

Facility Fence Line Monitoring using Passive Samplers

Eben D. Thoma

U.S. EPA, Office of Research and Development, National Risk Management Research Laboratory, 109 TW Alexander Drive, E343-02, Research Triangle Park, NC 27711, USA

Michael C. Miller and Kuenja C. Chung

U.S. EPA Region 6, 1445 Ross Avenue, Suite 1200, 6PD, Dallas, TX 75202, USA

Nicholas L. Parsons and Brenda C. Shine

U.S. EPA, Office of Air Quality Planning and Standards, 109 TW Alexander Drive, E143-01, Research Triangle Park, NC 27711, USA,

ABSTRACT

In 2009, the U.S. EPA executed a year-long field study at a refinery in Corpus Christi, Texas, to evaluate the use of passive diffusive sampling technology for assessing time-averaged benzene concentrations at the facility fence line. The purpose of the study was to investigate the implementation viability and performance of this type of monitoring in a real world setting as part of U.S. EPA's fence line measurement research program. The study utilized 14-day time-integrated Carbopack X samplers deployed at 18 locations on the fence line and at two nearby air monitoring sites equipped with automated gas chromatographs. The average fence line benzene concentration during the study was 1075 pptv with a standard deviation of 1935 pptv. For a six-month period during which wind direction was uniform, the mean concentration value for a group of downwind sites exceeded the mean value of a similar upwind group by 1710 pptv. Mean value differences for these groups were not statistically significant for the remaining six-month time period when wind directions were mixed. The passive sampling approach exhibited acceptable performance with a data completeness value of 97.1% ($n = 579$). Benzene concentration comparisons with auto gas chromatographs yielded an r^2 value of 0.86 and slope of 0.90 with an approximately ($n = 50$). A linear regression of duplicate pairs yielded an r^2 of 0.97, unity slope, and zero intercept ($n = 56$). In addition to descriptions of technique performance and general results, time series analyses are described, providing insight into the utility of two-week sampling for source apportionment under differing meteorological conditions. The limitations of the approach and recommendations for future measurement method development work are also discussed.

38

39 **IMPLICATIONS**

40 Improved knowledge of air pollution concentrations at the industrial facility fence lines is a topic
41 of increasing environmental importance. Fence line and process monitoring can yield many
42 benefits ranging from enhanced risk management to cost savings through improved process
43 control. Efforts are underway within the U.S. EPA to develop and test a variety of cost effective
44 fence line monitoring strategies for potential use in a range of research and regulatory
45 applications. Among these, passive diffusive sampling is emerging as a promising technique for
46 time-integrated fence line monitoring applications.

47

48 **INTRODUCTION**

49 Development of cost effective and robust methods for detecting fugitive emissions and
50 monitoring air pollution concentration levels at industrial facility fence lines and remediation site
51 boundaries can yield many benefits. Implementable fence line and process monitoring systems
52 can enhance protection of public health and worker safety, advance emission inventory
53 knowledge, and realize cost savings by helping reduce product loss. A primary requirement for a
54 fence line monitoring system is that it provide adequate spatial coverage for determination of
55 representative pollutant concentrations at the boundary of the facility or operation. In an ideal
56 scenario, fence line monitors would be placed so that any fugitive plume originating within the
57 facility would have a high probability of intersecting one or more sensors, regardless of wind
58 direction. Sufficient measurement coverage can be accomplished using a small number of open-
59 path instruments¹⁻⁶ or through deployment of a larger number of point monitors. With either
60 approach, applications that require high detection sensitivity, chemical speciation, and fast time
61 response demand laboratory-class instrumentation which comes with significant capital and
62 operational cost. Currently, the expense of high performance, near real-time fence line
63 monitoring systems is likely perceived by industry to outweigh benefits. This is evidenced by
64 the lack of significant voluntary adoption causing potential benefits to go largely unrealized.

65

66 As part of U.S. EPA's fugitive emission research program, a variety of cost effective fence line
67 and process monitoring approaches are under investigation with aim to improve understanding

and facilitate broader access to these technologies. Under the program, both time-resolved and time-integrated measurement approaches are being explored. In long-term assessment or screening applications where sensitivity and speciation are important but time response is not critical, deployment of time-integrated passive diffusive samplers (PSs) with subsequent laboratory analysis is a promising and cost-effective fence line monitoring approach. This paper presents the results of a year-long field study using PSs to quantify fence line benzene concentrations at a refinery in Corpus Christi, TX. The objectives of the study were to evaluate the implementation feasibility, cost, and performance of the PS fence line monitoring approach and to assess the effectiveness of time-integrated sampling for source apportionment under varying meteorological conditions.

Flint Hills Resources collaborated with U.S. EPA in execution of this study by granting permission to deploy the PSs and by allowing access to their on-site leak detection and repair contractor for sample deployment. The study was performed at the Flint Hills West Refinery in Corpus Christi, TX which has a nominal crude oil refining capacity of approximately 260,000 bbl/day. The West Refinery includes typical refining operations such as fluid catalytic cracking and distillate hydrocracking, delayed coking, and associated petrochemical extraction and conversion process units. For the study period, production was relatively consistent although there were regularly scheduled maintenance and periodic shutdown and startup activities. Since the emphasis for this study was on the use and performance of the PS measurement approach and not on assessment of the actual emissions from the refinery, no attempt was made to gather detailed process or operation information. Due to the relative consistency of production throughout the year and the time-integrated nature of the measurement, it is believed that day to day production variability had little impact on observations or the data groupings suggested below.

EXPERIMENTAL METHODS

The use of PSs with a variety of designs and sorbent materials for ambient monitoring applications has been documented in the literature⁷⁻¹³ with much effort related to the development of monitoring protocols for the European Community Directive 2000/69/EC and daughter directives that set limits on ambient concentrations of hazardous air pollutants including

benzene. The current study utilized Carbopack X sorbent (≈ 650 mg) in ceramic-lined Perkin-Elmer (PE) tubes (Supelco, Inc., Bellefonte, PA), 6 mm in dia. by 90 mm length, with laboratory analysis by thermal desorption gas chromatograph (TurboMatrix ATD, PerkinElmer Instruments LLC, Shelton, CT and Saturn 2000 GC/MS, Agilent, Santa Clara, CA). Information on use of Carbopack X sorbent for determination of the concentration of benzene and other volatile organic compounds in ambient air¹⁴⁻¹⁷ along with details on the custom Carbopack X PE tubes and laboratory analytical procedures used in this study are summarized by McClenney, Mukerjee, and others.¹⁶⁻¹⁹

For this study, a two-week PS deployment schedule was utilized. Each PS was exposed to ambient air for a 14-day period (P) and then replaced with an unexposed PS. A total of 26 PS sets, designated P1 through P26, were deployed from December 3, 2008, to December 2, 2009. The PS set change was executed between 8:00 a.m. and 11:30 a.m. and required approximately 1.5 hours to complete with additional time for record keeping and shipping to the laboratory for analysis. For cost efficiency, samples were analyzed and samplers were reconditioned for redeployment in batches requiring multiple sets of PSs to be used to prevent sampling discontinuity. The PSs were covered with a rain shield and attached to the boundary fence of the facility at approximately 1.5 m above the ground. The samplers were changed by the facility leak detection and repair (LDAR) contractors who were trained by EPA representatives in proper procedures prior to the study. Additional information on study execution can be found in the quality assurance project plan.²⁰

The PSs were deployed at 18 locations on the fence line of the Flint Hills Refinery West Facility in Corpus Christi, TX, and at two Texas Commission on Environmental Quality (TCEQ) continuous air monitoring station (CAMS) sites: C633, south of the facility (Fig. 1); and C634, located approximately 10 km east of the facility (not shown). The PS locations (loc) are labeled by their approximate angular position as observed from the center of the facility with north representing zero degrees. The configurations of the PSs were fixed for the study with the exception of loc 40, 50I, and 60 which were added during P12 to help diagnose high observed concentrations in the vicinity of loc 50. Duplicate and field blanks were deployed at loc 180 and C633, with duplicates added to loc 360 during P22. TCEQ CAMS sites C633 and C634

performed automated gas chromatograph (GC) benzene measurements providing one hour average concentration values (Clarus Model 500 GC, Perkin-Elmer, Waltham, MA) and PSs were placed at both locations for comparison purposes. Also shown in Figure 1 are TCEQ CAMS sites C631 and C632, which did not operate auto GCs but provided total nonmethane organic carbon (TNMOC) measurements and meteorological data useful for future comparisons.

The PS data set produced by the year-long deployment consisted of 579 samples, including 56 duplicates and 49 field blanks. Seventeen samples were excluded from the analysis due to combination of tube damage or deployment issues ($n = 6$) and laboratory equipment malfunction ($n = 11$), yielding a data completeness value of 97.1%. The benzene concentration data for 10 samples exceeded the demonstrated linearity range of 4071 pptv for the analytical system utilized and, as a consequence, these values contain additional uncertainty estimated to be below 20%. Further information on the PS configuration, deployment, and laboratory analysis can be found in the quality assurance project plan and supplemental information.²⁰

RESULTS AND DISCUSSION

The objective of this study was to gain information on the implementation feasibility and measurement performance of the two-week passive samplers in a real-world fence line deployment scenario. Information such as overall data completeness, duplicate and field blank data, site to site trend consistency, and comparisons with automated gas chromatographs help form a basis for judging the efficacy of the overall measurement approach. The results section begins with a description of meteorological conditions encountered during the study and PSs validation data. An overview of the combined fence line results by location and period are then presented. This information is followed by a discussion of time series results and upwind vs. downwind comparisons under uniform and mixed wind direction conditions. The latter data is important because it provides valuable insights on the general utility of time-integrated monitoring for determining a facility's contribution to the observed fence line concentrations.

