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# Small Tributaries Pollutants of Concern Reconnaissance Monitoring: Pilot Evaluation of Source Areas Using PCB Congener Data

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## Preface

This is one of two companion reports that were prepared. A second report prepared by Lester McKee, Alicia Gilbreath, Jennifer Hunt, Jing Wu, Don Yee, and Jay Davis focused on the use of loads and yields for identifying areas of potential high leverage. It was titled “Small Tributaries Pollutants of Concern Reconnaissance Monitoring: Loads and Yields-based Prioritization Methodology Pilot Study”. It can be downloaded at <https://www.sfei.org/documents/small-tributaries-pollutants-concern-reconnaissance-monitoring-loads-and-yields-based>

## Acknowledgements

We appreciate the support and guidance from members of the Sources, Pathways, and Loadings Workgroup of the Regional Monitoring Program for Water Quality in San Francisco Bay. The detailed workplan behind this project was developed through the Small Tributaries Loading Strategy (STLS) Team, including Jim Scanlin (Alameda Countywide Clean Water Program), Bonnie de Berry (San Mateo Countywide Water Pollution Prevention Program), Lucile Paquette (Contra Costa Clean Water Program), Chris Sommers (Santa Clara Valley Urban Runoff Pollution Prevention Program), and Richard Looker and Jan O’Hara (Regional Water Board). Helpful written reviews of this report were provided by Lisa Sabin, Bonnie de Berry, Richard Looker, Daniel Cain (USGS Menlo Park, CA) and Barbara Mahler (USGS Austin, TX).

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# Small Tributaries Pollutants of Concern

## Reconnaissance Monitoring: Pilot Evaluation of Source Areas Using PCB Congener Data

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### Executive Summary

PCB congener profiles can be used to help identify source areas that contribute most to the PCB mass exported from the watershed via stormwater and to illustrate variability in PCB mobilization from source areas over time. A method is presented for estimating the contributions of different Aroclor mixtures to the congener profiles of samples of stormwater and sediment. The method is based on the use of indicator congeners that are representative of each of the four most commonly used Aroclors. In this report, the method was applied in three watersheds. In the Pulgas Pump Station watershed, stormwater and sediment had high concentrations with a unique congener profile, dominated by congeners indicative of a combination of Aroclors 1242 and 1260. The concentrations and congener profiles in sediment suggest that there are two distinct source areas in the watershed that combine to create the mix of 1242 and 1260 that is dominant in stormwater at the Pump Station. The data indicate that if PCB flux from one of these areas could be eliminated, loads from the watershed would be reduced by 50% or more. For the Coyote Creek watershed, the similarity in congener profiles for the highest concentration sediment samples and the stormwater samples suggest that the important source areas in the watershed have been identified, and that reduction of loading from an area at the south end of the Charcot Avenue Storm Drain watershed would yield the greatest reduction in export at the Coyote Creek station. The concentrations and congener profiles in stormwater and sediment from the Guadalupe River watershed indicate the presence of one source area that is likely a substantial contributor to PCB export from the watershed, but that all of the significant sources areas may not yet have been identified.

### Introduction

PCBs were manufactured and used as complex mixtures of individual PCBs, referred to as PCB congeners. In North America, the only producer of PCBs was the Monsanto Company, which marketed them under the trade name Aroclor from 1930 to 1977. A series of different mixtures was produced, each referred to as an Aroclor, and each with varying degrees of overall chlorine content. The different mixtures were used for different purposes. The congener composition of the various Aroclor mixtures has been reported in the literature (e.g., Schulz et al. 1989, Frame et al. 1996a,b).

As a consequence of the use of Aroclor mixtures, PCBs are also present in the environment as complex mixtures of congeners. The congener profiles observed in samples of Bay sediment and water generally represent a combination of the most heavily used Aroclors (i.e., Aroclors 1254

and 1260). Watershed source areas, on the other hand, often have simpler profiles that are dominated by single Aroclors that were used in specific applications on these properties. Stormwater flowing out of the watersheds has a congener profile that is an aggregation of the combined contributions of inputs from watershed source areas.

Routine analysis of data on PCB concentrations in stormwater, storm drain sediment, and other matrices typically uses the sum of the concentrations of PCB congeners as the index of contamination. This approach yields a great deal of valuable information. Additional valuable information, however, can be obtained by examining the congener profiles of stormwater, storm drain sediment, and source area soils. The congener profiles can be used to help identify source areas that contribute most to the PCB mass exported from the watershed by stormwater and to illustrate variability in PCB mobilization from source areas over time.

This section presents the results of a preliminary effort to compare congener profiles in stormwater at the bottom of three Bay Area watersheds and in sediment samples collected upstream.

## Methods

The PCB congener data for stormwater included in this analysis were generated by studies conducted by SFEI. Data for sediment were generated by studies conducted by BASMAA agencies. The data for stormwater and sediment were compiled into a set of Excel spreadsheets.

Sets of indicator congeners were selected to represent each of the commonly used Aroclors: 1242, 1248, 1254, and 1260. Complete congener profiles for each of these Aroclors as reported in Frame et al. (1996b) are shown in Figure 1. Four indicator congeners were selected for each Aroclor (Figure 1, Table 1). The indicator congeners have the following key characteristics:

1. they are relatively unique to the designated Aroclor mixture; and
2. they are a major contributor to the overall sum of PCBs.

Each set of four indicator congeners accounts for approximately equal contributions to the overall sum of 209 PCB congeners, ranging from 24% for the 1248 indicators (PCBs 44, 49, 66, and 70) to 30% for the 1254 indicators (PCBs 87, 101, 110, 118) and the 1260 indicators (PCBs 149, 170, 180, 187).

It should be noted that the four Aroclors are only a subset of the full set of mixtures that were marketed and used. Frame et al. (1996b) provides the congener profiles for other commercial mixtures. The congener profiles for Aroclors 1016 and 1262 are very similar to those for Aroclors 1242 and 1260, respectively. In this report, these profiles are referred to nominally as 1242 and 1260 profiles.

The protocol for generating data for the indicator congeners included the following steps (Figure 2).

1. Available data included samples with 40 congeners analyzed and with 209 congeners analyzed. To generate consistent percent contribution data, the analysis was limited to data for 40 congeners common to all samples.

2. The sum of 40 congeners ( $\Sigma\text{PCB40}$ ) was calculated for each sample. Results below reporting limits were set to zero.
3. The percent contribution of each of the congeners to  $\Sigma\text{PCB40}$  was calculated.
4. For each Aroclor, an index was computed as the sum of the percent contributions of the indicator congeners for each Aroclor. For example, the Aroclor 1242 index is the sum of the percent contributions for congeners 18, 28, 31, and 33 (Figure 2).
5. To standardize the indices for each Aroclor, they were expressed as a percentage of the sum of the indices for the four major Aroclors (1242, 1248, 1254, and 1260) (Figure 2).
6. For visual assessment of the maps in this section, the data for the Aroclor indices were binned into the following categories (Figure 2):
  - a. greater than or equal to 40% of the sum of the four Aroclor indices (primary contributor);
  - b. greater than or equal to 20% and less than 40% of the sum of the four Aroclor indices (secondary contributor); and
  - c. less than 20% of the sum of the four Aroclor indices (minor contributor).
7. Samples with concentrations below 10 ng/g are not shown. When samples have low concentrations, data for many of the congeners are censored and the percent contribution values become very noisy. Given the greater uncertainty and low influence of these values on mass loads, these samples were flagged as being unreliable for congener profile analysis.

## Results and Discussion

### Pulgas Pump Station South Watershed

During the period from February 17, 2011 to March 31, 2014, PCBs in stormwater at the outlet of the Pulgas Pump Station South watershed were measured in 33 samples from nine storms (Figure 3).  $\Sigma$ PCB40 concentrations in stormwater at this location have been among the highest measured throughout the Bay Area, and include the 2 highest values (maximum of 6,300,000 pg/L) and another 3 within the top 10 for the entire Bay Area dataset. Four of these high values were measured in one storm that occurred on November 19, 2013. The median  $\Sigma$ PCB40 concentration in stormwater at this location (23,000 pg/L) is elevated relative to concentrations measured in stormwater at other locations (median concentration for the entire Bay Area dataset [n=658] is 8,400 pg/L), and the mean concentration at Pulgas (390,000 pg/L) is very high.

The congener profiles in the 33 stormwater samples from Pulgas Pump Station South had a unique pattern, dominated by congeners indicative of a combination of Aroclors 1242 and 1260 (Figure 3). The prominence of the contribution of Aroclor 1242 is especially unusual. The Aroclor 1242 contribution ranged from a low of around 10% in the storm on February 17, 2011, to a high of 90% in the storm on November 19, 2013, the same day that the extremely high  $\Sigma$ PCB40 concentrations was measured. The temporal variability in Aroclor contributions from the same watershed provides an indication of differential mobilization of source areas within the watershed between storms and within storms. The variation in profiles did not have a clear correlation with flow at the Pump Station (Figure 3). The Aroclor 1242 contribution was generally high across all of the storms, accounting for an mean of 49% of the sum of the indices. The mean contribution of Aroclor 1260 was 29%. The mean contributions of Aroclors 1248 and 1254 were 14% and 7%, respectively. This is an unusually low contribution of Aroclor 1254. Aroclor 1242 dominates the stormwater congener profile for this watershed, with a generally high contribution across all storms and an especially high contribution to the extremely high concentration samples on November 19, 2013; Aroclor 1260 is a secondary contributor.

The concentrations and congener profiles in sediment from the Pulgas Pump Station South watershed (Figure 4, Appendix 1) suggest that there are two distinct source areas that combine to create the mix of Aroclors 1242 and 1260 that is dominant in stormwater at the Pump Station. Particularly noteworthy is the sample PUL22 collected in the northeastern part of the watershed. This sample had an exceptionally high  $\Sigma$ PCB40 concentration (193,000 ppb), approximately 1,000-fold higher than most of the other samples in the watershed. Nearly all of the contributions for this sample were from Aroclors 1242 (63%) and 1248 (34%), with 0% from 1260. Another sample (PUL4) from this same geographic area also had a profile dominated by Aroclor 1242 and a relatively high  $\Sigma$ PCB40 concentration (2,500 ppb). The extremely high concentration in the PUL22 sample, the very distinct and unusual associated congener profile, and the small size of the watershed strongly indicate that this source area is a major contributor to the high PCB loads that are exported from Pulgas Pump Station South watershed. These data suggest that if PCB flux from this source area could be eliminated, loads from the watershed would be reduced by 50% or more.

Most of the other sediment samples in this watershed, especially those with relatively high concentrations (over 1000 ppb), had congener profiles dominated by Aroclor 1260. These observations are consistent with the dominant presence of Aroclor 1260 in the stormwater at the Pump Station. The sediment samples with high concentrations were clustered in the southern part of the watershed. These samples generally were strongly dominated by Aroclor 1260 congeners, with 1260 indices greater than 85% in many cases. Collectively these samples indicate the presence of another important source area in the southern part of the watershed.

The congener data suggest that the PCB uses leading to sediment contamination of the two source areas may have been very different (Aroclors 1242 and 1260 had very different chemical properties and generally different applications), but the wide array of uses of each of the different mixtures makes it difficult to be more precise about this based on the congener data alone.

### Coyote Creek Watershed

PCBs in stormwater were measured in seven samples from three storms during December 17, 2004 to January 11, 2005 at the Coyote Creek station (Figure 5). The  $\Sigma$ PCB40 concentrations in stormwater for the seven samples at this location (median of 3,500 pg/L) were less than the median for the stormwater dataset as a whole (8,400 pg/L). They were also much lower than the median concentrations for Pulgas Pump Station South (23,000 pg/L) and Guadalupe River (17,000 pg/L).

The congener profiles measured in the seven stormwater samples were very consistent, dominated by a combination of Aroclors 1260 and 1254. The contribution of the 1260 index varied within a narrow range, from 47% to 65%, with a mean of 55%. The 1254 index ranged from 28% to 35%, with a mean of 30%. Aroclors 1248 and 1242 were minor contributors, averaging 11% and 5% of the sum of the indices, respectively. The variation in profiles did not have a clear correlation with creek flow (Figure 5).

The similarity in congener profiles between the highest concentration sediment samples (Figures 6a-c, Appendix 1) and the stormwater samples suggest that the important source areas in the watershed have been identified, and that reduction of loading from an area at the south end of the Charcot Avenue Storm Drain watershed would yield the greatest reduction in export at the Coyote Creek station. The two highest sediment concentrations were for two samples collected at the south end of the Charcot Avenue Storm Drain watershed, both of which were dominated by Aroclor 1260 (SC-SJY-10-I at 12,000 ppb and SC-SJY-10-H at 2,000 ppb) (Figure 6a). The sediment sample with the third highest concentration (SC-SJY-07-A at 1,600 ppb) was collected at the north end of the Ridder Park Storm Drain watershed and consisted almost entirely of equal amounts of Aroclors 1254 and 1260 (Figure 6b). There were nine other samples with moderately elevated  $\Sigma$ PCB40 concentrations (between 100 and 1000 ppb) and all but one of these were dominated by Aroclor 1254, 1260, or a combination of the two (Figures 6a-c). The high concentrations and congener profiles at the source area at the south end of the Charcot Avenue Storm Drain watershed match the profile in stormwater at the Coyote Creek station, suggesting that reduction of flux from this area should be a top priority.

