the mean angle of flow in de-

124 grees from north. We then artificially rotate the plumes so that they are normalized to  
 125 one direction (due north) and overlay them to map out monitoring wells relative to the  
 126 leak point and direction of flow and regardless to actual location. Coordinate math was  
 127 done using the sf package (Pebesma, 2018) and bearing directions were calculated using  
 128 the stplanr package (Robin Lovelace & Richard Ellison, 2018). Data cleaning relied  
 129 on the tidyverse package (Wickham et al., 2019). To weight monitoring wells, benzene  
 130 concentrations were multiplied by the distance in meters of the monitoring well from the  
 131 LOP. Lines were then created using existing bearings for each monitoring well from the  
 132 LOP and lengths from weighted distances. Lines were then redrawn end to end and the  
 133 mean linear direction was calculated as the bearing between the LOP and the end vertex  
 134 of the final weighted line (Figure 2).

### Example of Plume Mean Linear Direction Calculation



135 **Figure 2.** Illustration of mean direction calculation. Panel A shows actual locations and con-  
 136 centrations of benzene relative to LOP. Panel B shows weighted vector math result with mean  
 137 linear direction calculation.

138 For area analyses, we included all benzene samples in Geotracker which were taken  
 139 at LUST cleanup sites and were analyzed as either ug/L or mg/L (91.3% of all samples).

Measurements in mg/L were converted to ug/L. In total, we included 3,495 sites which had at least 3 monitoring wells with benzene concentrations exceeding 5 ug/L so that a two-dimensional space could be delineated. These sites contained 63,916 spatially unique monitoring wells, with 1,545,731 benzene samples, 526,060 of which met or exceeded 5 ug/L.

## 2.5 Statistical Analysis

To determine if there is a statistically significant difference in plume sizes depending on whether a site exhibited boundary exceedance or plume capture we used the Wilcoxon test. If sites exhibiting plume capture are significantly different then sites exhibiting boundary exceedance, it could indicate that testing at sites that exhibit boundary exceedance are not effectively monitoring the plumes. Finally, we show the measured distances from the LOP for all monitoring wells used in the two-dimensional analysis to contextualize the findings of the Wilcoxon test.