Meteorology

The 14-day average of hourly wind direction (WD), scalar wind speed (SWS), vector resultant wind speed (RWS), temperature (T), and relative humidity (RH) data recorded by the C633

site²¹ are summarized in Table 1. The SWS represents a simple average of hourly values of wind speed for the two-week period. The RWS was determined by first calculating the orthogonal vector components (north = 0 °, east =90°) for each hourly reading, averaging individual components for the period, then calculating the magnitude of the resulting vector. The RWS increases from zero with decreasing WD variability, approaching the value of SWS when winds are highly uniform over the two week period. The difference in RWS and SWS is one of several ways to quantify the degree of wind direction uniformity which is important for time-integrated sampling approaches. Confidence in meteorological data acquired from the TCEQ CAMS site is bolstered by State's quality assurance requirements and additionally by well-correlated cross checks with nearby CAMS sites for important meteorological variables.

In comparison to other parts of the U.S., Corpus Christi exhibits strong wind speeds and periods of highly uniform wind direction which can have a significant effect on comparative analysis with time-integrated monitors. In preparation for discussion on this point, two six-month groupings of wind data from the study are presented in Figure 2. Figure 2a shows a wind rose for a grouping of P1-P6 coupled with P20-P26 and reflects a period of relatively mixed wind directions. Figure 2b shows a grouping of P7-P19 exhibiting a continuous six month period when the wind direction was more uniformly from the southeast. For the grouping of Fig. 2a, the average difference in SWS minus RWS is 7.0 mph, whereas for the more uniform case the difference is 2.8 mph. A six month grouping of neighboring periods was chosen for simplicity with period cut-off decided by comparing the SWS and RWS values for individual periods.

PS Validation Results

Benzene concentration data determined by PSs were compared to the 14-day average of 1 hour data from the GCs at the C633 and C634 sites. A linear regression of PS and GC data (Figure 3) shows an unconstrained r^2 value of 0.86 and slope of 0.90 ($n = 50$ using average values for 26 duplicate pairs at C633). The Method Detection Limit (MDL) for the PS was determined to be 35 pptv and the MDL for the GC was found by TCEQ to be 50 pptv for benzene for the study period. Figure 3 utilizes all reported GC data which includes a significant number of hourly values below the MDL (25%) with a disproportionate number occurring in the P7-P19 periods with winds away from the facility. As an example, for P14-P19, only 1036 of a possible 3427

GC values were above the MDL. For the same time period, the average value of the PS concentrations at the GC locations was 139 pptv with a minimum of 85 pptv, significantly above the MDL, owing to the time-integrated nature of the sampling approach. The y-intercept value of 142.2 pptv in Figure 3 is largely determined by the decision to include all available GC data in the comparison. Removing all GC data below the MDL gives a linear regression r^2 value of 0.78, a slope of 0.87 and a y-intercept of 91.85 pptv. These data comparisons ultimately depend on the definition of Minimum Quantization Limit (MQL) and the choice for assignment of fixed values for below MQL entries. This highlights a difficulty in comparing time-integrated and time-resolved approaches which is not of major concern for current discussion on fence line monitoring where levels significantly above MDL are of primary importance.

The range of comparison for the PS and GC data (≈ 100 pptv to ≈ 1000 pptv) is somewhat lower than optimal for validation purposes. The low upper limit on two-week average concentrations at the TCEQ sites was due in part to their locations that were significantly displaced from the fence line of the facility. While not optimal, the upper limits of comparison are reasonable when considering the overall PS study average for fence line locations was ≈ 1000 pptv. To achieve higher ranges of comparison, future field studies should consider co-deployment of PS and GC on the fence line of facility near areas of high expected concentration. In addition to Figure 3, time series comparisons of C633 GC and C633 PS providing further validation information are discussed in a subsequent section.

Duplicate PSs were located at C633 and loc 180 for all periods, and at loc 360 for P22 through P26 (Figure 4). Concentrations of duplicate pairs ranged from approximately 100 pptv to 1200 pptv with a linear regression $r^2 = 0.97$, unity slope, and near zero intercept, $n = 56$. The average difference in the duplicate values was 8.5% with a maximum of 33% occurring for a low range reading (229 pptv vs. 333 pptv). Duplicates were added to loc 360 during P22 in response to high readings observed in P14 and P15. The delay in deployment of the duplicates was due to the batch processing of samples, which delayed data availability. Field blanks deployed at loc 180 and C633 had an average value of 8.0 pptv with a standard deviation of 6.2 pptv, $n = 49$. Supplemental table S1 contains all duplicate, GC, and field blank data for the study.²⁰

PS Fence Line Results

A total of 454 PSs were deployed at 18 fence line sites around the facility (Fig. 1). Combining all fence line PS results, the mean benzene concentration was 1075 pptv with a standard deviation (s) of 1935 pptv. The PS median value was 709 pptv with a minimum of 122 pptv and a maximum of 29280 pptv. With fence line-deployed duplicates averaged, 8.5% of readings were above 2000 pptv, 21.2% were between 1000 and 2000 pptv, and 70.3% were below 1000 pptv. Fence line PS data, along with the off-site C633 PS data, are summarized by location in Figure 5. The C633 PS has a mean benzene concentration value of 318 (s = 160) pptv, slightly below neighboring fence line sites, loc 250 ($\approx$ 630 m away) with a mean value of 416 (s = 183) pptv, and loc 270 ($\approx$ 510 m away) with a mean value of 395 (s = 121) pptv. The differences in the means of C633 compared with loc 250 and separately with loc 270 are statistically significant at $\alpha = 0.05$ with t-test p-values of 0.042 and 0.048, respectively. The ability to detect differences in PSs deployed on the fence line and at proximate off-site locations is potentially important in future gradient-based source comparison strategies.

PS benzene concentration values on the predominately upwind southern fence line, consisting of loc 130 through loc 250, show a group mean of 613 (s = 353) pptv, lower than the northern fence line (loc 310 through loc 50) having a group mean of 1840 (s = 3169) pptv with group mean difference p-value < 0.001 . Excluding the two extreme outliers at loc 360, the northern fence line group mean is 1512 (s = 1494) pptv with similar group mean difference p-values.

Figure 6 shows PS benzene concentration data for a subset of fence line locations by sampling period (loc 40, 50I, and 60 are not included due to incomplete sets). The mean values and number of outliers (values that extend beyond 1.5 times interquartile range) are somewhat higher in the warmer months and lower in the cooler months. It is not known if these differences are due to higher emissions or to the effects of atmospheric conditions on ground level concentrations at different times of the year. Since PSs comparisons with auto GC show little seasonal variation (next section), these differences are not believed to be due to measurement bias.

As discussed in the text associated with Figure 2, it can be informative to form two six-month groupings of PS results from neighboring time periods. This is performed here with the spatially integrated data of Figure 6 and in a subsequent section by resolving the locations into upwind and downwind subgroups. The mixed wind direction six-month group (Fig. 2a) contains cooler months (average $T = 68^{\circ}\text{F}$) and has a mean benzene concentration value of 798 ($s = 414$) pptv, $n = 188$. The uniform wind direction grouping (Fig. 2b) has a higher average temperature ($T = 80^{\circ}\text{F}$) and a mean concentration value of 1288 ($s = 2799$) pptv, $n = 192$. There is a statistically significant difference in group means ($p = 0.017$) for these sets. For this data comparison, 88.5% of readings above 2000 pptv occur in the P7-P19 uniform wind group. These observed differences were not due to changes in refinery operations as production levels were confirmed to be relatively consistent throughout the study period.

Time Series Comparisons

Techniques for temporal analysis of fence line monitoring data are determined in large part by the time resolution of the measurement. For example, monitoring schemes with time resolutions less than one hour can utilize intra-day trend analysis and metrological comparisons to help apportion local source contributions. The time-integrated nature of the PS approach makes it less useful in this context; however, important information on longer-term temporal and spatial trends can be gained through time series comparisons. Since the implementation cost of the PS approach is lower than similar density deployments of time-resolved monitors, passive sampling has clear advantages for acquisition on longer-term trend information.

Figure 7 examines the southern fence line benzene concentrations from the C633 auto GC, the collocated C633 PS, and the average of two nearby sites, loc 250 and loc 270. Similar trends in the concentrations are evident. For example, comparatively lower concentrations in P7 and P9 through P19 are observed for both the PS and auto GC even though the overall average concentration for the fence line sites is higher for these periods (Fig. 6). Basic wind direction expressed as the percentage of winds coming out of the southern hemisphere is shown on the secondary y-axis. During periods P7, P11, and P14-P20, winds are directionally towards the north, transporting facility source signal away from the southern fence line samplers, resulting in lower observed concentrations. A linear regression comparison of C633 PS data

with a percentage of southerly winds yields an unconstrained r^2 value of 0.87. This relatively high correlation indicates that the PS readings are likely influenced by emissions transported from the facility and also that the two-week time-integrated sampling approach is able to register changes in prevailing wind orientation with respect to the source.

The similarity in the time series for the fence line PS (loc 250 and loc 270) and the offsite PS (C633) provides some confidence that the mobile sources using Interstate Highway 37, located between the observation points (Fig. 1), are not producing significant interfering benzene signal. If this were the case, divergence in the time series with changing prevailing winds would be expected. The time series shown in Figure 7 also provides supporting validation information for the PS by showing similar period-to-period variations of the PS compared to the auto GC. Similar comparative results were also observed for the C634 site. These comparisons, taken over the year-long study, provide some evidence that seasonal changes in temperature and humidity have little effect in PS performance for the range of conditions encountered in this field campaign.