## Guadalupe River Watershed

An extensive dataset is available for PCB concentrations in stormwater at the Guadalupe River station: 125 samples measured in 25 storms from November 2002 through March 2014.

$\Sigma$ PCB40 concentrations at this location (median of 17,000 pg/L, mean of 24,000 pg/L) have been high relative to the stormwater dataset as a whole (median of 8,400 pg/L). The median concentration in stormwater at the Guadalupe River station is of a similar magnitude as the median at Pulgas Pump Station South, although the mean is much lower than the Pulgas Pump Station South mean.

The congener profiles at the Guadalupe station have been very consistent, with essentially equal and substantial contributions of Aroclors 1254 and 1260 (41 and 40%, respectively) and small contributions of Aroclors 1242 and 1248 (Figure 7). The contributions of Aroclors 1254 and 1260 varied within fairly restricted ranges: 23-62 and 20-65%, respectively. Aroclors 1248 and 1242 were minor contributors, averaging 12 and 7%, respectively. On a few occasions, Aroclor 1242 had a higher contribution, contributing a maximum of 37% in October 2004. This suggests the periodic mobilization of PCBs from a source area that usually is of secondary importance. The variation in profiles did not have a correlation with river flow (Figure 7).

The concentrations and congener profiles in sediment from the Guadalupe watershed (Figures 8, 9a-I, Appendix 1) indicate the presence of one source area that is likely a significant contributor to PCB export from the watershed, but that other significant sources areas may not yet have been identified. The only area in this large watershed with sediment concentrations above 1000 ppb is region G (Figure 9g). Two samples in this region near the same parcel had high concentrations: SC-SJY-47-J at 7100 ppb and SC-SJY-47-D at 2000 ppb. These samples had very similar congener profiles, dominated by Aroclors 1254 and 1260: 42% 1254 and 50% 1260 at SC-SJY-47-J, and 43% 1254 and 54% 1260 at SC-SJY-47-D. Region G also had eight samples that were distributed slightly more widely geographically (over a three-block area) with concentrations between 100 and 1,000 ppb. These eight samples had congener profiles that were all dominated by Aroclor 1254, Aroclor 1260, or both.

Region A was the only other region with sediment concentrations above 100 ppb (Figure 9a), but this area lies outside of the boundary of the watershed for the Guadalupe River station.

Although the congener profiles from the source area in region G match the profiles in stormwater at the downstream end of the watershed, the concentration data suggest that there may be other unidentified source areas. The median concentration in stormwater, based on a very extensive dataset, was of a similar magnitude to that of stormwater at Pulgas Pump Station South, yet the sediment concentrations in the Pulgas Pump Station South watershed were much higher than the sediment concentrations in the Guadalupe watershed.



## References

- Frame, G.M., R.E. Wagner, J.C. Carnahan, J.F. Brown Jr., R.J. May, L.A. Smullen, and D.L. Bedard. 1996a. Comprehensive, quantitative, congener-specific analyses of eight Aroclors and complete PCB congener assignments on DB-1 capillary GC columns. *Chemosphere* 33: 603-623.
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- Schulz, D.E., G. Petrick, and J.C. Duinker. 1989. Complete characterization of polychlorinated biphenyl congeners in commercial Aroclor and Clophen mixtures by multidimensional gas chromatography-electron capture detection. *Environ. Sci. Technol.* 23: 852-859.

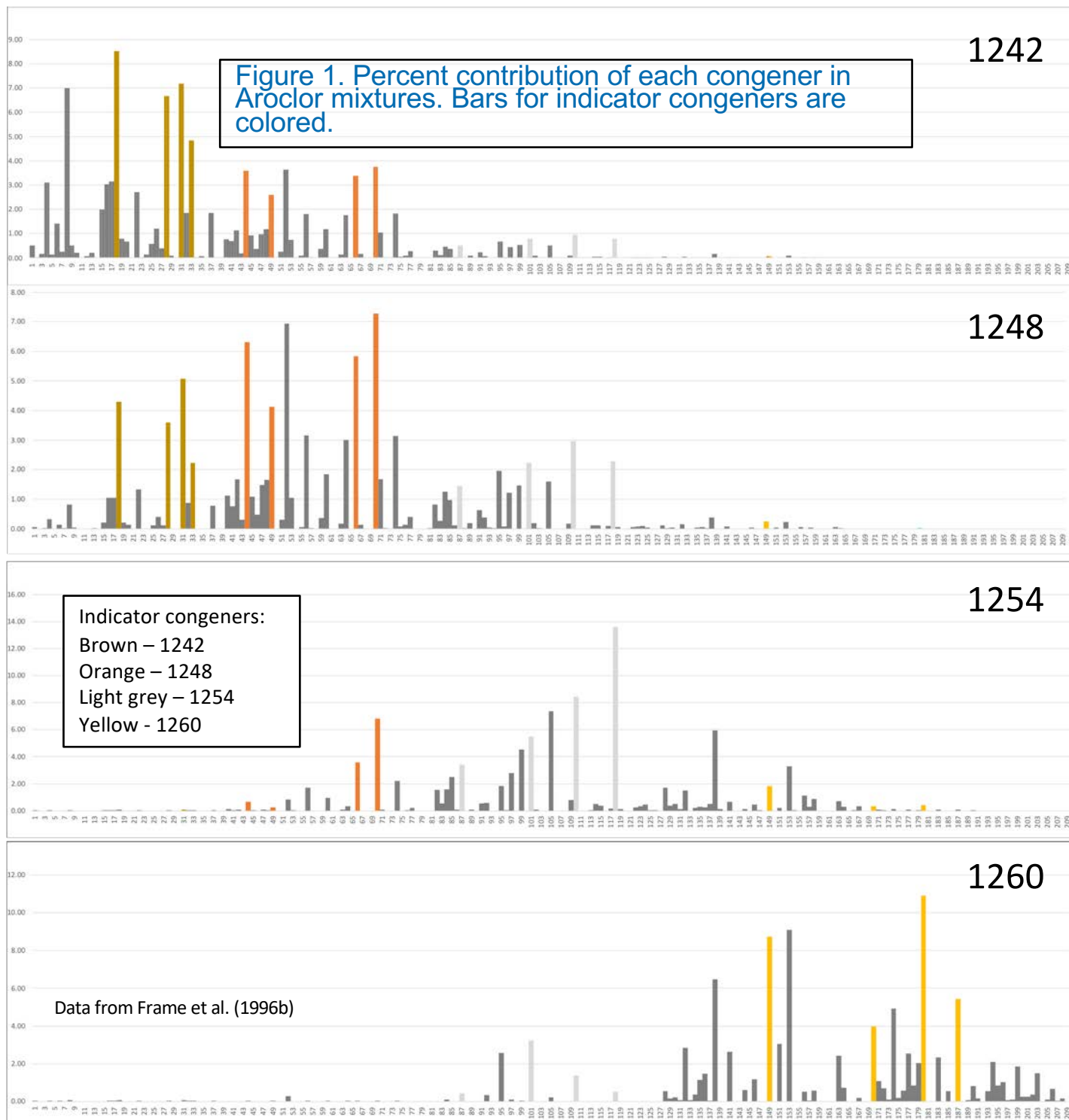


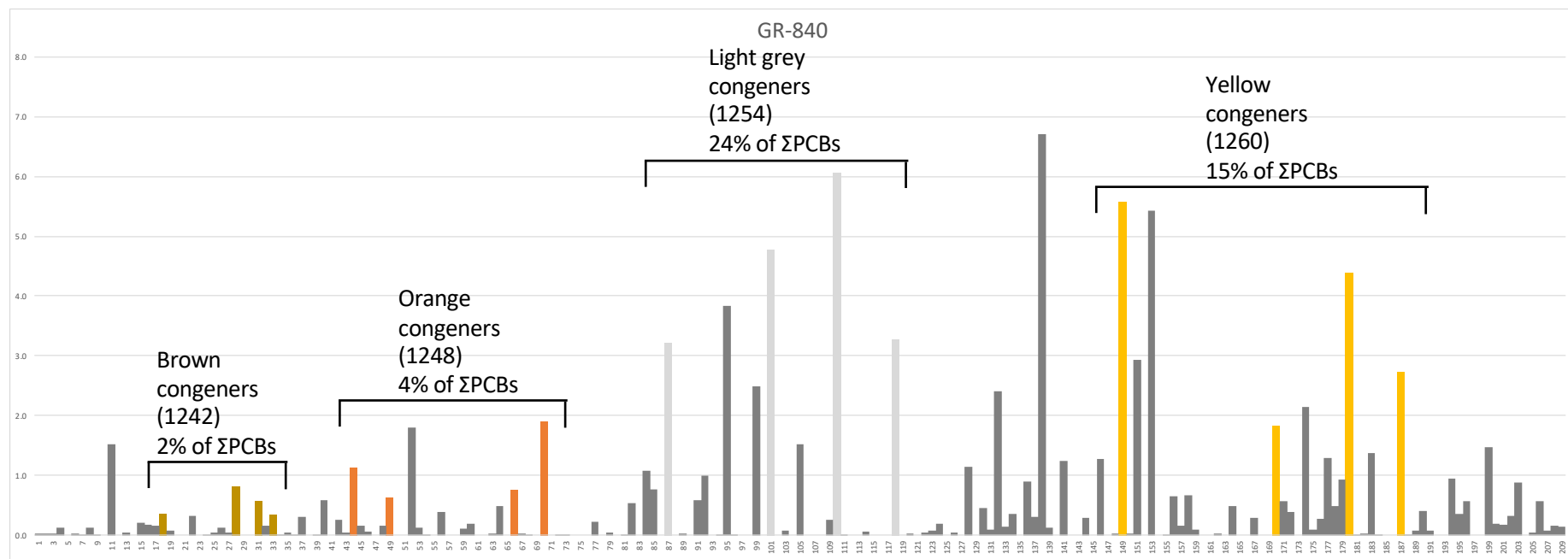
Table 1. Indicator congeners for the main Aroclors.

% of Sum PCBs for  
Indicator  
Congeners in Each  
Aroclor

Highlighted cells  
show the indicators

		<b>1242</b>	<b>1248</b>	<b>1254</b>	<b>1260</b>
	<b>18</b>	8.53	3.79	0.17	0.05
	<b>28</b>	6.86	4.58	0.13	0.03
	<b>31</b>	7.34	5.27	0.20	0.04
	<b>33</b>	5.01	2.22	0.11	0.03
	<b>44</b>	3.55	5.70	1.49	0.04
	<b>49</b>	2.52	4.15	0.68	0.01
	<b>66</b>	3.39	6.53	2.29	0.02
	<b>70</b>	3.73	7.34	5.16	0.04
	<b>87</b>	0.46	1.28	3.70	0.41
	<b>101</b>	0.69	2.06	6.76	3.13
	<b>110</b>	0.83	2.76	8.86	1.33
	<b>118</b>	0.66	2.32	10.47	0.49
	<b>149</b>	0.06	0.29	2.74	8.75
	<b>170</b>	0.00	0.03	0.44	4.11
	<b>180</b>	0.00	0.12	0.55	11.38
	<b>187</b>	0.00	0.05	0.17	5.40
% from 4 Indicators		28	24	30	30

Figure 2. Percent contributions of each congener to the sum of 40 PCBs for an example stormwater sample from the Guadalupe River.



Overall Sum of the Indicator Congeners = 45% of  $\Sigma$ PCBs

Normalized Percentages

1242 = 2%/45% = 5%

1248 = 4%/45% = 10%

1254 = 24%/45% = 53%

1260 = 15%/45% = 32%

Purple: Primary contributor (>40% of sum of indices)

Blue: Secondary (20-40%)

White: Low contributor (<20%)

Figure 3. Aroclor indices in stormwater at the outlet of Pulgas Pump Station South over time.