## 3 Results

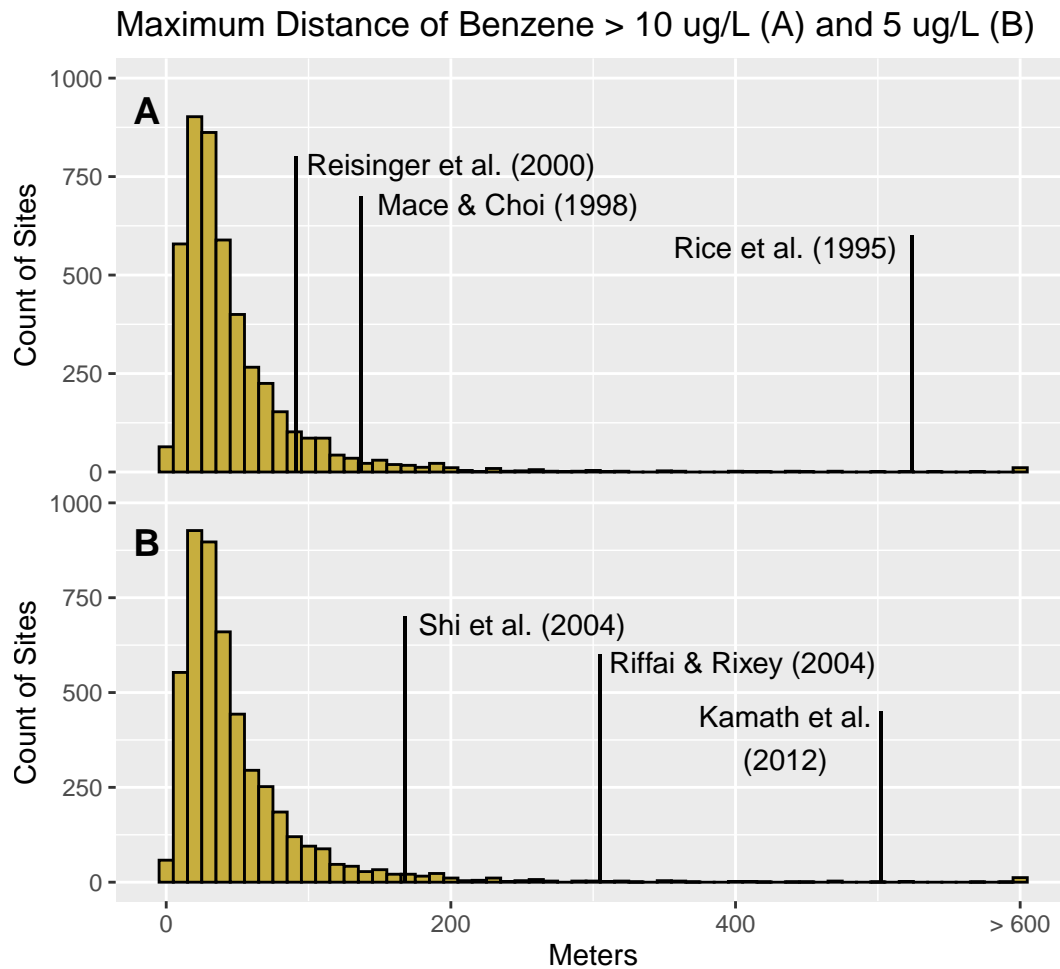
### 3.1 Maximum Plume Distance

Plume maximum distances were calculated for 5,624 sites which had measurable distances (at least 2 unique monitoring wells) with  $\geq 10 \text{ ug/L}$  and 5,881 sites which had measurable distances with  $\geq 5 \text{ ug/L}$  (Figure 3). The median distance for plumes delineated at 10 ug/L was 27.7249 meters. The 90th percentile distance of plumes delineated at 10 ug/L was 84.2 meters. The median distance for plumes delineated at 5 ug/L was 29.42471 meters. The 90th percentile distance of plumes delineated at 5 ug/L was 87.4 meters

Figure 3 shows the maximum distance benzene that was measured from the point of origination. The 90th percentile for benzene distance is 595 feet for 5 ug/L which falls within the findings of Connor et al. (2015).

### 3.2 Directionally Normalized Plumes and Study Areas

We found 3,495 plumes with at least 3 points with benzene concentrations  $\geq 5 \text{ ug/L}$ . We calculated mean linear direction of benzene flow and rotated each plume to due north.



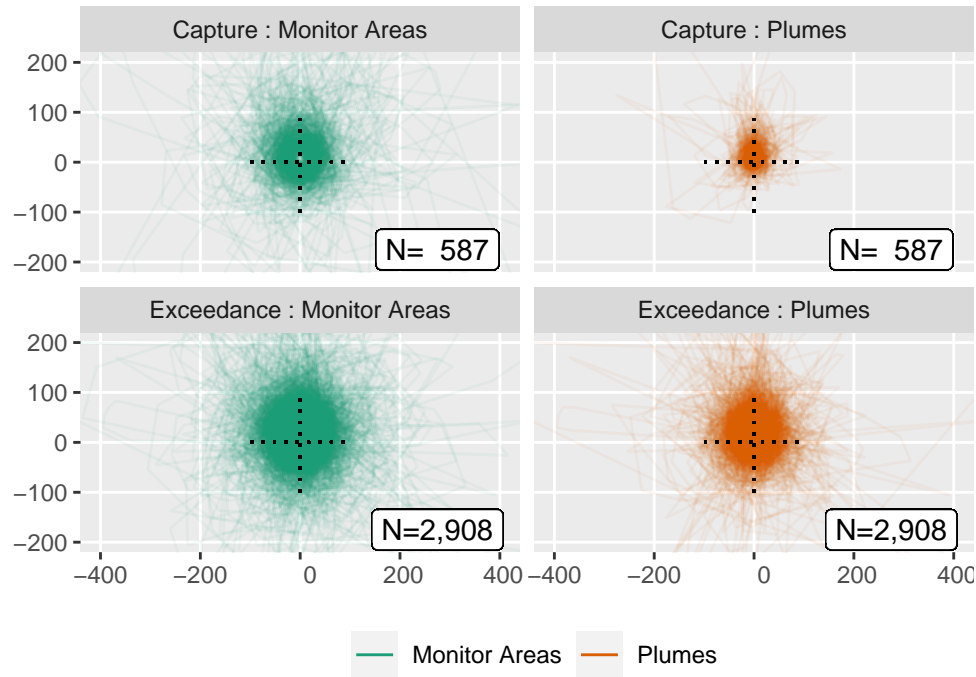
**Figure 3.** Histogram of maximum measured distance of benzene plumes in meters using thresholds of 10 ug/L (A) and 5 ug/L (B). Maximum distances from previous studies are overlaid. The width of bins is 10m.