Ideally, the fence line PSs should be deployed away from obstructions which can impede wind flow and also away from potential interfering sources outside of the fence line. Both of these situations can lead to elevated concentrations measured by the PS that are not due to the observed facility. Time series analysis along with deployment of additional diagnostic samplers can be used to help understand elevated PS readings and to identify PS siting and interfering source issues. Figure 8 shows PS benzene concentrations in the neighborhood of loc 50 (Fig 1.), which is positioned in a complicated environment including complex local topography and potential neighboring sources. The ground level to the southwest, near loc 50I, is elevated by approximately 2 m compared to the location of loc 50. This local topography could cause complex wind flow (channeling or vortices) in the neighborhood of loc 50 potentially affecting measured concentrations. Potential sources such as the barge loading operations to the north and the wastewater treatment to the southeast are outside the defined fence line. Location 50 exhibited the first notably high concentration during P7 and, in response to this reading, several additional PS sites were implemented (loc 40, 50I, and 60) during P12. These samplers also showed somewhat elevated concentrations prior to P20, but the results are difficult to correlate

with loc 50 values or wind direction. For this fence line location, the combination of topography and additional potential sources makes it difficult to draw conclusions about emissions from the primary observed target, the facility to the southwest. For example, the PS at loc 50I is inside the fence line, closer to the potential facility sources (tanks). Due to proximity, we would expect higher concentrations at loc 50I compared to loc 50 if the primary source were the observed facility, all other factors being equal. Additionally, the three highest readings at loc 50 occur during P7, P11, and P16 with a high percentage of winds from the south (Fig. 7) and more specifically from the southeast (Fig 2b). This fact, coupled with the relative response of neighboring PSs, implies that the wastewater treatment area outside the defined fence line is a likely interfering source.

A strength of PS-based fence line monitoring is in providing cost-effective, high spatial density long-term monitoring capability. As evidenced by the results of Figure 8, a weakness of time-integrated monitoring lies in its inability to apportion contributions to the measured concentration in complex source and micrometeorological conditions. In cases where additional source apportionment capability is required, the PS approach can be selectively augmented through the use of time-resolved fence line monitoring coupled with wind direction analysis.

The time series of Figure 9 illustrates the elevated nature of data acquired downwind of the facility and also provides some perspective on extreme outlier readings. In comparison to upwind site loc 130, the downwind sites register consistently higher benzene concentrations, especially during P7-P19 where winds are uniformly from the southeast. The two highest readings were recorded at loc 360 during P14 and P15 (29,280 pptv and 20,007 pptv, respectively). These outlier values are significantly elevated compared to the third highest reading of 8891 pptv (loc 20, P11) and are ≈ 6 standard deviations displaced from the northern fence line group average of 1840 pptv. At approximately 5 times the demonstrated analytical linearity range for this study, the accuracy of the P14 and P15 outlier readings is uncertain. However, the occurrence of significantly elevated values at loc 360 during these periods is not unexpected when considering the elevated neighboring observations in the time series of Figures 8 and 9.

Two-week integrated PS readings at the 30,000 pptv level are somewhat difficult to understand since if these readings are not due to gross analytical error, they are a result of either sustained elevated concentrations transported by the wind to the sampling location or a shorter time duration intense spike in local concentration in close proximity to the PS caused by a transient source. Since the two similar outlier values were produced from separate sorbent tubes and analyzed during different laboratory runs, it is unlikely that analytical error is the cause of the elevated readings. The explanation of sustained elevated benzene concentrations at the PS is somewhat unlikely considering loc 360 is over 300 m distant from the nearest above-ground facility structure (tanks to the south east, Fig. 1). These observations do not preclude the presence of a below-ground emission or a temporary source not obviously part of the facility fence line observation. An unknown or temporary source, such as a rail car, could have been located in very close proximity to the loc 360 PS thereby causing a large integrated response.

A local benzene spike could include an actual emission or could be attributed to a sample handling issue. As an example of the latter, the field operators were instructed not to refuel their vehicles prior to sample handling to reduce the chance that gasoline vapor entrained on their hands could provide an intense concentration spike to the PS when uncapped during deployment. This type of sample corruption could affect two successive sampling periods as both the pick-up of the deployed PS and the placement of the new PS occur at similar times. This type of deployment error can be investigated by looking at neighboring samples (loc 20 and loc 330), which in this case were deployed within seven minutes before and after the loc 360 P15 PS and did not show abnormally high results. In future PS protocol development work, placement of secondary samplers with offset deployment schedules could assist in diagnosing outlier issues. These secondary samplers could be analyzed only when abnormal results arise to minimize cost for this diagnostic.

Upwind vs. Downwind Comparisons

A primary objective of any fence line monitoring strategy is to positively identify the observed facility's contribution to the measured concentrations. One way to accomplish this is by comparing the concentrations registered by the monitors stationed upwind (UW) of the facility with downwind (DW) sampling locations with the difference indicative of emissions. Since

meteorological conditions change over time, the designation of UW and DW monitors is mutable. When using time-resolved fence line monitoring instrumentation, this UW vs. DW comparison is accomplished by reviewing measured concentration data in conjunction with simultaneously acquired meteorological data. When using two-week time integrated PSs, this approach is less viable, especially in cases where the wind direction is mixed.

To investigate this effect, we can compare uniform and mixed wind direction scenarios by using the two six month periods defined in Figure 2. An UW group, consisting primarily of southern fence line sites (loc 90 through loc 270), and a DW group (loc 290 through loc 20) can be formed for both the P1-P6, P20-P26 mixed wind direction case (Fig. 2a) and the P7-P19 uniform wind direction case (Fig. 2b.) For the mixed wind direction case, the UW mean is 768 ($s = 366$) pptv and the DW mean is 718 ($s = 297$) pptv [Fig 10(a)]. Differences in these group means are not statistically significant (p -value = 0.330). For the uniform wind direction case, the UW mean of 487 ($s = 277$) pptv is significantly lower than the DW mean, 2197 ($s = 4361$) pptv with a p -value = 0.003 [Fig 10(b)]. Excluding the two high outliers at loc 360, the DW mean becomes 1473 ($s = 1371$) pptv with an improved p -value of <0.001 for a mean difference comparison with the UW samples. Comparing across the mixed and uniform wind direction cases, the UW means are also statistically different from each other at the 99% CI. For multi-month groupings of two-week PSs, it is possible to resolve UW and DW differences in the case of highly uniform wind direction. However, it is difficult to draw conclusions on facility contributions to the measured fence line concentrations using a simple UW-DW approach for the mixed wind direction case that may be more typically encountered in other areas of the U.S.

To further investigate the effects of wind direction, Figure 11 plots the percentage difference in UW and DW benzene concentrations with a metric indicative of wind direction uniformity formed by calculating the percentage difference in the scalar and resultant vector wind speeds (SWS and RWS in Table 1). For periods with uniform wind direction, SWS and RWS are similar, so emissions from the facility are transported toward the DW sampling locations a high percentage of the time, resulting in a larger difference in the UW and DW concentrations. As the difference in SWS and RWS increases, the temporal overlap of the facility-generated plume is more equally shared between the UW and DW samplers, so their percentage difference decreases

and actually becomes slightly negative during the winter months as the UW leg experiences higher concentration on average. The relationship expressed in Figure 11 depends on the definition of UW and DW sites which may change throughout the year based on site-specific metrological conditions.

The ability to resolve statistically significant differences in PS concentrations using fence line deployed PSs depends on the degree of wind direction uniformity and also on factors such as sampling time integration, wind speed (degree of stagnation), and on the offset distance of PS from facility sources (dilution effects). At 14 days, the time duration of sampling used for this study was judged to be an optimal trade-off between time resolution and cost. To help increase the diagnostic capability of the two-week PS approach, future protocol development could include a significant number of off-fence line sites set back from the primary monitors so as to allow concentration gradient analysis to aid in deciphering facility contributions under mixed wind direction cases. The reduction in concentration by atmospheric dispersion along the gradient will help provide source apportionment information. Additionally, ways to systematically define UW and DW site groups based on statistical comparisons of concentrations on a rotating sector basis should be explored.

CONCLUSIONS

This field demonstration provides first-level validation data for the PS fence line monitoring approach while informing future method development needs. With high data completeness rates, the year-long study provides evidence that the approach is relatively robust and implementable by modestly trained personnel. Based on cost figures from the current study, the expense for commercial application of a standardized method is projected to be below \$200 per sample for a single component analysis. The implementation factors for the PS approach are attractive in comparison to similar density deployments of time-resolved monitoring technologies which can come at much higher capital and operational costs.

The PS fence line concept can provide useful information on overall concentration levels and potential problem areas on the facility fence line using simple source identification techniques such as upwind-downwind comparisons, temporal trend investigation, and gradient analysis. A

weakness of the time-integrated approach is found when attempting source apportionment in complex environments. In this event, elevated concentration areas found in the PS screen can be further investigated with selective use of time-resolved monitoring where deemed necessary. The use of PS alone or in combination with optimally deployed time-resolved monitors can form the basis for cost effective and flexible fence line monitoring strategies.

Remaining method development questions center on establishment of PS performance with a wider concentration range and the expansion to compounds other than benzene. Future validation work should consider GC placement at downwind fence line locations to expand the range of comparison and potentially include the deployment of spikes duplicate samples to investigate out gassing effects. New deployment strategies must also be developed to allow effective source apportionment for the observed facility in areas with mixed wind directions and higher percentages of stagnant conditions. These deployment strategies are envisioned to include a gradient sampling approach with PS monitors placed progressive distances from the fence line. Another area for improvement is optimized duplicate deployment strategies to provide additional quality assurance information in the event of anomalous primary readings. For cases of complex sources or joint property fence line deployments, low-cost open-path, time-resolved monitoring will be evaluated as a way to cost effectively augment the PS screening approach.

ACKNOWLEDGMENTS

This work reflects the contributions of many individuals. In particular, the authors acknowledge the efforts of Jan Golden and Eric Kaysen with Flint Hills Resources for their collaboration; Karen Oliver, Hunter Daughtrey, Tamira Cousett, and Herb Jacumin with Alion Science and Technology for analytical support under EPA ORD contract EP-D-05-065, Mark Modrak of ARCADIS for project coordination under EPA ORD contracts EP-C-04-023 and EP-C-09-027 and many individuals with Shaw Environmental, Inc., for deployment of the passive samplers. We would like to thank Edward Michael, Vincent Torres, and David Allen with the University of Texas and David Brymer and Chris Owen with TCEQ for their assistance in acquiring auto GC validation data. We appreciate the direction and support of Robin Segall, Jason DeWees, Raymond Merrill, and ConnieSue Oldham with U.S. EPA's Office of Air Quality Planning and

Standards and the quality assurance assistance of Bob Wright and Dr. Joan Bursey with U.S. EPA's Office of Research and Development.