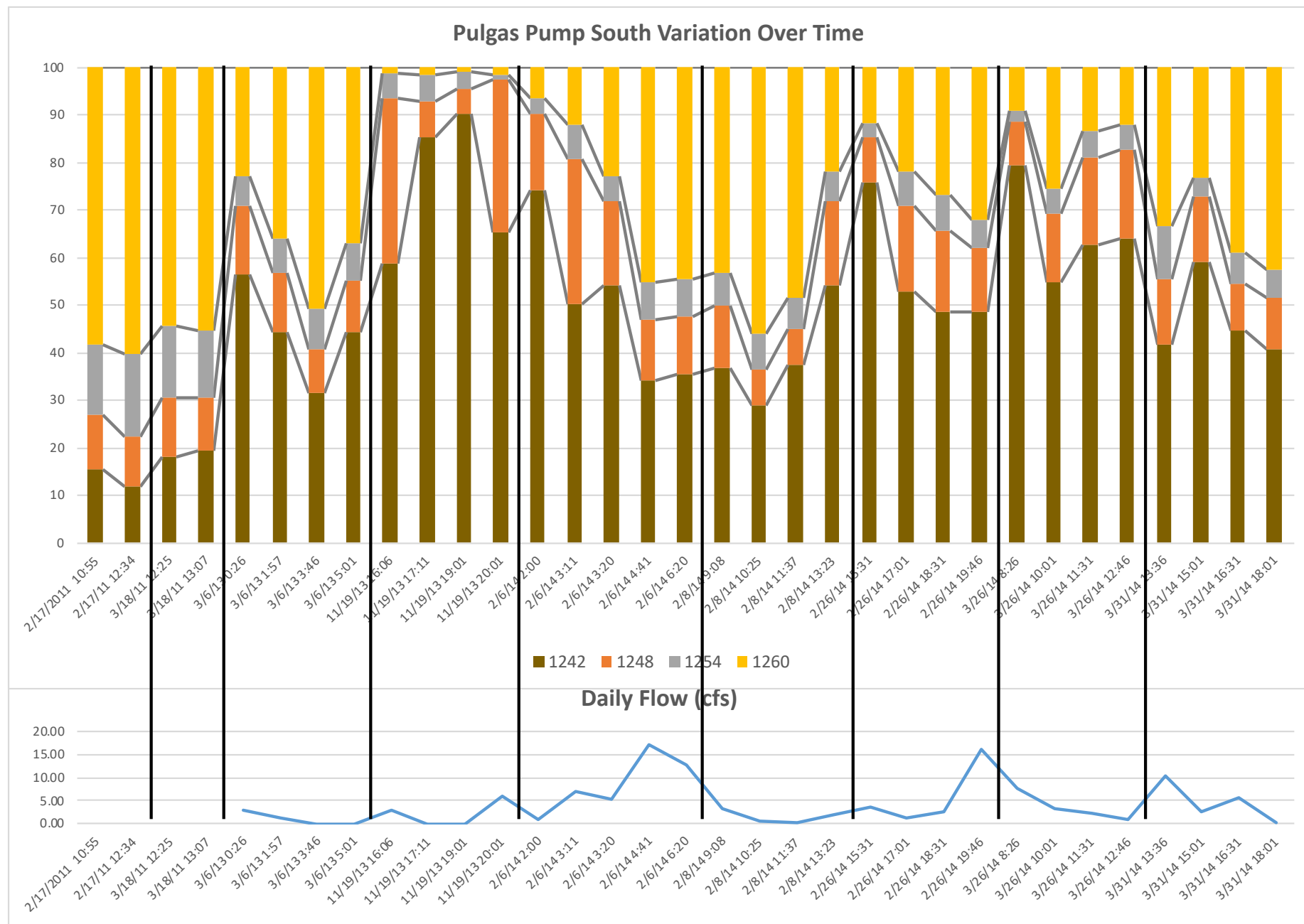


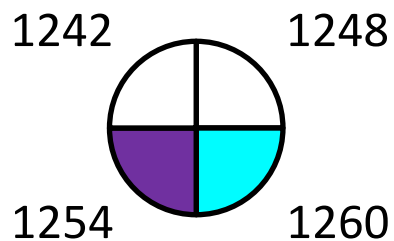
Figure 4. Aroclor indices in sediment in the Pulgas Pump Station South watershed.

Purple: Primary contributor (>40% of sum of indices)

Blue: Secondary (20-40%)

White: Low contributor (<20%)

Pink: Unreliable profiles due to low concentrations



Sum of 40 Congeners (ppb)

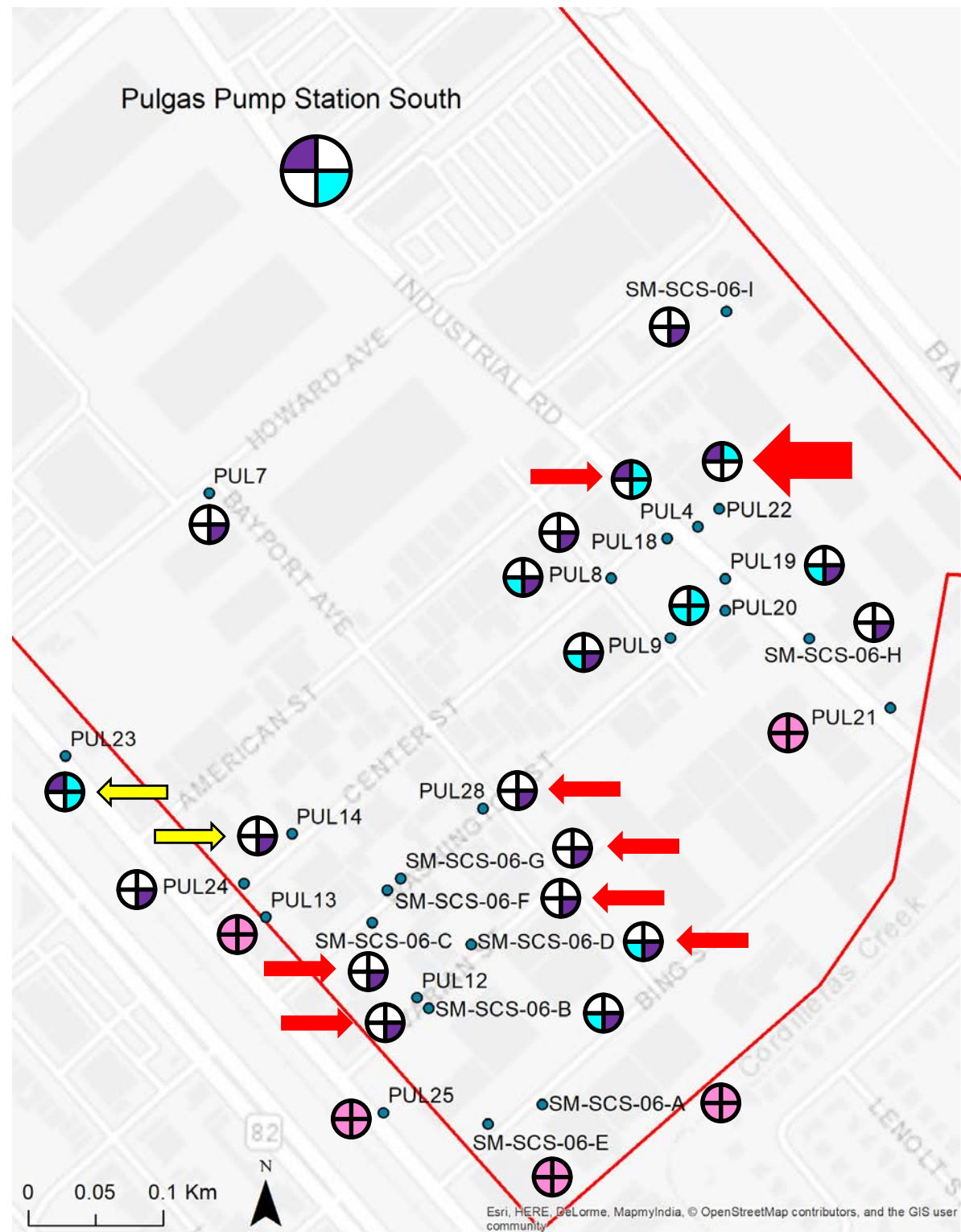


Figure 5. Aroclor indices in stormwater at Coyote Creek over time.

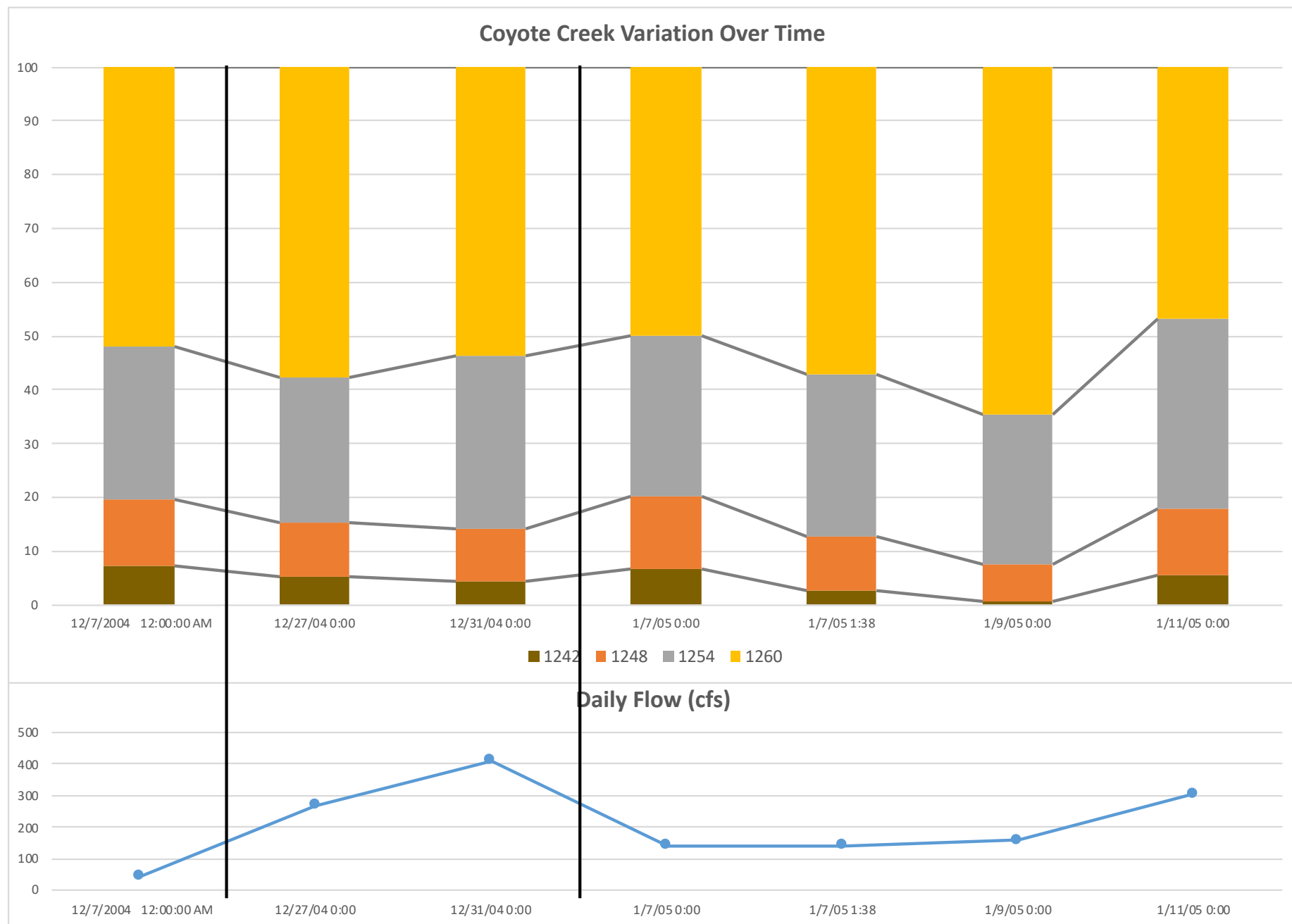


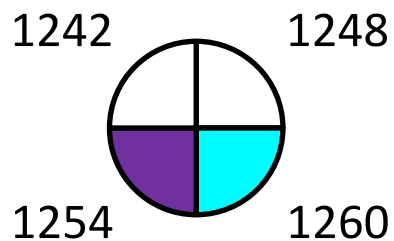
Figure 6a. Aroclor indices in sediment in the Coyote Creek watershed: Charcot Avenue.

Purple: Primary contributor (>40% of sum of indices)

Blue: Secondary (20-40%)

White: Low contributor (<20%)

Pink: Unreliable profiles due to low concentrations



Sum of 40 Congeners (ppb)

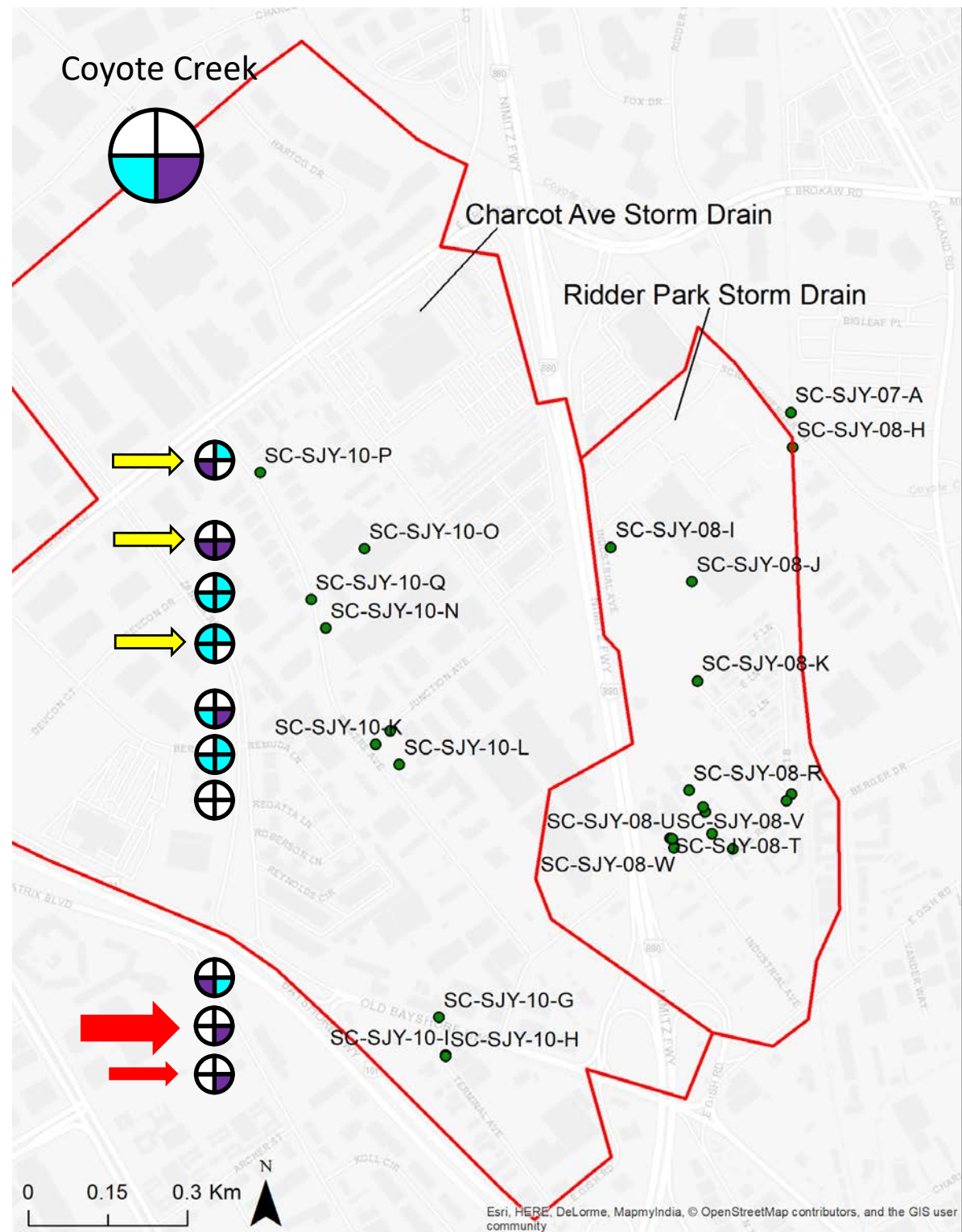
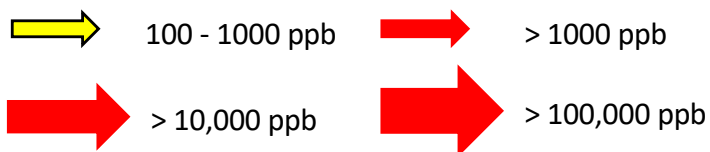