Each plume was overlaid by shifting the leak origination point to the coordinates (0,0) in the California albers projection.

### 3.3 Wilcox Test

2,908 of 3,495 cleanup sites had an exceedance of 5 ug/L at the testing boundary (83.20458). Figure 4 illustrates that when plumes are completely captured (spatially), they are generally smaller than if plumes extend to the boundary of a monitoring network. The results of the Wilcox test (Table 1) show a significant difference between the measured plume areas at sites where boundary exceedance was observed and at sites where entire plume capture was observed (figure 5). Plume areas are statistically larger at sites



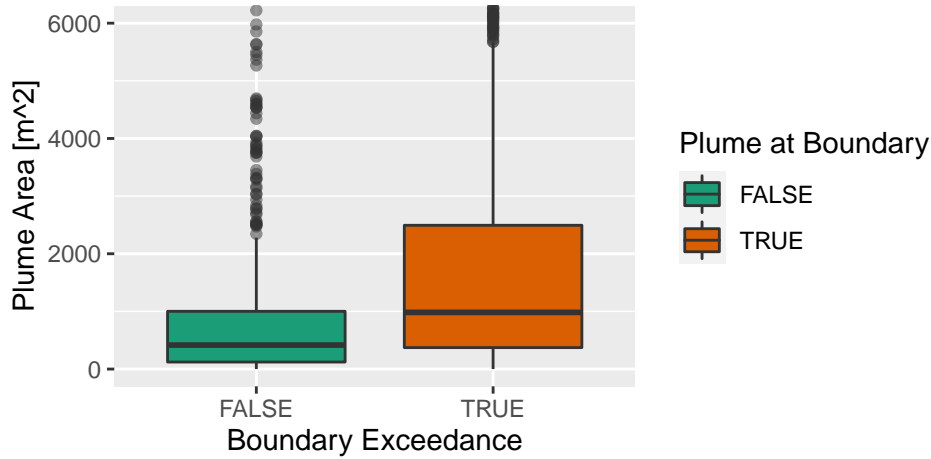


**Figure 4.** Visualization of all monitoring areas and plume areas superimposed on top of each other. Line transparency = 95 percent.

where plumes were entirely captured, and the majority of plumes exhibited boundary exceedance across their monitoring well extents. The median plume area where plume capture was observed was 416 m<sup>2</sup>. The median plume area where boundary exceedance was observed was 983 m<sup>2</sup>, more than twice as much area as plumes that were spatially captured.

**Table 1.** Wilcox Test Results

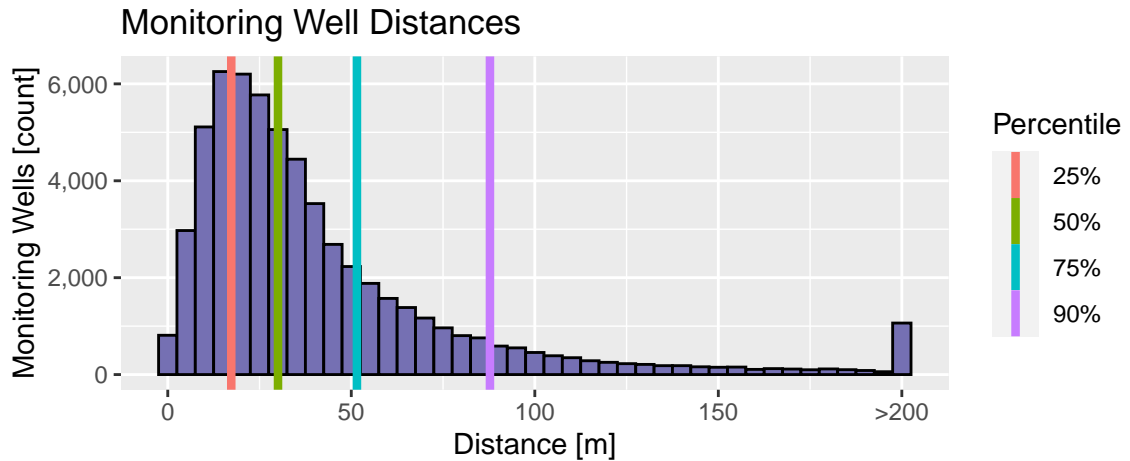
Y	Group 1	Group 2	n1	n2	Statistic	p	Effect
Area_m	FALSE	TRUE	587	2908	559822	0	0.2228



**Figure 5.** Visualization of plume areas by whether they exhibited boundary capture (green/left) or boundary exceedance (brown/right).