DISCLAIMER

This article has been reviewed by the Office of Research & Development, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the agency nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

REFERENCES

1. Fischer, C.; van Haren, G.; Chaudhry, A.; Weber, K. Detection of potential leakage at a biogas production plant with open-path FTIR measurement techniques - A case study. *Gefahrst. Reinhalt. Luft* **2006**, 66 (10), 426-430.
2. Mickunas, D. B., Zarus, G.M., Turpin, R.D.,; Campagna, P. R. Remote optical sensing instrument monitoring to demonstrate compliance with short-term exposure action limits during cleanup operations at uncontrolled hazardous waste sites. *J. of Hazard. Mater.* 1995, 43, 55-65.
3. Takach, S. F., Schulz, S.P., Minnich, T.R., Scotto, R.L. Results of Gas Technology Institute's ORS methods development project for perimeter air monitoring during MGP site cleanups. *Proceedings of the 101st Annual Conference of the Air & Waste Management Association, Portland, OR, June 24-27, 2008; A&WMA: Pittsburgh, PA, 2008; Paper #756.*
4. Lin, C. S.; Liou, N. W.; Chang, P. E.; Yang, J. C.; Sun, E. Fugitive coke oven gas emission profile by continuous line averaged open-path Fourier transform infrared monitoring. *J. Air & Waste Manage. Assoc.* **2007**, 57 (4), 472-479.
5. Ciaparra, D.; Aries, E.; Booth, M. J.; Anderson, D. R.; Almeida, S. M.; Harrad, S. Characterization of volatile organic compounds and polycyclic aromatic hydrocarbons in the ambient air of steelworks. *Atmos. Environ.* **2009**, 43 (12), 2070-2079.

6. Thoma, E. D.; Secrest, C.; Hall, E. S.; Jones, D. L.; Shores, R. C.; Modrak, M.; Hashmonay, R.; Norwood, P. Measurement of total site mercury emissions from a chlor-alkali plant using ultraviolet differential optical absorption spectroscopy and cell room roof-vent monitoring. *Atmos. Environ.* **2009**, *43* (3), 753-757.
7. Brown, R. H. Environmental use of diffusive samplers: evaluation of reliable diffusive uptake rates for benzene, toluene and xylene. *J. Environ. Monit.* **1999**, *1* (1), 115-116.
8. Ballach, J.; Greuter, B.; Schultz, E.; Jaeschke, W. Variations of uptake rates in benzene diffusive sampling as a function of ambient conditions. *Sci. Total Environ.* **1999**, *244*, 203-217.
9. Brown, R. H. Monitoring the ambient environment with diffusive samplers: theory and practical considerations. *J. Environ. Monit.* **2000**, *2* (1), 1-9.
10. Buzica, D.; Gerboles, M.; Plaisance, H. The equivalence of diffusive samplers to reference methods for monitoring O₃, benzene and NO₂ in ambient air. *J. Environ. Monit.* **2008**, *10* (9), 1052-1059.
11. Woolfenden, E. Sorbent-based sampling methods for volatile and semi-volatile organic compounds in air. Part 2. Sorbent selection and other aspects of optimizing air monitoring methods. *J. Chromatogr. A* **2010**, *1217*, (16), 2685-94.
12. Pfeffer, H. U.; Breuer, L. BTX measurements with diffusive samplers in the vicinity of a cokery: Comparison between ORSA-type samplers and pumped sampling. *J. Environ. Monit.* **2000**, *2* (5), 483-486.
13. Technical Committee CEN/TC 264, Ambient air quality standard method for measurement of benzene concentrations - Part 4: Diffusive sampling followed by thermal desorption and gas chromatography. BS EN 14662-4:2005, British Standards Institution: London, England, 2005.

14. Strandberg, B.; Sunesson, A. L.; Olsson, K.; Levin, J. O.; Ljungqvist, G.; Sundgren, M.; Sallsten, G.; Barregard, L. Evaluation of two types of diffusive samplers and adsorbents for measuring 1,3-butadiene and benzene in air. *Atmos. Environ.* **2005**, *39* (22), 4101-4110.
15. Martin, N. A.; Marlow, D. J.; Henderson, M. H.; Goody, B. A.; Quincey, P. G. Studies using the sorbent Carbopack X for measuring environmental benzene with Perkin-Elmer-type pumped and diffusive samplers. *Atmos. Environ.* **2003**, *37*, (7), 871-879.
16. McClenney, W. A.; Oliver, K. D.; Jacumin, H. H.; Daughtrey, E. H.; Whitaker, D. A. 24 h diffusive sampling of toxic VOCs in air onto Carbopack X solid adsorbent followed by thermal desorption/GC/MS analysis - laboratory studies. *J. Environ. Monit.* **2005**, *7* (3), 248-256.
17. McClenney, W. A.; Jacumin, H. H., Jr.; Oliver, K. D.; Daughtrey, E. H., Jr.; Whitaker, D. A. Comparison of 24 h averaged VOC monitoring results for residential indoor and outdoor air using Carbopack X-filled diffusive samplers and active sampling--a pilot study. *J. Environ. Monit.* **2006**, *8* (2), 263-9.
18. Mukerjee, S.; Oliver, K. D.; Seila, R. L.; Jacumin, H. H., Jr.; Croghan, C.; Daughtrey, E. H., Jr.; Neas, L. M.; Smith, L. A. Field comparison of passive air samplers with reference monitors for ambient volatile organic compounds and nitrogen dioxide under week-long integrals. *J. Environ. Monit.* **2009**, *11* (1), 220-227.
19. Mukerjee, S.; Smith, L. A.; Norris, G. A.; Morandi, M. T.; Gonzales, M.; Noble, C. A.; Neas, L. M.; Ozkaynak, A. H. Field method comparison between passive air samplers and continuous monitors for VOCs and NO₂ in El Paso, Texas. *J. Air & Waste Manage. Assoc* **2004**, *54* (3), 307-319.
20. U.S. E.P.A, Facility fence line monitoring using passive samplers; Quality Assurance Project Plan and supplementary data tables; Office of Research and Development, National Risk Management Research Laboratory, Durham, NC, 2010. Supplemental material to Thoma, E. D.;

et al. Facility fence line monitoring using passive samplers. *J. Air & Waste Manage. Assoc.* **2011**, 61 (<issue number>), <page numbers>; available at <supplemental URL>.

21. Texas Commission on Environmental Quality, Continuous air monitoring station data, At web site: <http://www.tceq.state.tx.us/compliance/monitoring/air/monops/agc/autogc.html> accessed October 10, 2010.

About the Authors

Eben Thoma is a scientist with EPA's Office of Research and Development, National Risk Management Research Laboratory in Research Triangle Park NC. Nick Parsons is an environmental engineer and Brenda Shine is a chemical engineer with EPA's Office of Air Quality Planning and Standards in Research Triangle Park NC. Mike Miller and Kuenja Chung (recently retired) are environmental scientists with EPA Region 6 in Dallas TX. Address correspondence to: Eben Thoma, 109 TW Alexander Drive, E343-02, RTP NC 27711; phone: +1- 919-541-7969; fax: +1-919-541-0359; e-mail: thoma.eben@epa.gov.

591 **Table 1.** Summary of PS fence line meteorological data by period.

Period	End Date (mm/dd/yy)	WD (deg)	SWS (mph)	RWS (mph)	T (°F)	RH (%)
P1	12/17/08	210	11	1	57	58
P2	12/31/08	135	11	3	63	67
P3	1/14/09	191	11	2	60	60
P4	1/28/09	166	12	3	61	56
P5	2/11/09	157	13	8	62	58
P6	2/25/09	133	11	6	65	62
P7	3/11/09	169	16	13	69	62
P8	3/25/09	167	12	6	64	73
P9	4/8/09	190	13	4	71	47
P10	4/22/09	154	13	7	75	59
P11	5/6/09	138	19	18	80	68
P12	5/20/09	141	16	12	81	63
P13	6/3/09	173	9	6	80	64
P14	6/17/09	158	13	12	84	63
P15	7/1/09	151	12	11	86	63
P16	7/15/09	151	13	12	87	63
P17	7/29/09	151	15	14	87	62
P18	8/12/09	150	14	14	87	62
P19	8/26/09	146	11	10	87	61
P20	9/9/09	175	8	3	84	62
P21	9/23/09	191	8	1	82	66
P22	10/7/09	163	11	5	80	73
P23	10/21/09	132	12	5	75	68
P24	11/4/09	198	10	2	69	62
P25	11/18/09	191	9	3	68	67
P26	12/2/09	166	9	3	61	73

592
593
594
595
596
597
598

Figure 1. Overhead view of test site with locations of PS monitors and neighboring TCEQ CAMS sites indicated.

Figure 2. Wind rose summaries for (a) mixed wind direction grouping, P1-P6 combined with P20-P26; and (b) uniform wind direction grouping, P7-P19.

Figure 3. Comparison of PSs and TCEQ auto GC benzene concentration data from C633 and C634. Error bars indicate duplicate PS range values for C633 site.

Figure 4. Comparison of passive sampler (PS) and duplicates (DPS) for C633, loc 180, and loc 360 sites.

Figure 5. PS benzene concentration data for all sampling periods by location: ($\oplus$) mean, ($\square$) interquartile range (25%-75%), ($*$) outlier values. Two outlier values for loc 360 (29280 pptv, 20007 pptv) are off scale.

Figure 6. PS benzene concentration data for primary fence line locations by sampling period: ($\oplus$) mean, ($\square$) interquartile range (25%-75%), ($*$) outlier values. Loc 40, 50I, 60, and CAMS sites not included. Outlier values for loc 360 (29280 pptv, 20007 pptv) are off scale.