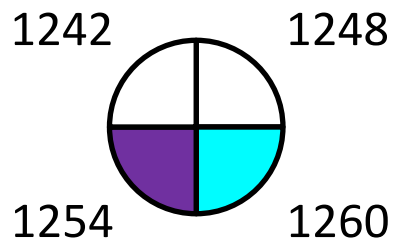
Figure 6b. Aroclor indices in sediment in the Coyote Creek watershed: Ridder Park (north).

Purple: Primary contributor  
(>40% of sum of indices)

Blue: Secondary (20-40%)

White: Low contributor (<20%)

Pink: Unreliable profiles due to low concentrations



Sum of 40 Congeners (ppb)

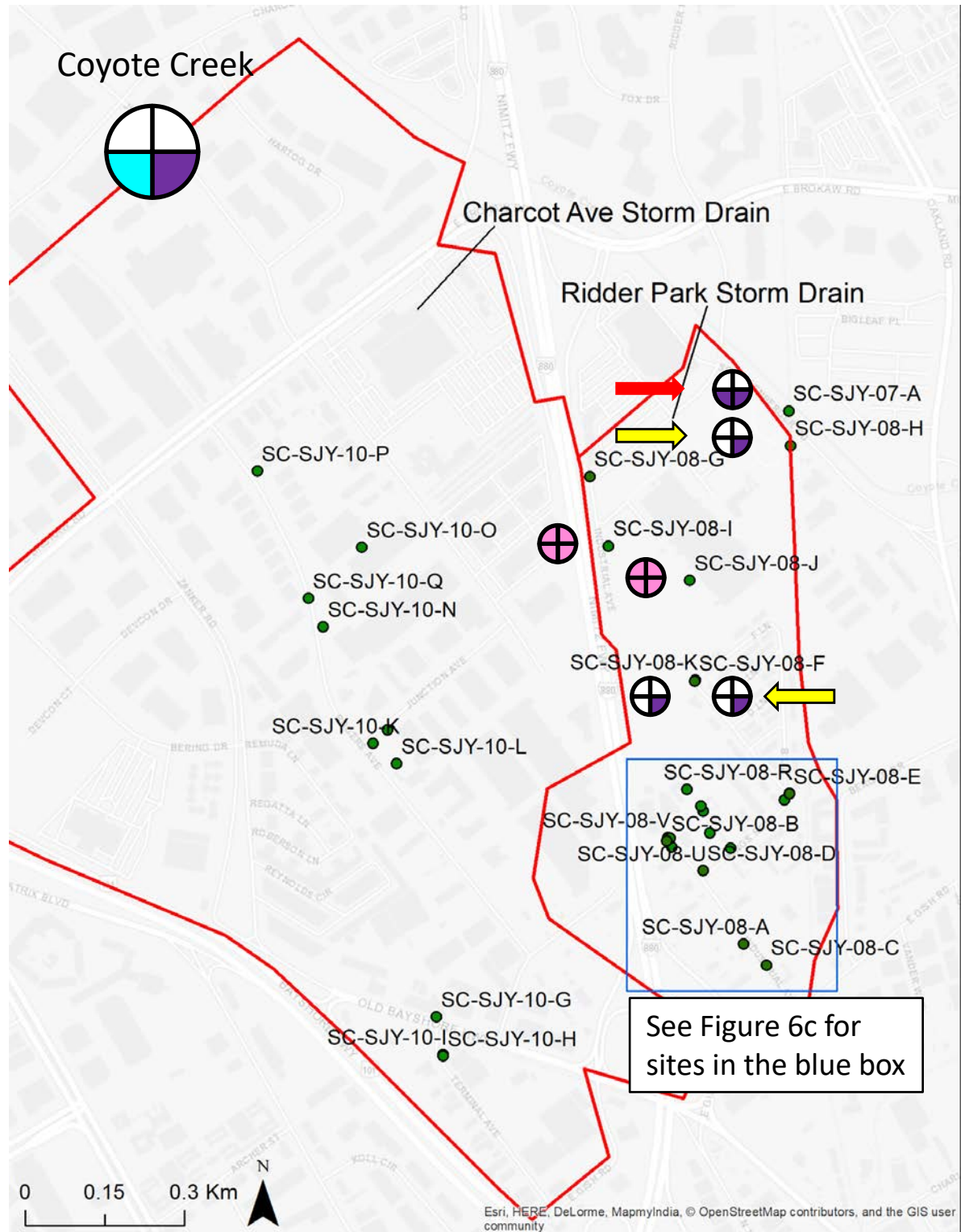
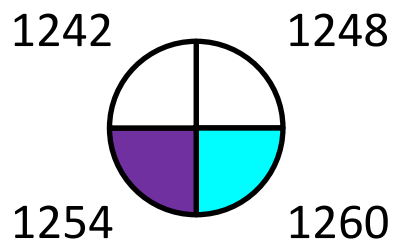


Figure 6c. Aroclor indices in sediment in the Coyote Creek watershed: Ridder Park (south).

Purple: Primary contributor (>40% of sum of indices)  
 Blue: Secondary (20-40%)  
 White: Low contributor (<20%)  
 Pink: Unreliable profiles due to low concentrations



Sum of 40 Congeners (ppb)

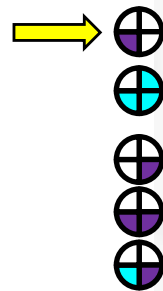


Figure 7. Aroclor indices in stormwater at Guadalupe River over time.

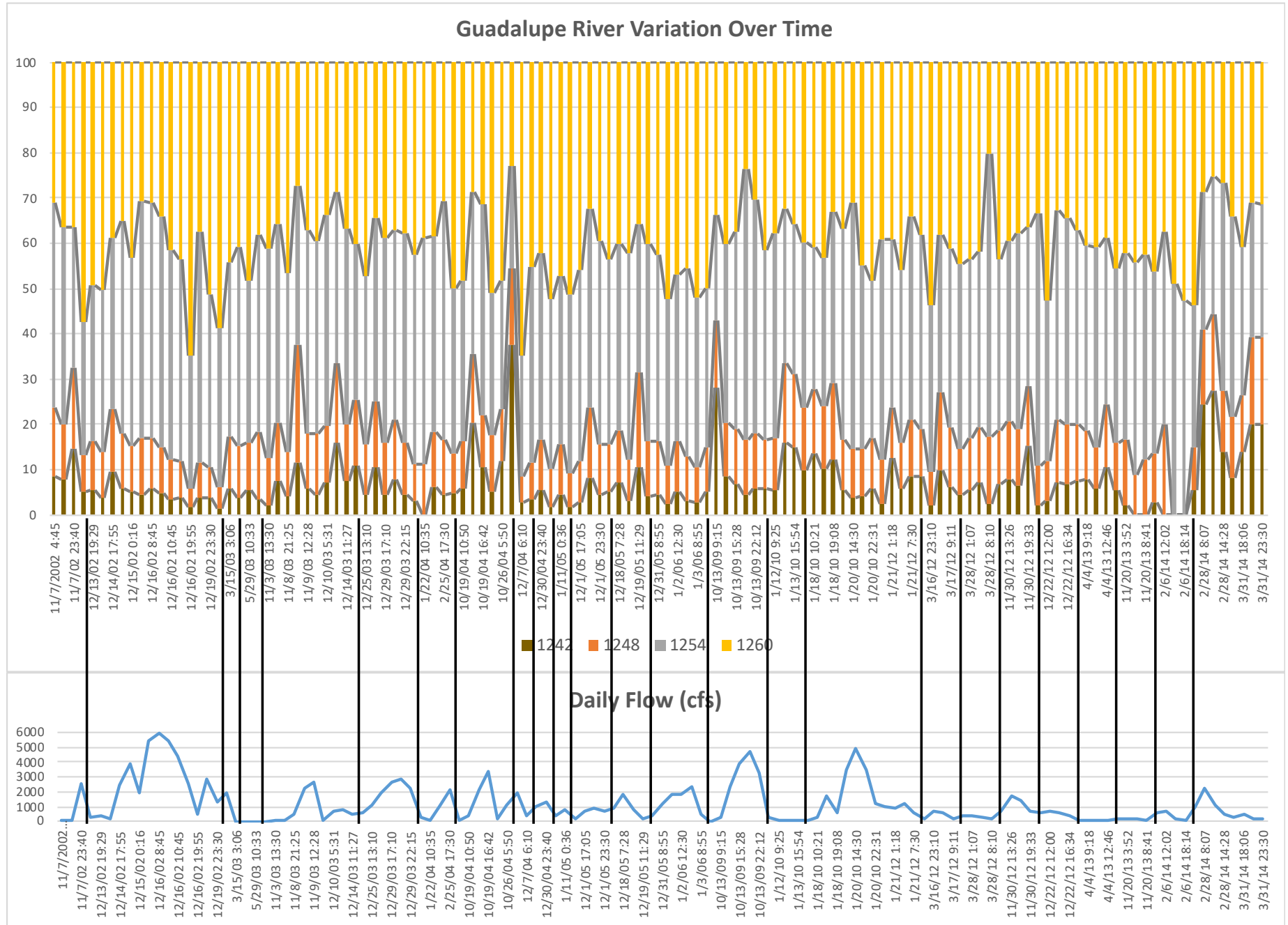


Figure 8. Map showing locations of the areas depicted in Figures 8a-i.

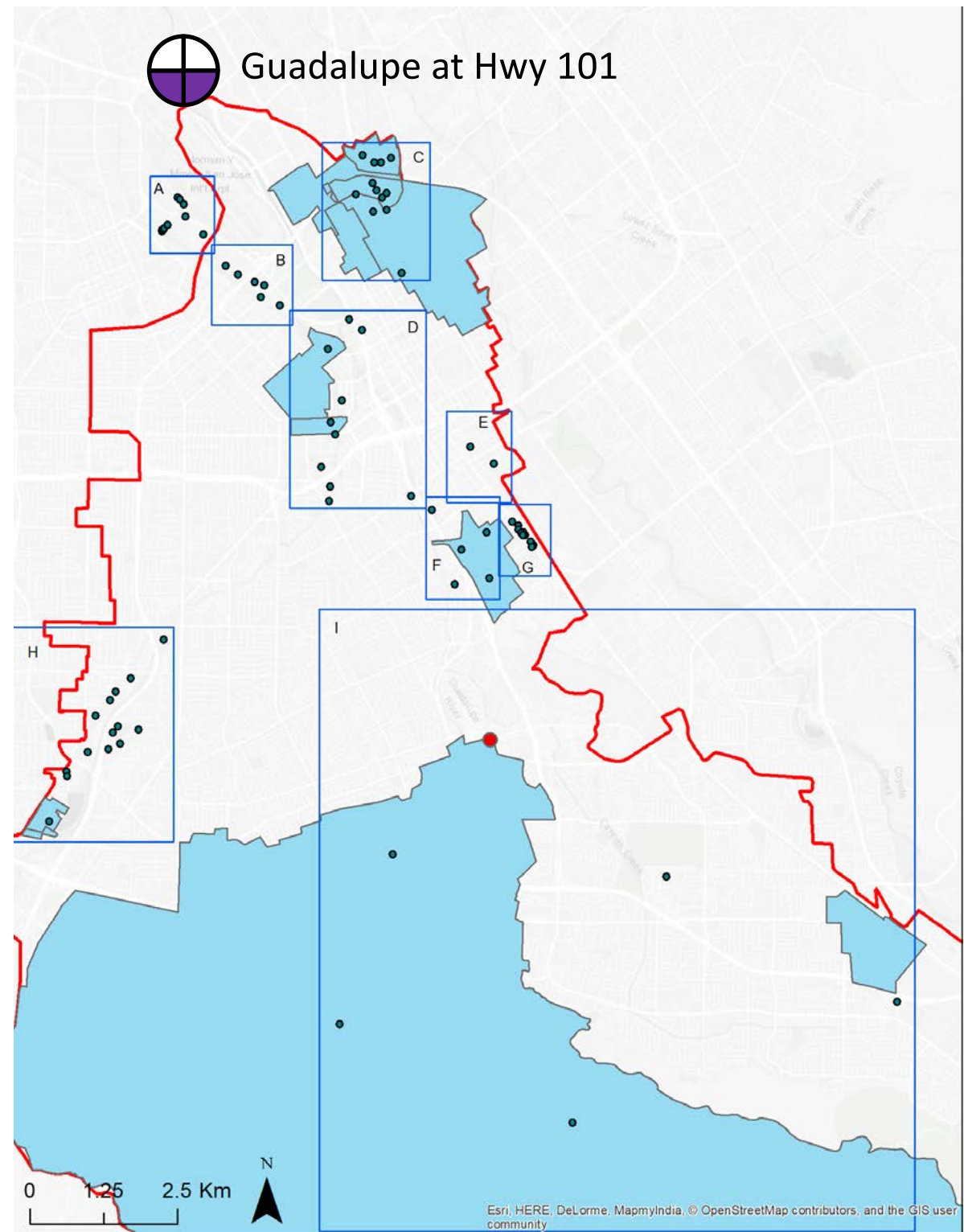
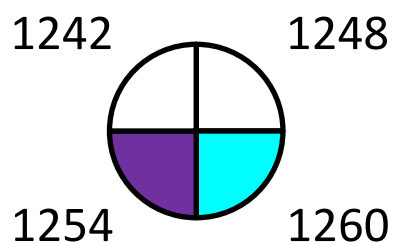




Figure 9a. Aroclor indices in sediment in the Guadalupe River watershed: region A.