### 3.4 Monitoring Well Distances

The distances of all spatially unique monitoring wells were measured from their respective LOPs. Figure 6 shows a histogram as well as the 25th, 50th, 75th and 90th percentiles of maximum benzene plume distances. The median distance of all monitoring wells from the LOP was 30.03 meters. 90% of monitoring wells were within 87.78 meters of the LOP.



**Figure 6.** Histogram of monitoring well distances used in area analysis with the 25th, 50th, 75th and 90th percentiles overlaid. Bin width = 5m

## 4 Conclusions & Discussion

While statistically, the maximum distance of 90% of plumes falls within the bounds of previous research, this is not necessarily the best way to consider potential impacts of petroleum hydrocarbons in the environment. California for example has particularly strict reporting requirements, meaning that even very small releases are documented, and the sites undergo soil and groundwater testing, leading to a disproportionate weighting of plumes towards smaller releases relative to documented releases in other states which have reporting requirements more aligned with federal regulations. However, there are still many plumes of concern that reach beyond the ninetieth percentile, in this case 589 sites. Further, our research finds that the vast majority of plumes recorded are likely larger than previously thought, with maximum distances that are longer than have been reported in the data. While previous research has not stated whether or not plumes were entirely captured by monitoring, it stands to reason that prior site investigations may have suffered from the same limitations as are present in the geotracker data. Limitations to testing often include both physical impediments and property boundaries. For example, many gas stations are located in urbanized areas, meaning that impervious, paved surfaces and other structures can limit the areas where testing is possible. Additionally, there may be several other private properties within a very small distance, making getting permission to test difficult. Releases can enter the ground in many ways. The release can originate underground, directly from a tank that has suffered corrosion, or from leaky piping connections, or it can originate on the surface from a spill or overfill and migrate into the ground directly, or through overland flow and via preferential pathways such as cracked pavement.

Our findings suggest that plumes are larger than the data suggests. Plumes are significantly larger when they are not captured by monitoring wells, suggesting that the sites which exhibit plume capture may be doing so simply because they are smaller in two-dimensional area. Larger plumes are less likely to be completely captured because the burden for doing so is higher. While the limitations of testing in the real world are clear, and are not likely to be overcome in their entirety, this research clearly shows that there is still much that is unknown about how benzene plumes move through the environment and how much area they can impact in unsafe levels. There is a need for better modelling and understanding of these plumes. If we are able to more effectively model the full extent of benzene plumes, we may be able to aid in future site investigations with-

out an additional burden on agencies responsible for site testing and characterization. While on-site sampling will always be the most reliable way to characterize a plume, additional modelling and understanding may help future site investigations to be more efficient by helping to prioritize monitoring well locations.

## Acknowledgments

The authors of this paper have no conflicts of interest to declare. The views expressed in this paper are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency. All analysis, statistics and spatial analyses were completed using R version 4.1.2. All California LUST data were obtained from the California Water Board’s Geotracker public portal ([https://geotracker.waterboards.ca.gov/data\\_download](https://geotracker.waterboards.ca.gov/data_download)). All code used in this research is publicly available on GitHub ([https://github.com/USEPA/ORD\\_Plume\\_Paper](https://github.com/USEPA/ORD_Plume_Paper)).