Figure 7. Time series of PS benzene concentration and wind data for the southern fence line area: ($*$) C633 auto GC, ($\circ$) passive samplers at C633 with error bars indicating duplicate range values, ($\bullet$) average of PSs at loc 250 and 270 with error bars indicating individual values, (Δ) percentage of winds from the south for the time period.

Figure 8. Time Series of PS benzene concentration data the northeastern fence line area: ($\blacktriangle$) loc 50, (Δ) loc 40, ($\bullet$) loc 60, and, ($\circ$) loc 50I with ($*$) loc 130 shown for comparison.

Figure 9. PS data by sampling period for the northern fence line area: ($\bullet$) loc 20, and ($\circ$) L360, with ($*$) L130 shown for comparison. Outlier values for loc 360 (29280 pptv, 20007 pptv) are off scale.

630 **Figure 10.** Comparison of upwind (loc 90 through loc 270) and downwind (loc 290 through loc
631 20) PSs data for six-month period groupings of Figure 2.

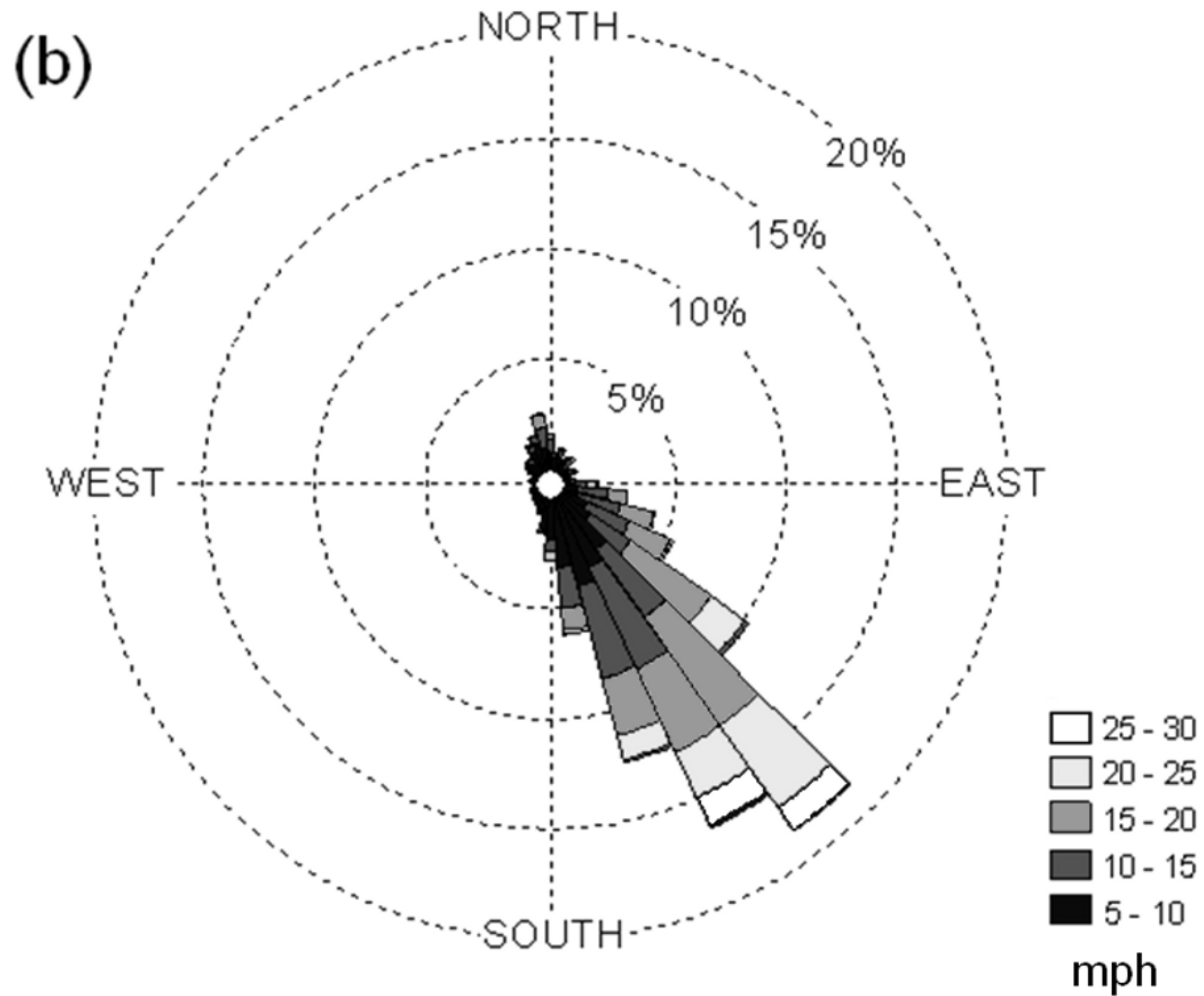
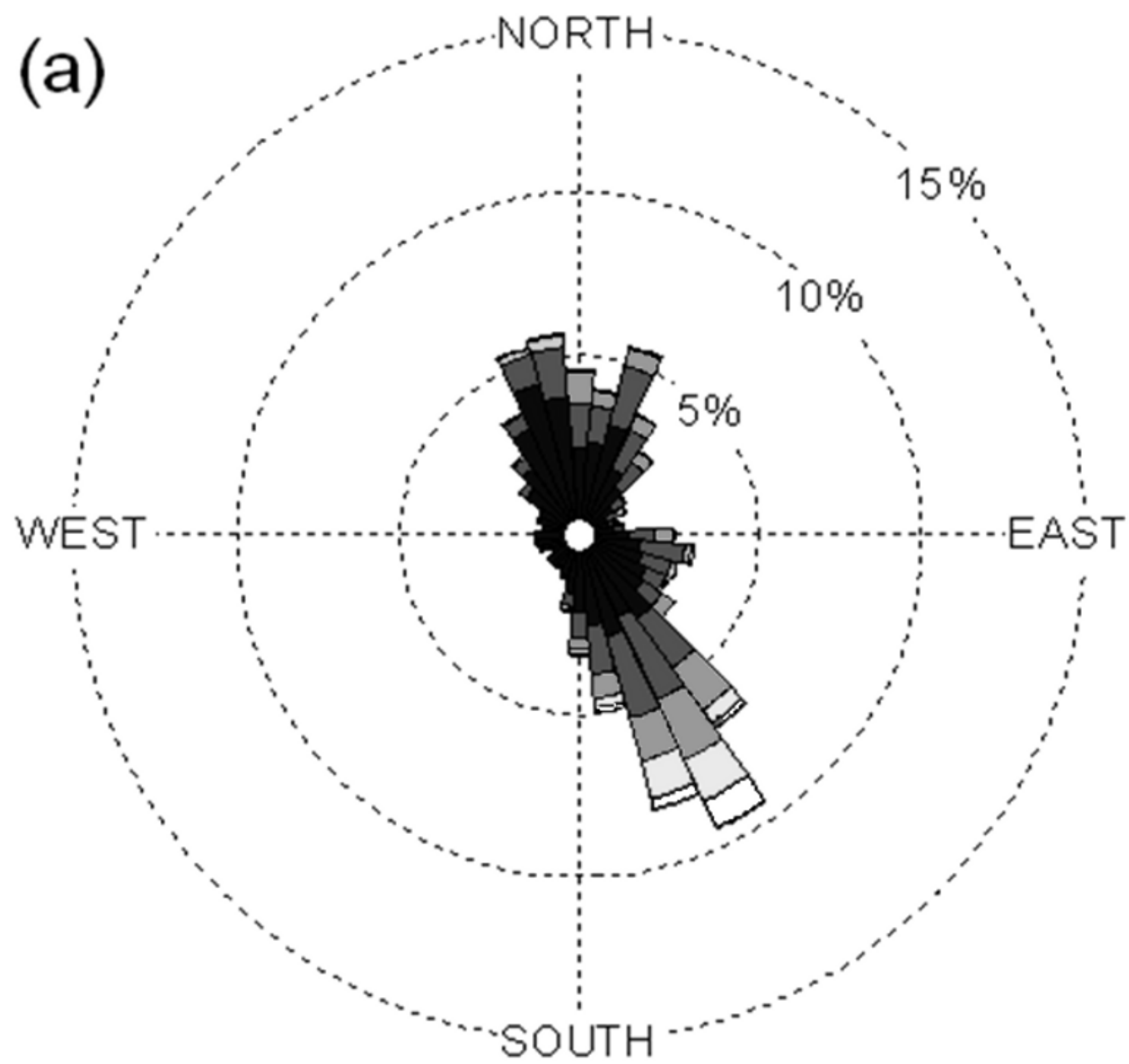
632

633 **Figure 11.** The percentage difference in upwind and downwind benzene concentrations
634 compared against a measure of wind direction uniformity.