Purple: Primary contributor (>40% of sum of indices)  
 Blue: Secondary (20-40%)  
 White: Low contributor (<20%)  
 Pink: Unreliable profiles due to low concentrations



Sum of 40 Congeners (ppb)

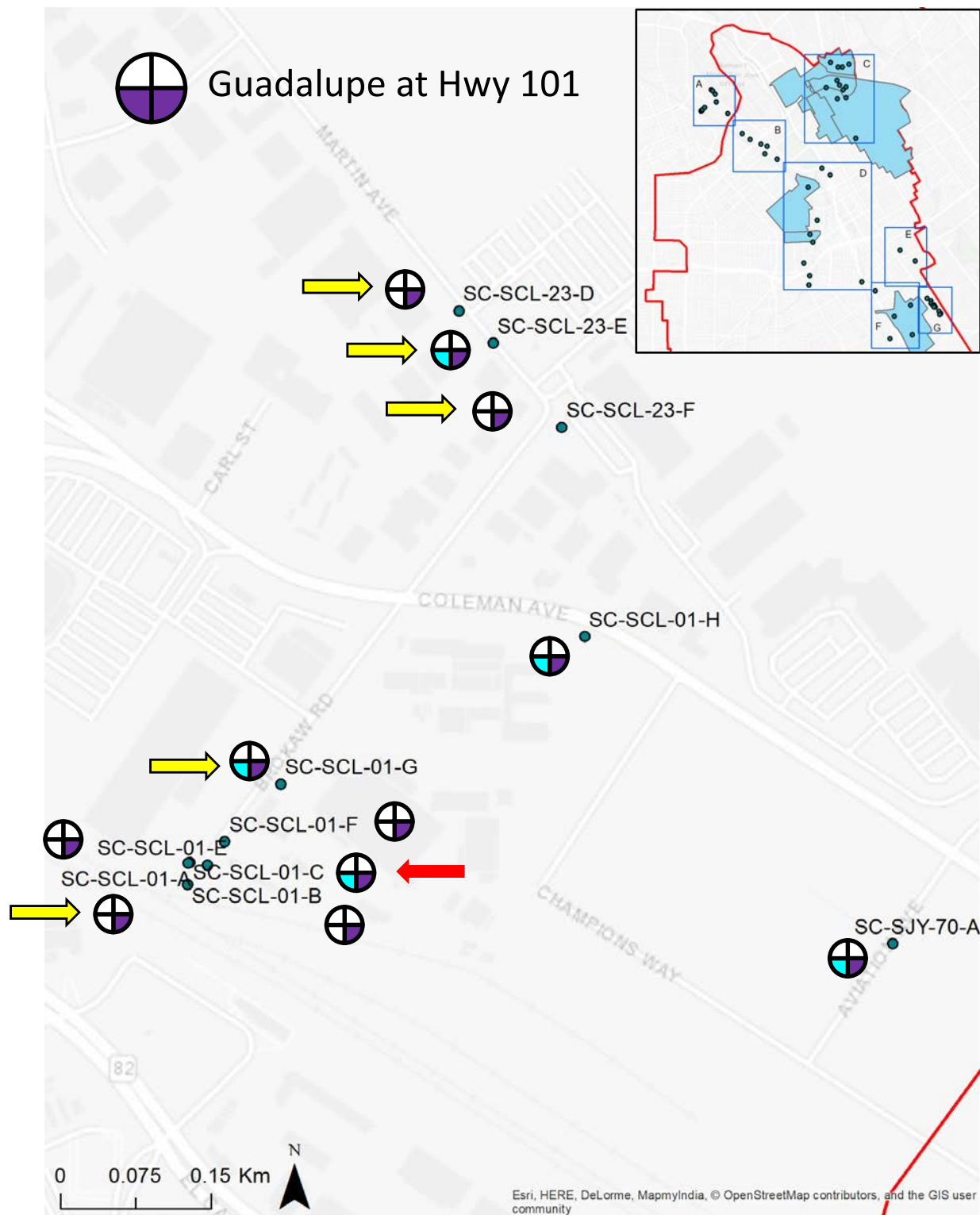


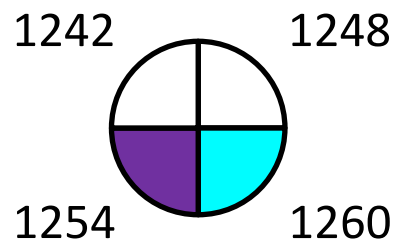
Figure 9b. Aroclor indices in sediment in the Guadalupe River watershed: region B.

Purple: Primary contributor (>40% of sum of indices)

Blue: Secondary (20-40%)

White: Low contributor (<20%)

Pink: Unreliable profiles due to low concentrations



Sum of 40 Congeners (ppb)

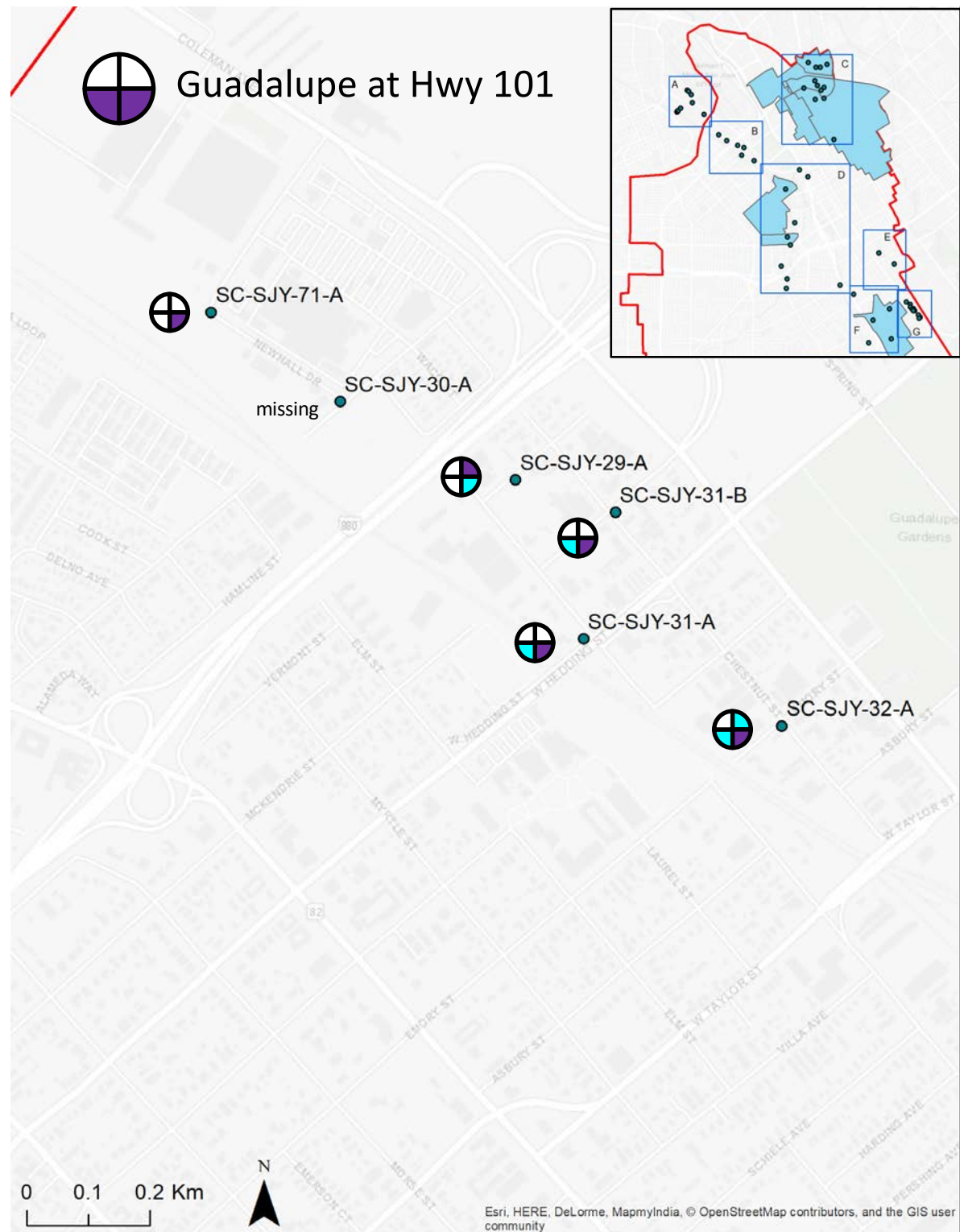
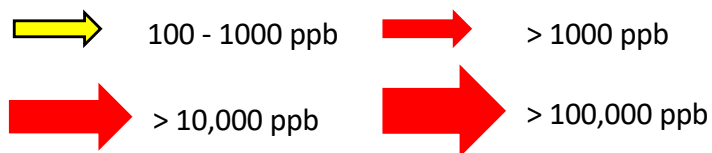
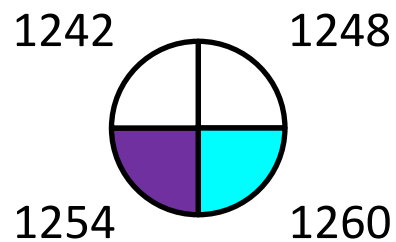


Figure 9c. Aroclor indices in sediment in the Guadalupe River watershed: region C.

Purple: Primary contributor (>40% of sum of indices)  
 Blue: Secondary (20-40%)  
 White: Low contributor (<20%)  
 Pink: Unreliable profiles due to low concentrations



Sum of 40 Congeners (ppb)