## References

- CA Water Board. (2022). *Geotracker: Download esi data*. Retrieved from [https://geotracker.waterboards.ca.gov/data\\_download\\_by\\_county](https://geotracker.waterboards.ca.gov/data_download_by_county) (Accessed: 2022-01-15)
- California Legislature. (1984). *Health and safety code - hsc division 20. miscellaneous health and safety provisions [24000 - 26250], chapter 6.7. underground storage of hazardous substances 25294*. [https://leginfo.ca.gov/faces/codes\\_displayText.xhtml?lawCode=HSC&division=20.&title=&part=&chapter=6.7.&article=](https://leginfo.ca.gov/faces/codes_displayText.xhtml?lawCode=HSC&division=20.&title=&part=&chapter=6.7.&article=) (Accessed: 2022-03-15)
- California Legislature. (2003). *Health and safety code - hsc division 20. miscellaneous health and safety provisions [24000 - 26250], chapter 6.7. underground storage of hazardous substances 25295.5*. [https://leginfo.ca.gov/faces/codes\\_displayText.xhtml?lawCode=HSC&division=20.&title=&part=&chapter=6.7.&article=](https://leginfo.ca.gov/faces/codes_displayText.xhtml?lawCode=HSC&division=20.&title=&part=&chapter=6.7.&article=) (Accessed: 2022-03-15)
- California Legislature. (2013). *Health and safety code - hsc division 20. miscellaneous health and safety provisions [24000 - 26250], chapter 6.7. underground storage of hazardous substances 25295*. [https://leginfo.ca.gov/faces/codes\\_displayText.xhtml?lawCode=HSC&division=20.&title=&part=&chapter=6.7.&article=](https://leginfo.ca.gov/faces/codes_displayText.xhtml?lawCode=HSC&division=20.&title=&part=&chapter=6.7.&article=) (Accessed: 2022-03-15)
- Connor, J. A., Kamath, R., Walker, K. L., & McHugh, T. E. (2015, 03). Review

- of quantitative surveys of the length and stability of mtbe , tba , and benzene plumes in groundwater at ust sites. *Groundwater*, 53(2), 195–206. Retrieved from <https://onlinelibrary.wiley.com/doi/10.1111/gwat.12233> doi: 10.1111/gwat.12233
- Kamath, R., Connor, J. A., McHugh, T. E., Nemir, A., Le, M. P., & Ryan, A. J. (2012, 04). Use of long-term monitoring data to evaluate benzene, mtbe, and tba plume behavior in groundwater at retail gasoline sites. *Journal of Environmental Engineering*, 138(4), 458–469. Retrieved from <http://ascelibrary.org/doi/10.1061/%28ASCE%29EE.1943-7870.0000488> doi: 10.1061/(ASCE)EE.1943-7870.0000488
- McHugh, T. E., Kulkarni, P. R., Newell, C. J., Connor, J. A., & Garg, S. (2014). Progress in remediation of groundwater at petroleum sites in california. *Groundwater*, 52(6), 898–907.
- Molson, J., Barker, J., Frind, E., & Schirmer, M. (2002). Modeling the impact of ethanol on the persistence of benzene in gasoline-contaminated groundwater. *Water Resources Research*, 38(1), 4–1.
- National Archives. (2022). *Code of federal regulations, title 40 / chapter 1 / subchapter 1 / part 280 / subpart e - release reporting, investigation, and confirmation.* <https://www.ecfr.gov/current/title-40/chapter-I/subchapter-I/part-280/subpart-E>. (Accessed: 2022-03-15)
- Pebesma, E. (2018). Simple Features for R: Standardized Support for Spatial Vector Data. *The R Journal*, 10(1), 439–446. Retrieved from <https://doi.org/10.32614/RJ-2018-009> doi: 10.32614/RJ-2018-009
- R Core Team. (2021). R: A language and environment for statistical computing [Computer software manual]. Vienna, Austria. Retrieved from <https://www.R-project.org/>
- Robin Lovelace, & Richard Ellison. (2018). stplanr: A Package for Transport Planning. *The R Journal*, 10(2). Retrieved from <https://doi.org/10.32614/RJ-2018-053>
- RStudio Team. (2020). Rstudio: Integrated development environment for r [Computer software manual]. Boston, MA. Retrieved from <http://www.rstudio.com/>
- Shih, T., Rong, Y., Harmon, T., & Suffet, M. (2004). Evaluation of the impact

295 of fuel hydrocarbons and oxygenates on groundwater resources. *Environmental*  
296 *Science & Technology*, 38(1), 42–48.

297 US EPA. (2021). *Semiannual report of ust performance measures*. [https://www.epa](https://www.epa.gov/system/files/documents/2021-11/ca-21-34.pdf)  
298 [.gov/system/files/documents/2021-11/ca-21-34.pdf](https://www.epa.gov/system/files/documents/2021-11/ca-21-34.pdf). (Accessed: 2022-03-  
299 15)

300 Wickham, H., Averick, M., Bryan, J., Chang, W., McGowan, L. D., François, R.,  
301 ... Yutani, H. (2019). Welcome to the tidyverse. *Journal of Open Source*  
302 *Software*, 4(43), 1686. doi: 10.21105/joss.01686