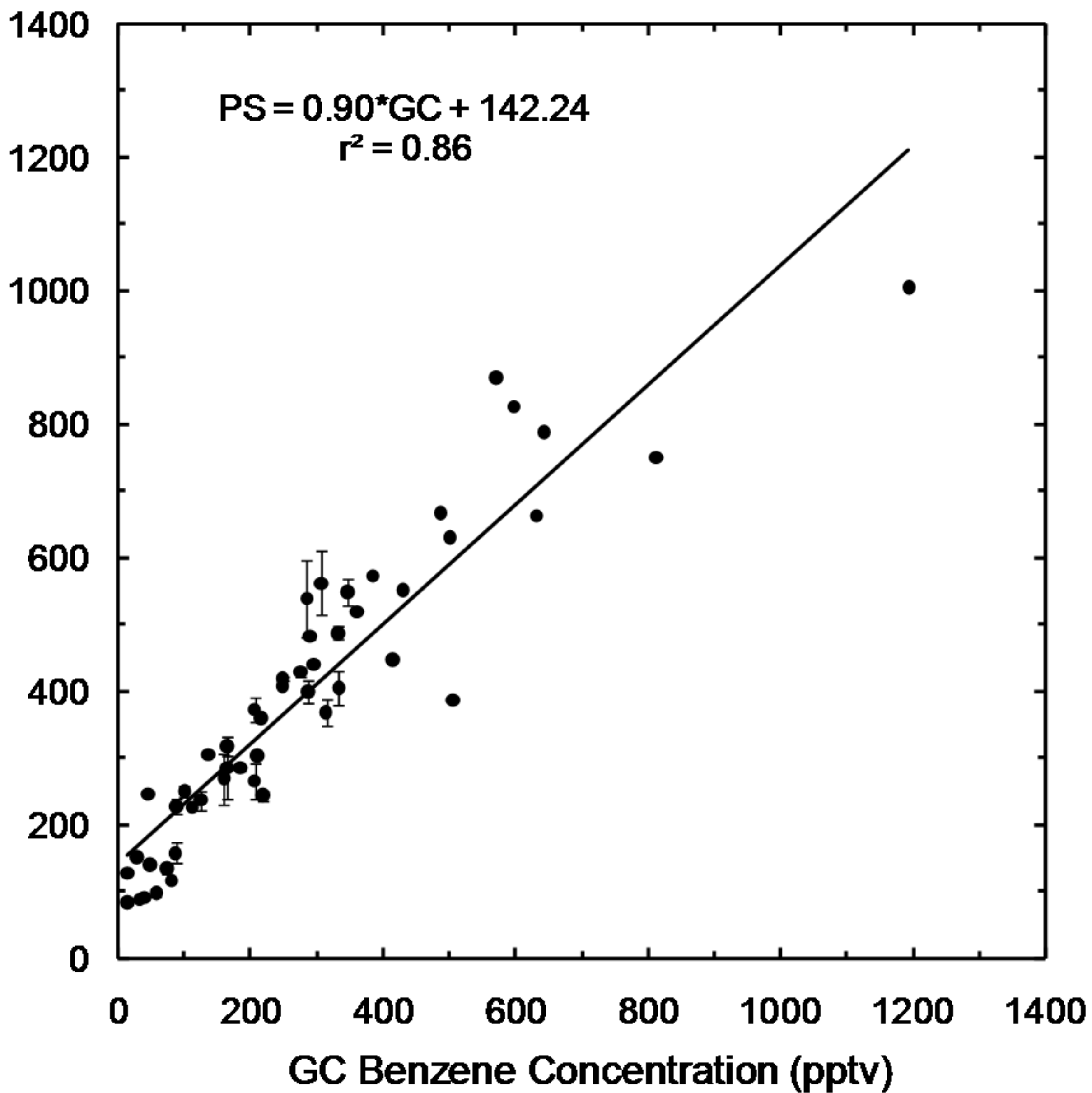
635

636

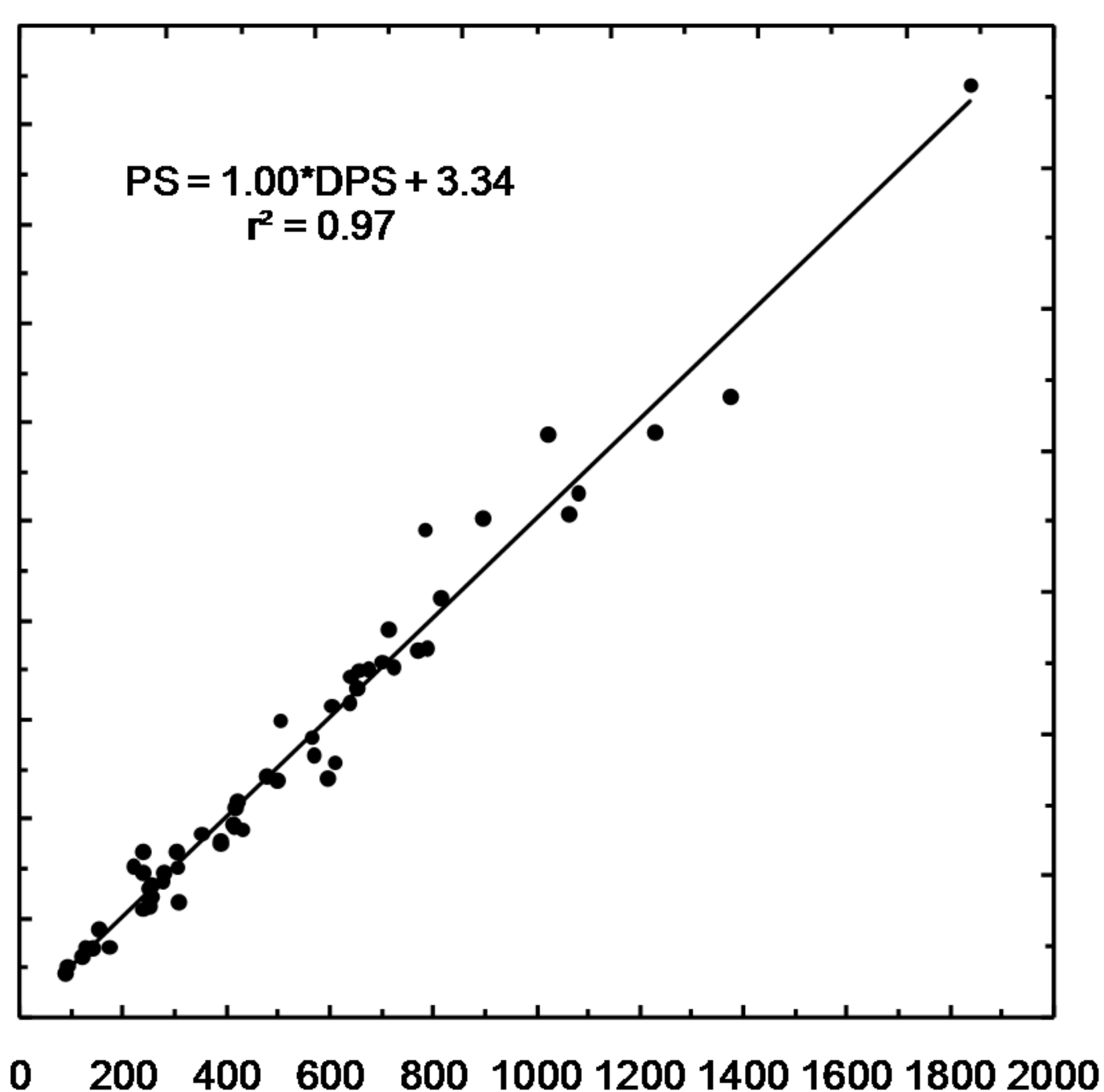




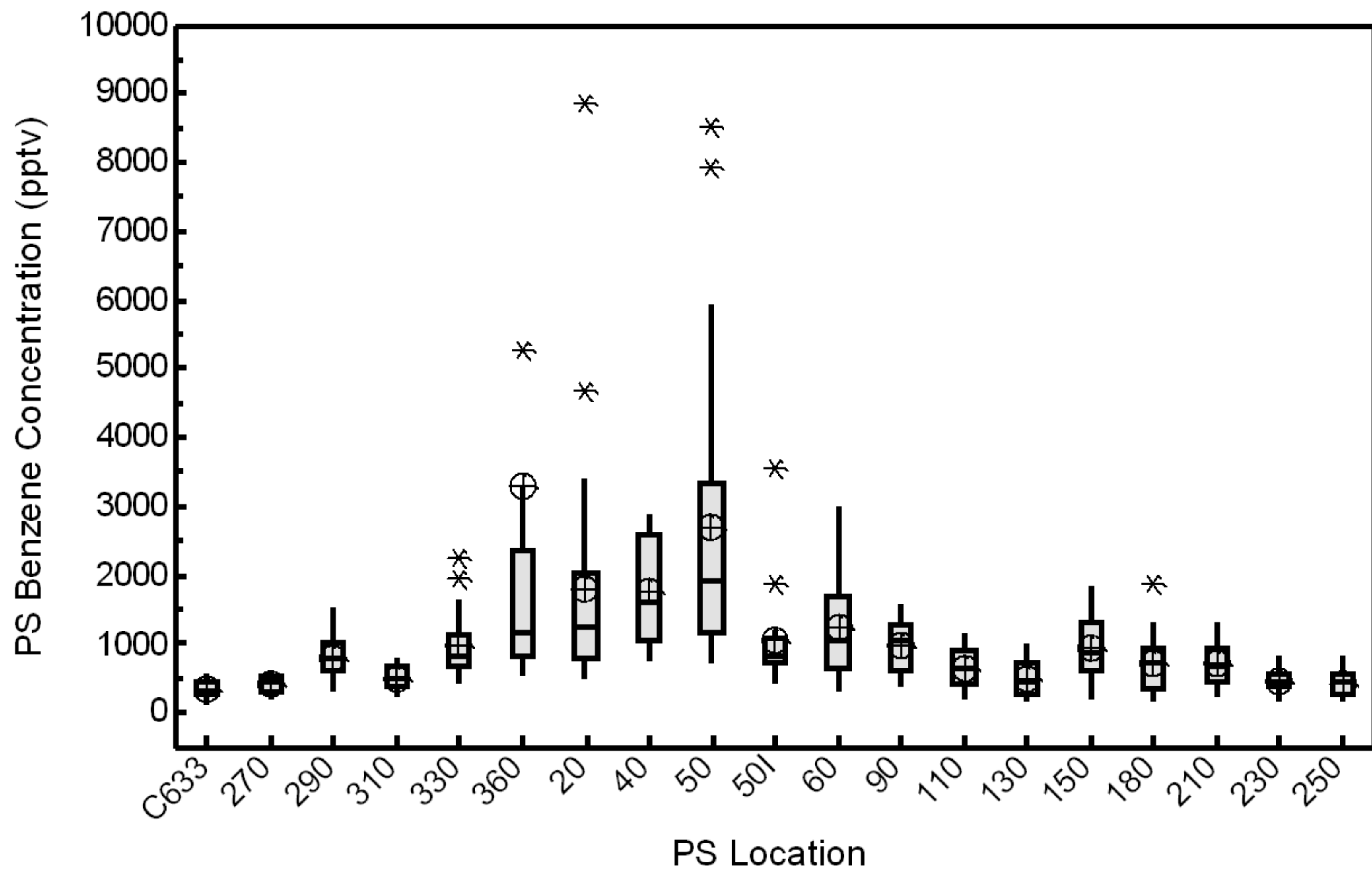
PS Benzene Concentration (pptv)