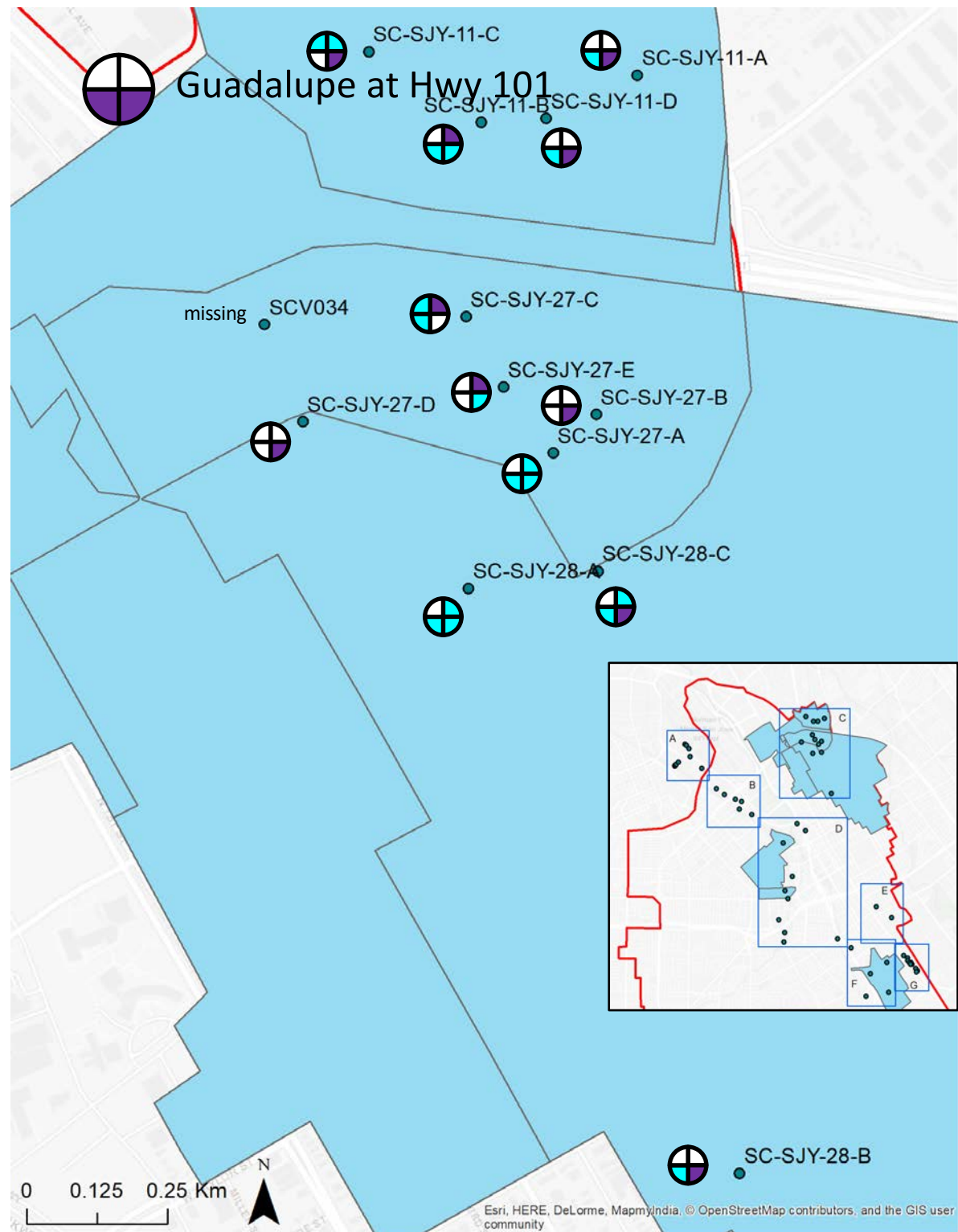
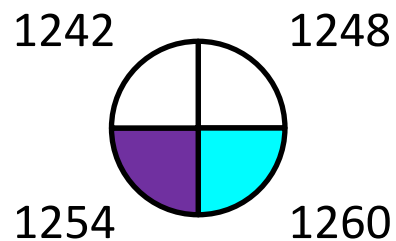


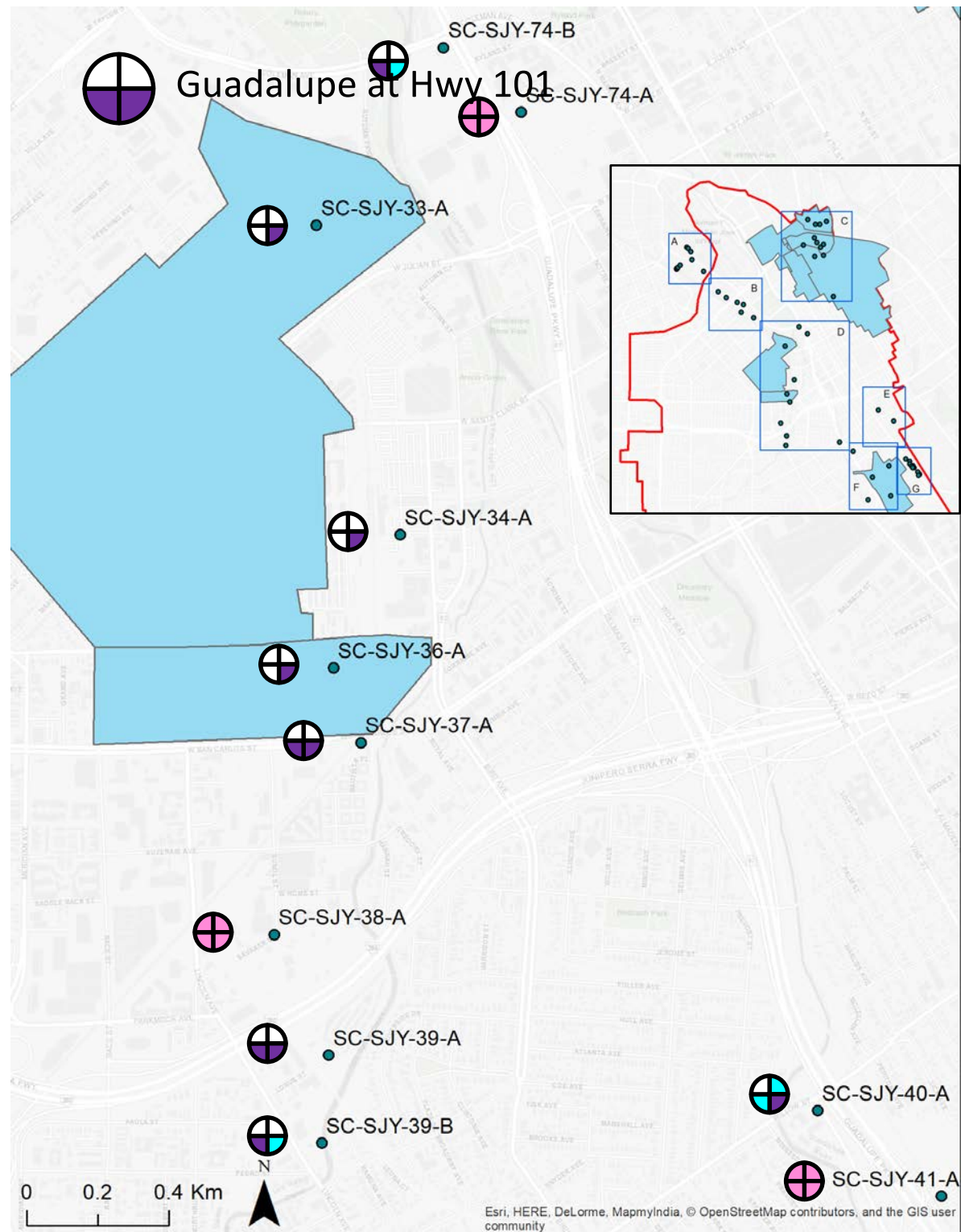


Figure 9d. Aroclor indices in sediment in the Guadalupe River watershed: region D.

Purple: Primary contributor (>40% of sum of indices)  
 Blue: Secondary (20-40%)  
 White: Low contributor (<20%)  
 Pink: Unreliable profiles due to low concentrations



Sum of 40 Congeners (ppb)





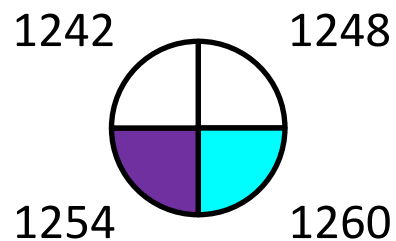
## Figure 9e. Aroclor indices in sediment in the Guadalupe River watershed: region E.

Purple: Primary contributor (>40% of sum of indices)

Blue: Secondary (20-40%)

White: Low contributor (<20%)

Pink: Unreliable profiles due to low concentrations



Sum of 40 Congeners (ppb)

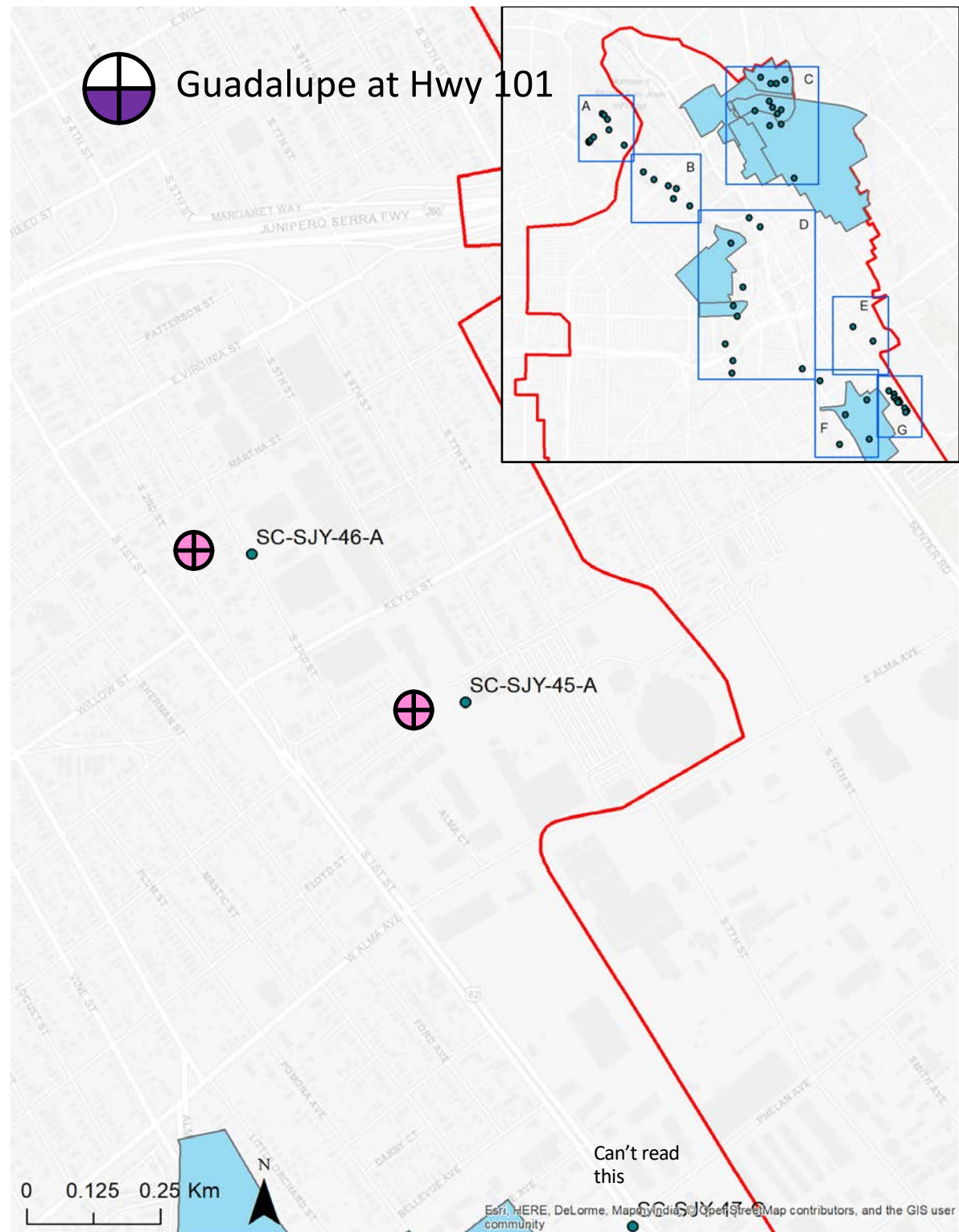
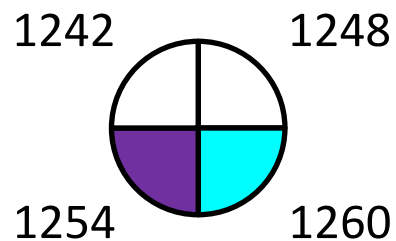


Figure 9f. Aroclor indices in sediment in the Guadalupe River watershed: region F.

Purple: Primary contributor (>40% of sum of indices)  
 Blue: Secondary (20-40%)  
 White: Low contributor (<20%)  
 Pink: Unreliable profiles due to low concentrations



Sum of 40 Congeners (ppb)

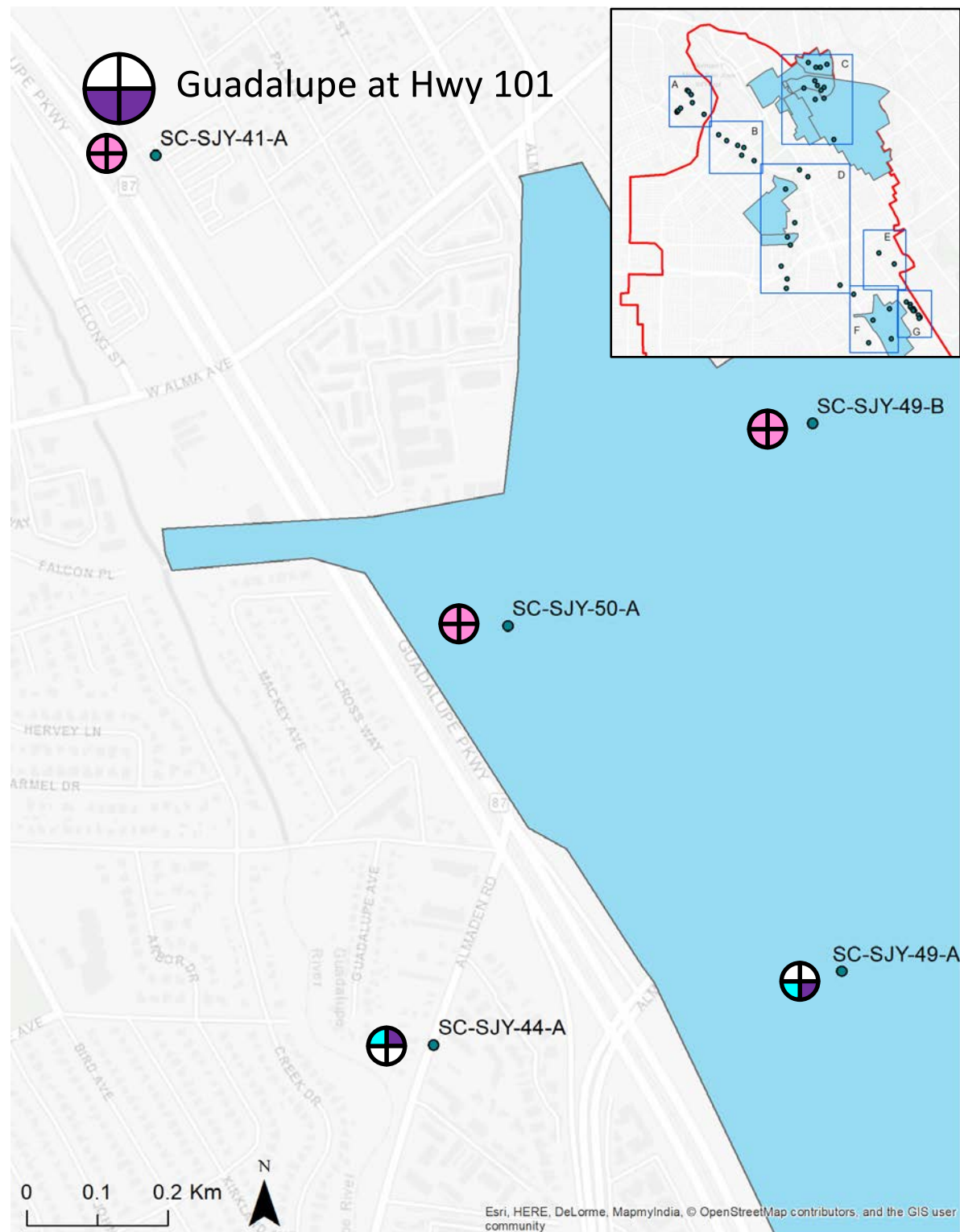


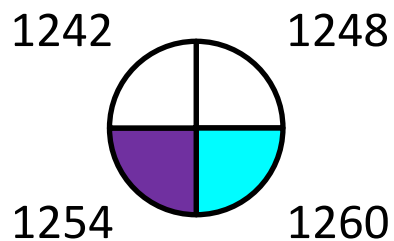
Figure 9g. Aroclor indices in sediment in the Guadalupe River watershed: region G.

Purple: Primary contributor (>40% of sum of indices)

Blue: Secondary (20-40%)

White: Low contributor (<20%)

Pink: Unreliable profiles due to low concentrations



Sum of 40 Congeners (ppb)

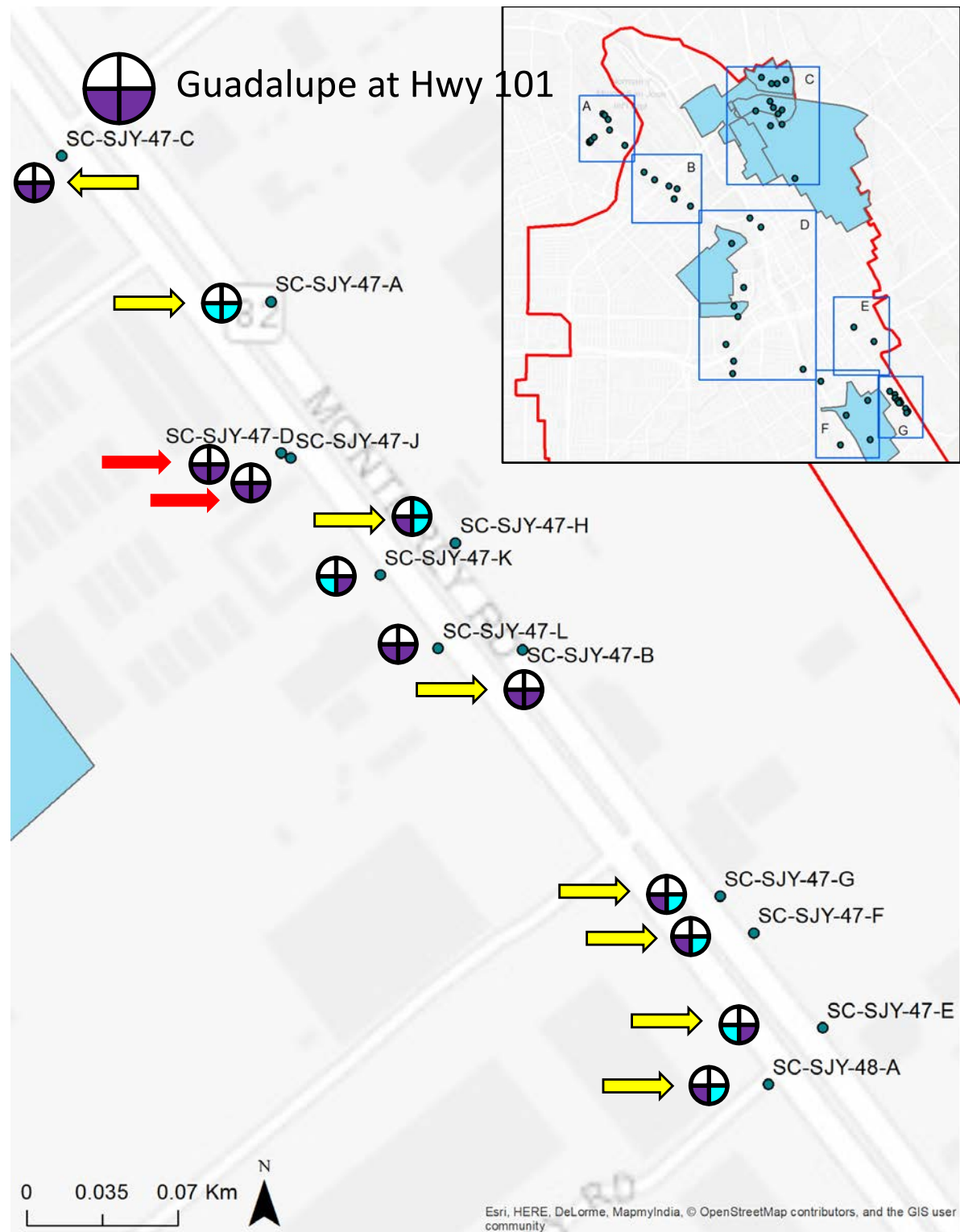
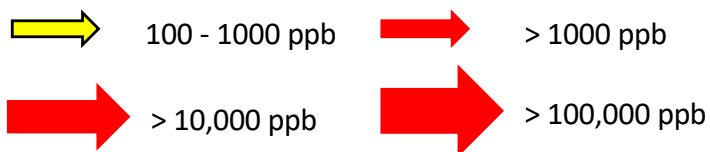




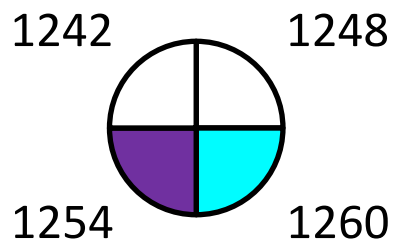
Figure 9h. Aroclor indices in sediment in the Guadalupe River watershed: region H.

Purple: Primary contributor (>40% of sum of indices)

Blue: Secondary (20-40%)

White: Low contributor (<20%)

Pink: Unreliable profiles due to low concentrations



Sum of 40 Congeners (ppb)

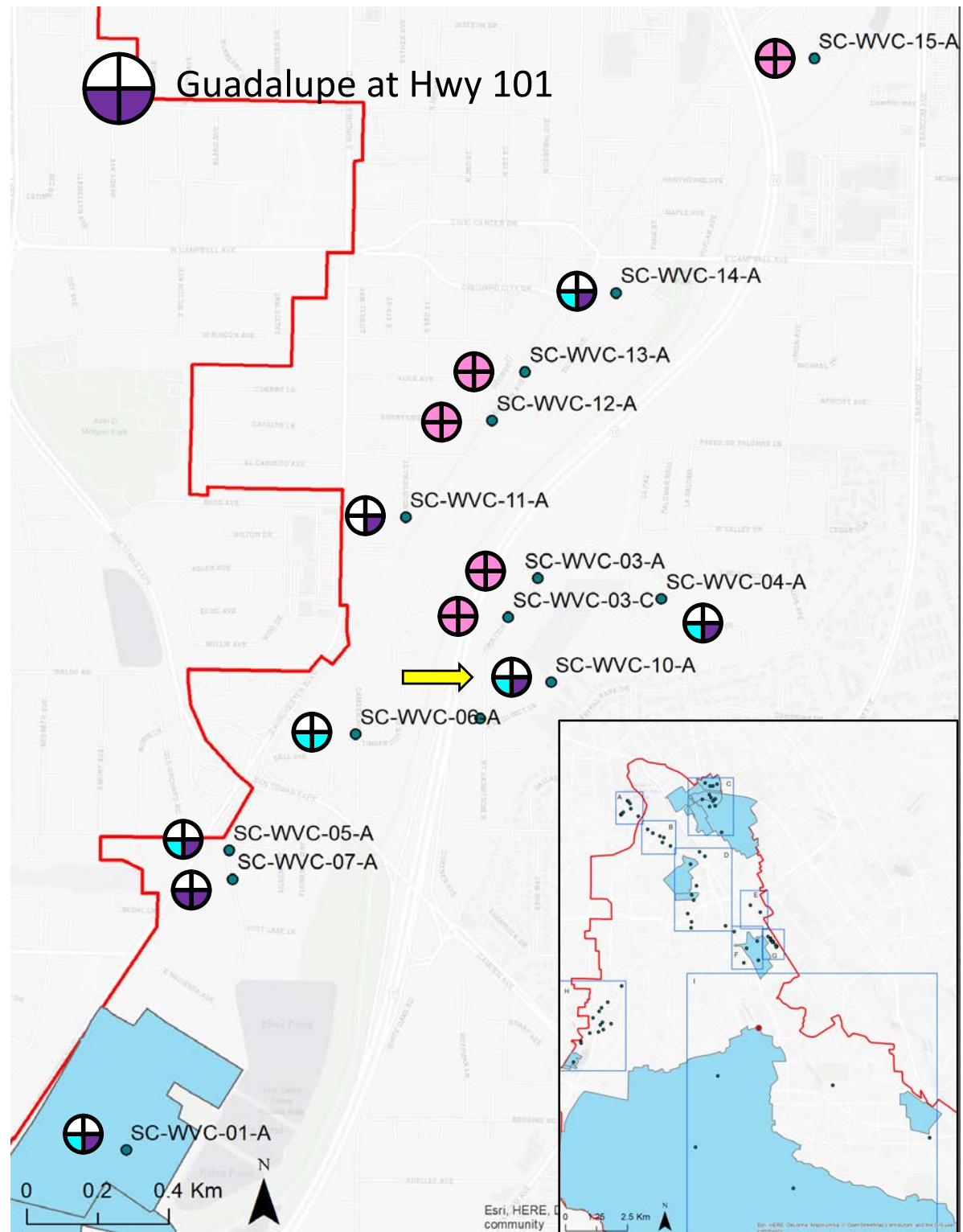


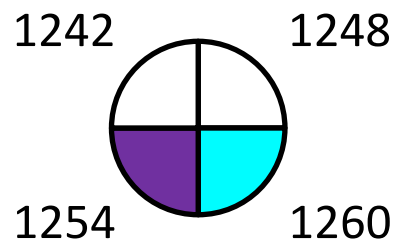
Figure 9i. Aroclor indices in sediment in the Guadalupe River watershed: region I.