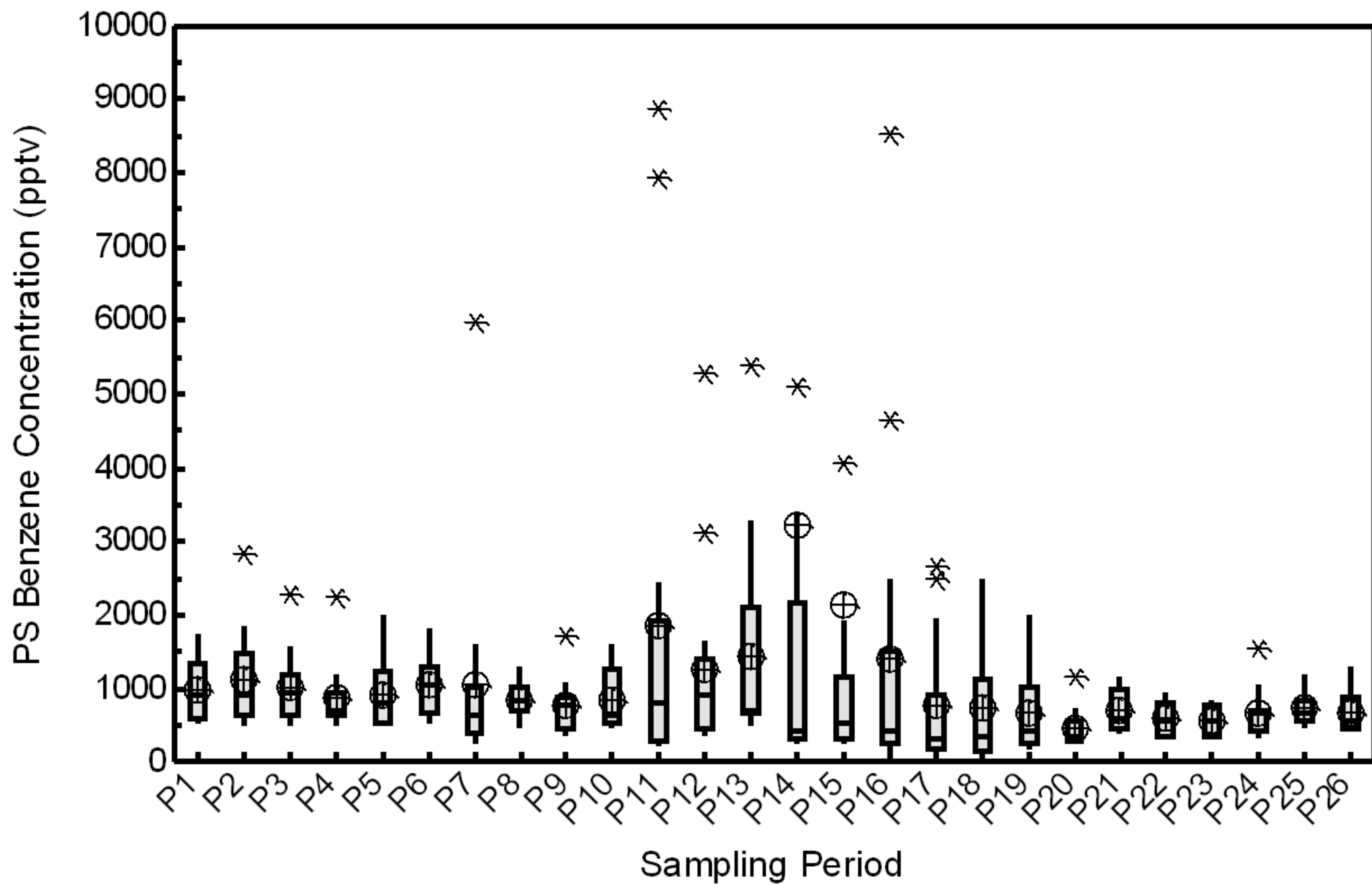


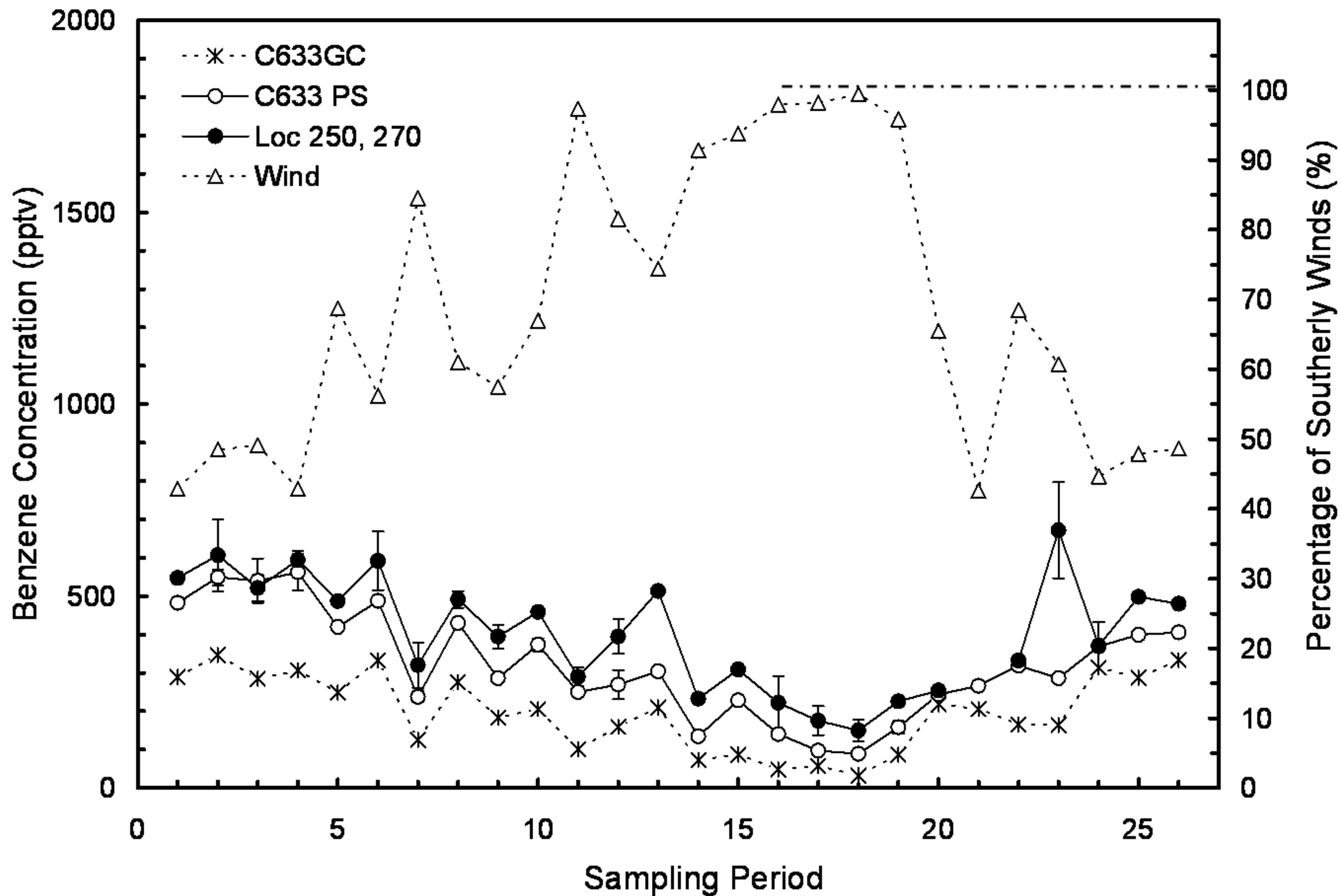
PS Benzene Concentration (pptv)

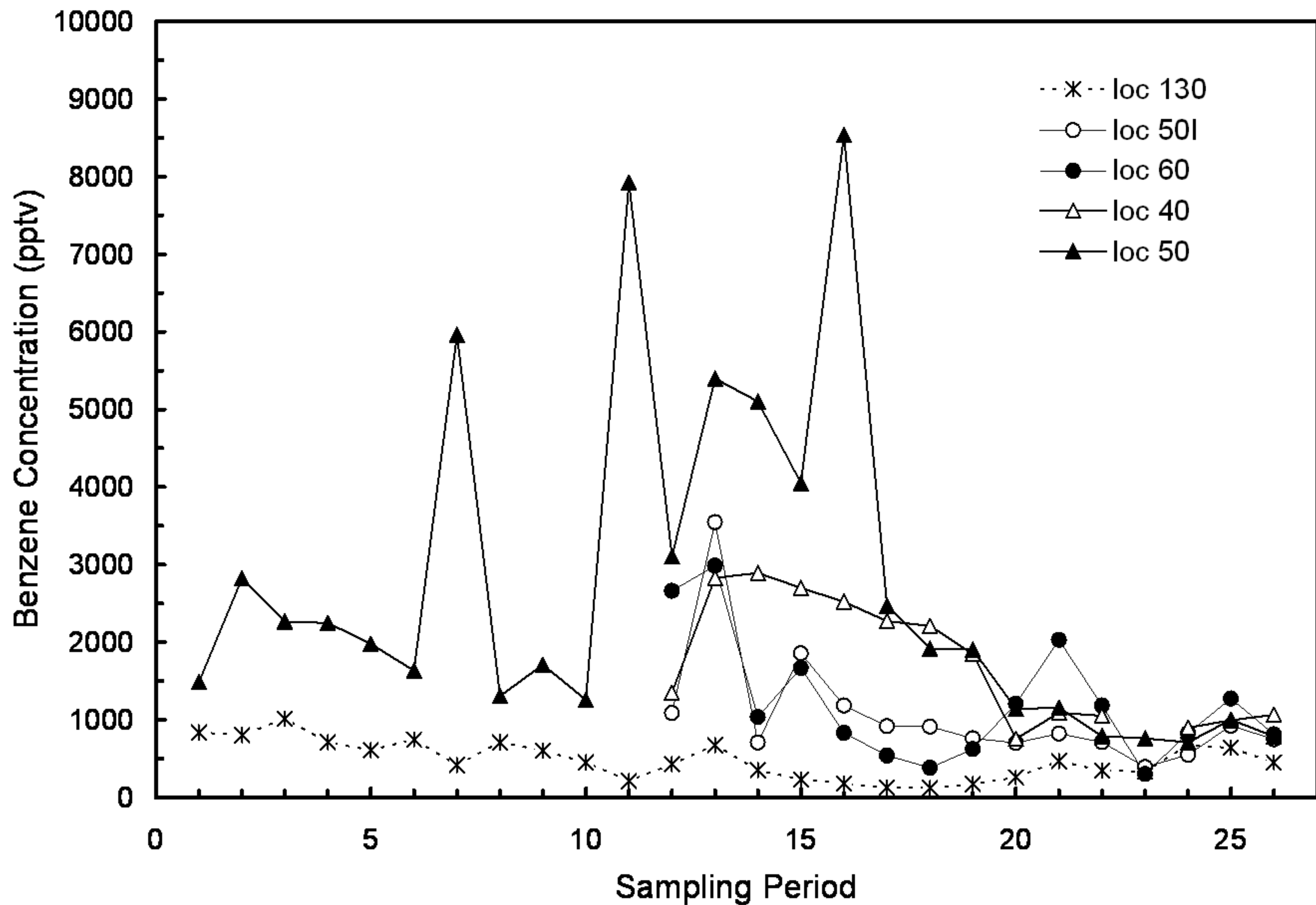


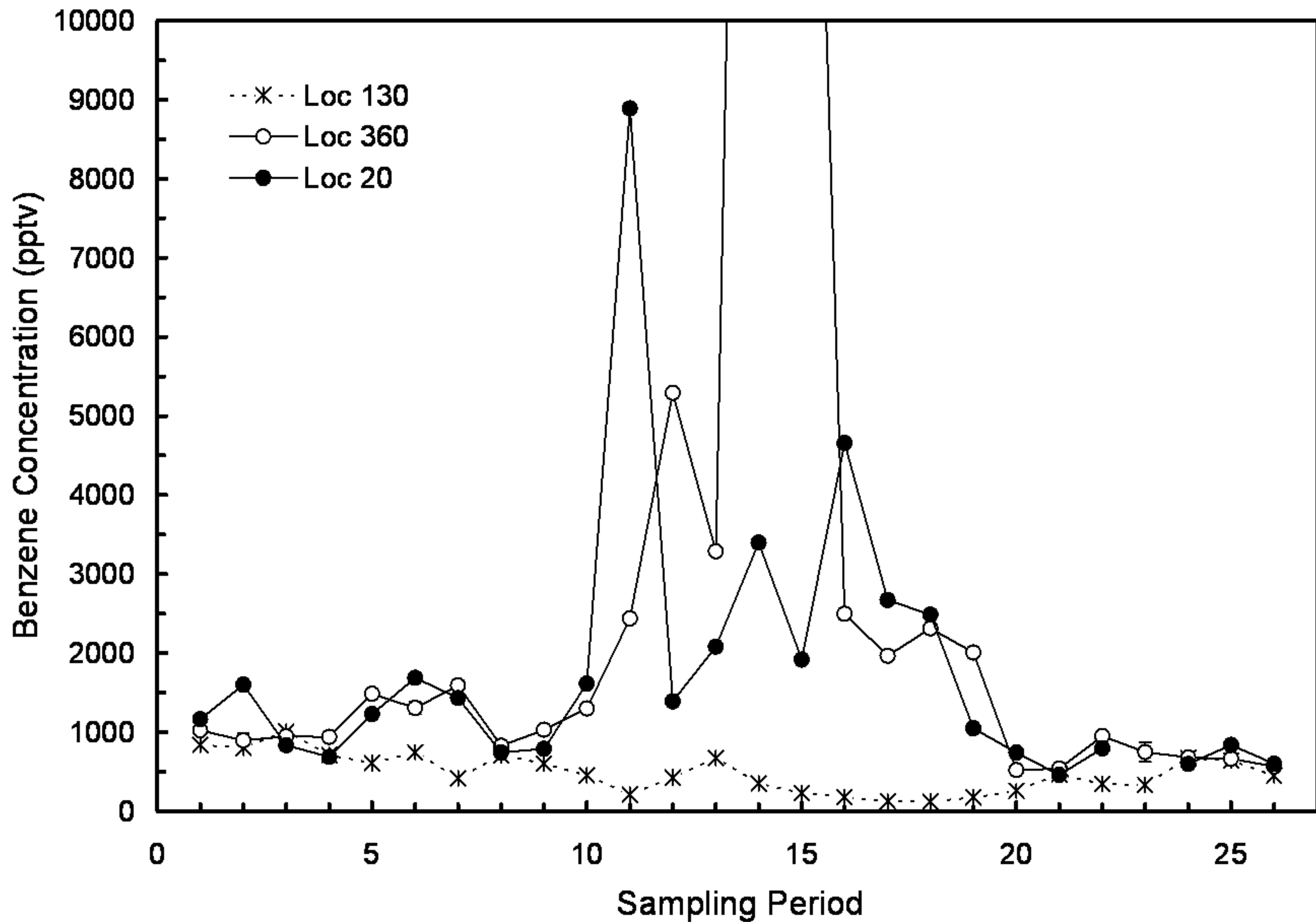
Duplicate PS Benzene Concentration (pptv)

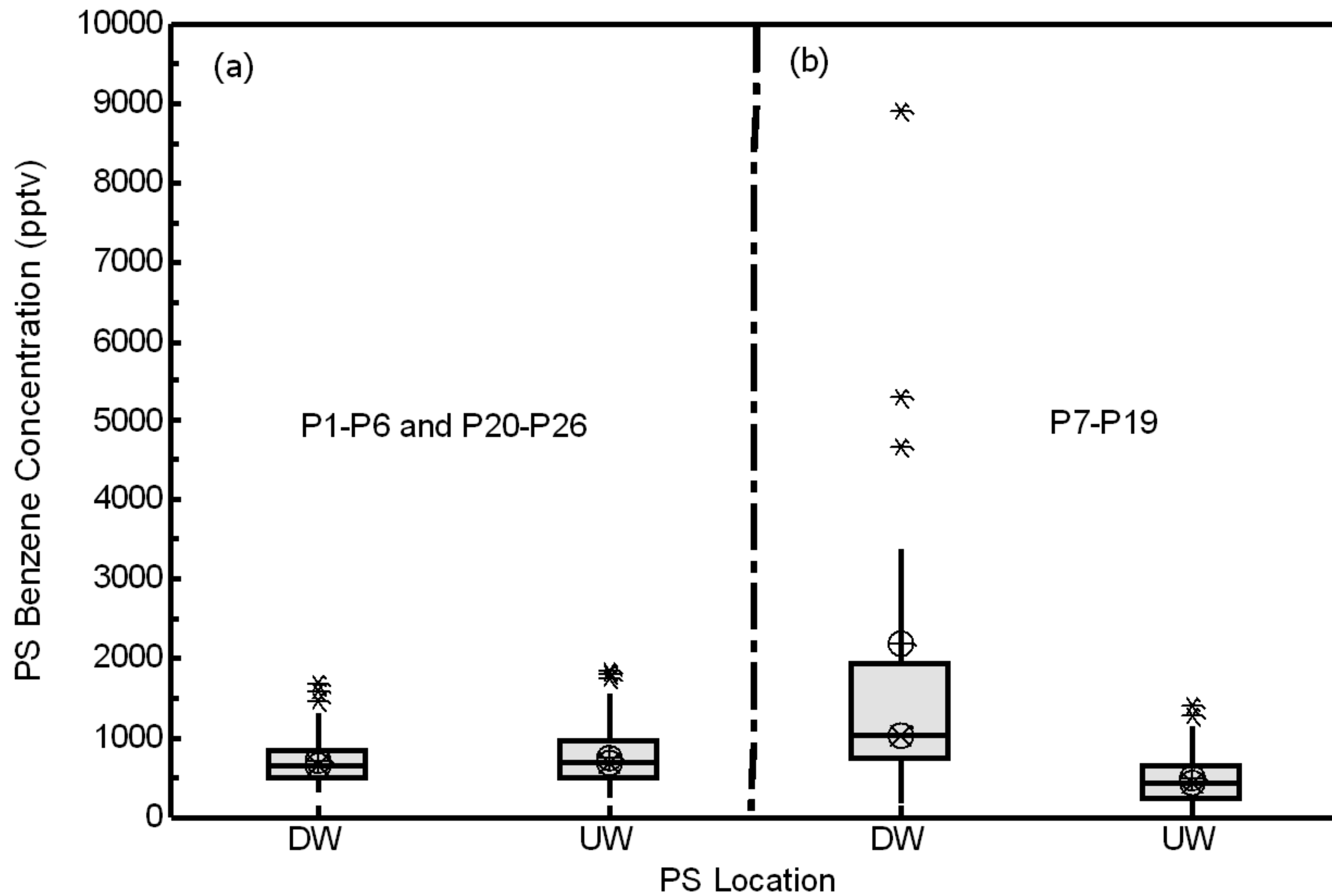












Upwind, Downwind (% dif.)