Purple: Primary contributor (>40% of sum of indices)

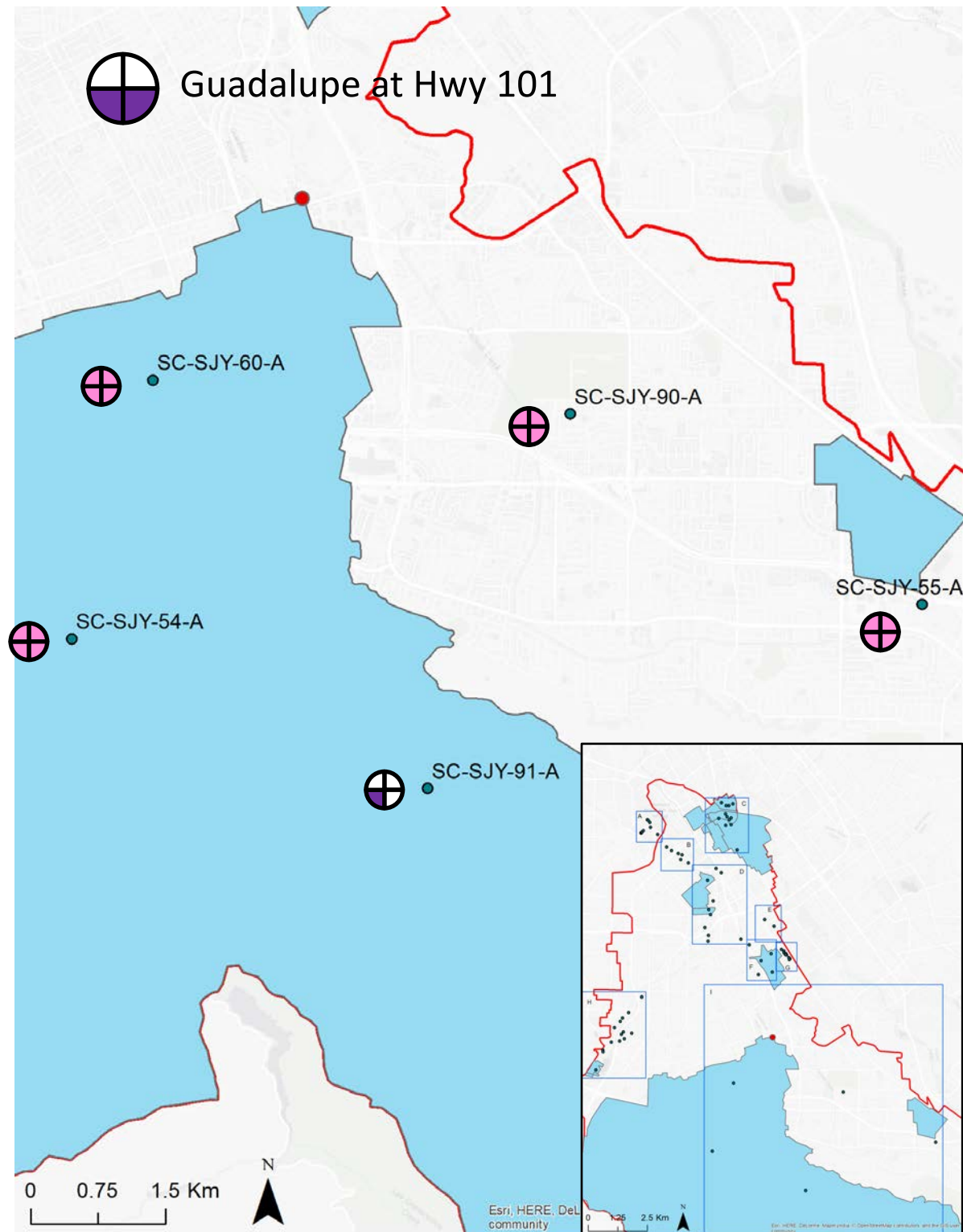
Blue: Secondary (20-40%)

White: Low contributor (<20%)

Pink: Unreliable profiles due to low concentrations

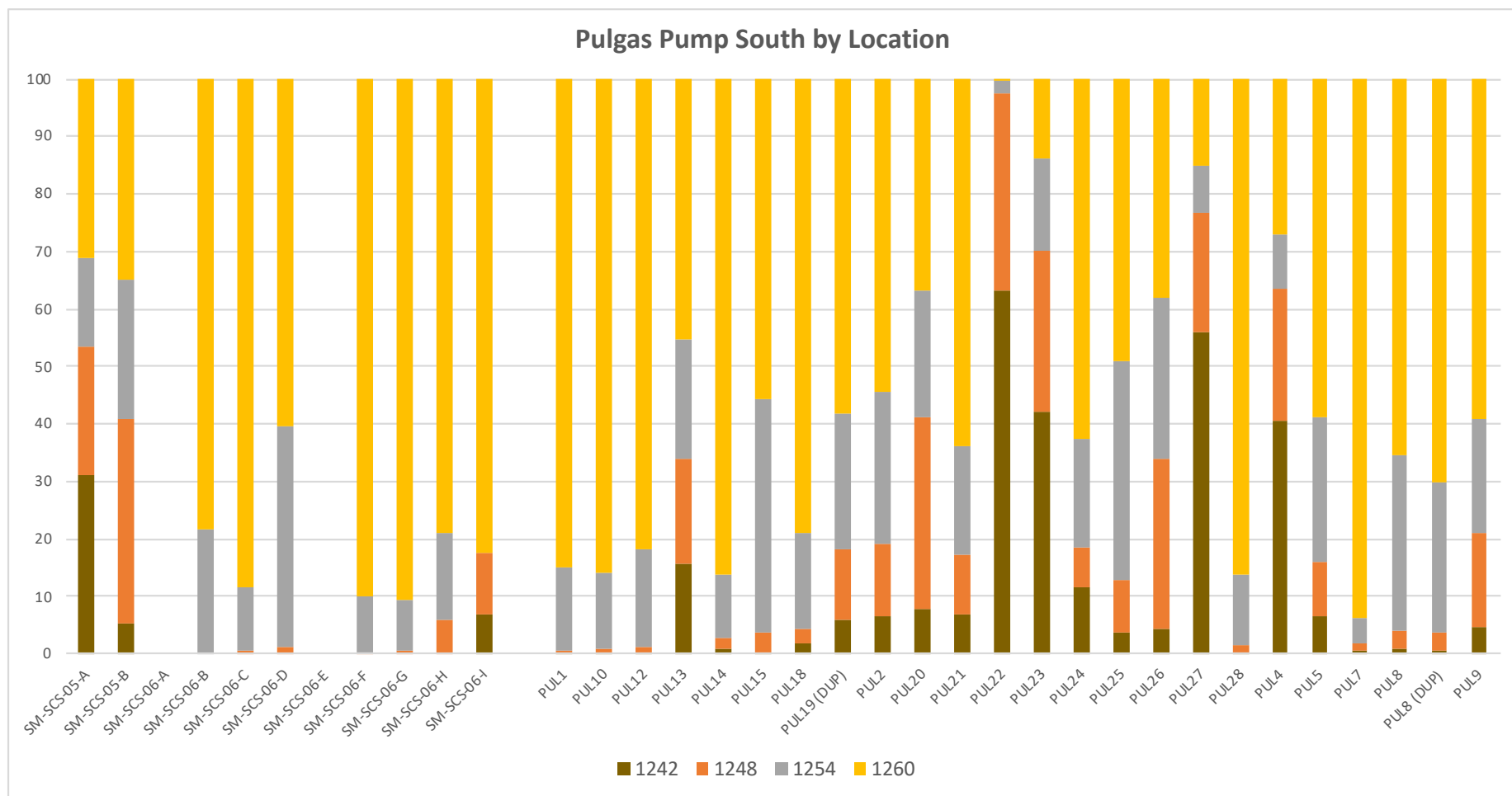


Sum of 40 Congeners (ppb)

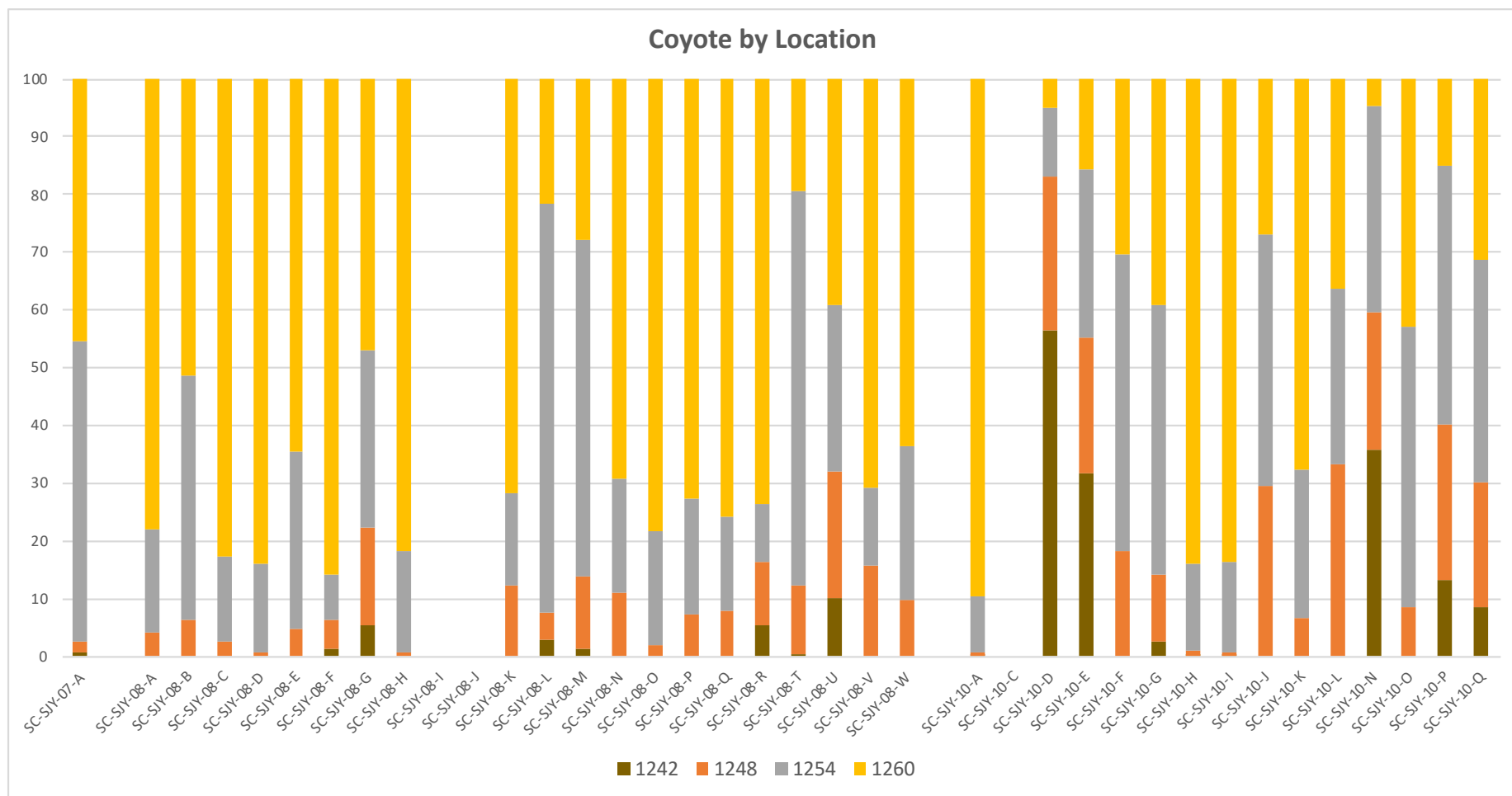


# Appendix 1

## Aroclor Contributions by Location

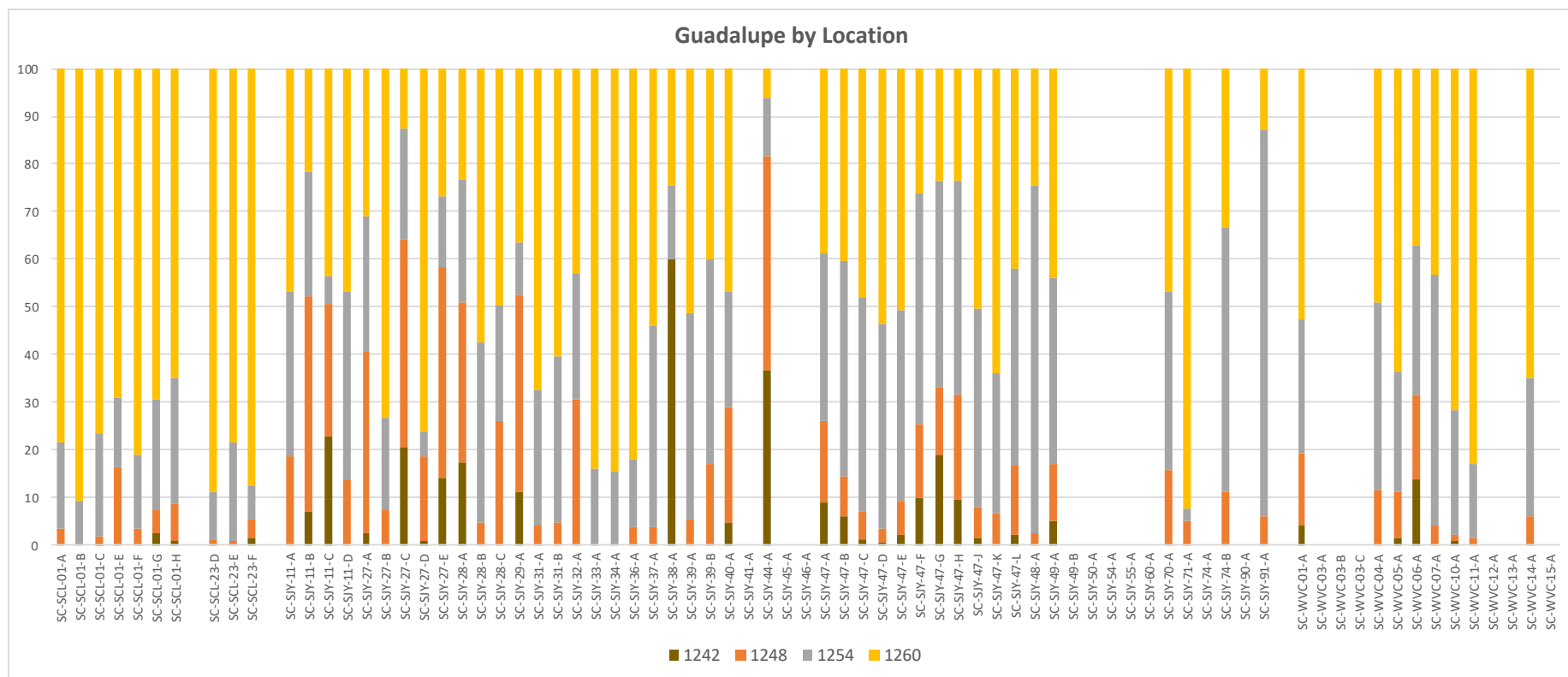


Some bars are missing because congener patterns were unreliable due to low  $\Sigma$ PCB concentrations (<10 ng/g).



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