



February 9, 2008

Mr. Gary Mauseth
Polaris Applied Sciences, Inc.
12509 - 130th Lane, NE
Kirkland, WA 98034-7713

RE: Evaluation of Environmental Chemistry Results Associated With the NOAA Report Entitled: "2008 Cosco Busan Oil Spill Assessing Toxic Injury to Pacific herring embryos and larvae in the San Francisco Bay. Draft Report September 2008.

Dear Mr. Mauseth,

As requested I have examined the NOAA report entitled **2008 Cosco Busan Oil Spill Assessing Toxic Injury to Pacific herring embryos and larvae in the San Francisco Bay. Draft Report September 2008**¹. The objective of my analysis was to determine if environmental chemistry data generated by NOAA supported their technical conclusions regarding type and source(s) of embryo and PEMD contamination at Cosco Busan oiled and reference (non-oiled) shoreline sites are valid and scientifically defensible.

Summary:

The preliminary technical conclusions based on the reported analysis of the Cosco Busan herring egg embryos and PEMD samples do not appear to be supported by the data (e.g., PAH concentrations). Detailed chemical analysis of the raw PAH laboratory results indicates that the figures in the report and associated conclusions presented in the text are invalid and do not represent an accurate assessment of the analytical results. Specifically, the PAH concentrations in the tissue samples are so low that the method blank contributes substantial concentrations of individual PAHs which are unrelated to any exposure to Cosco Busan oil. NOAA did not appear to consider this problem in the report which included simple statistics (e.g., mean and standard error) and graphical analysis of the test sites. For example in some tissue samples, the instrumental area response of the method blank is approximately the same as the instrumental area response in the sample (e.g., C2-phenanthrenes), yet these were not qualified² in the data report. These data were used to prepare summary graphics and conclusions that suggest that the mean concentrations of PAH in tissue samples from oiled sites (e.g., Keil Cove) are higher than the un-oiled reference sites. In addition, if one invokes the assumption in the report that the data are valid, simple and complex statistical analysis of the data do not indicate a Cosco Busan source. Although the PEMD samples did not have as extensive a blank problem, some of the data are compromised and the impacts of the blank/sample relationship should have been considered when preparing the interpretive report. When the mean PEMD PAH concentrations

¹ 2008 Cosco Busan Oil Spill Assessing Toxic Injury to Pacific Herring Embryos and Larvae in the San Francisco Bay. Draft Report September 2008.

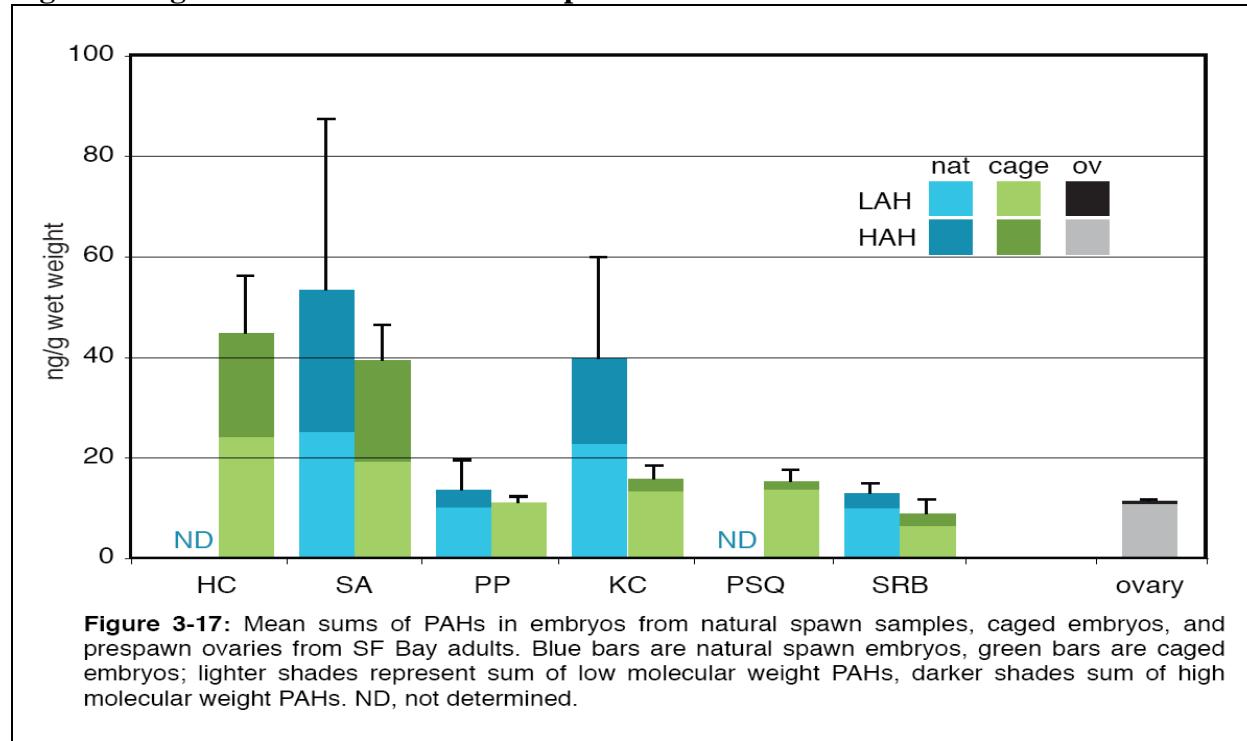
² Data that does not meet specific data quality objectives are qualified (e.g., B = blank) to alert the data user that there may be a problem with the chemical results.

for critical sites such as Kiel cove (oiled) are examined, and the method/procedural blank impacts are incorporated into the data interpretation process, there are no relevant PAH concentration or distribution differences relative to the reference (un-oiled, e.g., San Quentin) sites. Specifically, when the mean alkylated phenanthrenes concentrations between Keil Cove (oiled) and San Quentin (un-oiled reference) are compared, the San Quentin PEMD PAH results (mean values) are approximately same in concentration and distribution and document that the PAH distributions observed at Keil cove are derived from urban runoff. Based on my careful analysis of the data, the figures and conclusions presented in the report are not diagnostically informative. There are no chemical data to support the claim that herring embryos are impacted by Cosco Busan oil. The following discussion is a listing of my findings and the technical data that I relied on to reach my conclusions.

Findings:

Finding #1: Figure 3-17 is not useful because supporting embryo data is impacted by method blank contamination. The raw analytical data does not indicate that oiled sites have higher mean PAH concentrations than un-oiled sites.

Figure 1. Figure 3-17 from the NOAA report



Proof: The figure is confusing because the lower error bars are omitted from the plot that would show the concentration overlap at each site. Second, the individual herring egg PAH analyses used to construct this plot contain tissue PAH field results that are the same magnitude as the concentrations detected in the method blank, yet were included in the mean values. The impact of blanks is measured at the instrument level. If the instrument response of the field sample is less than 4X-5X the instrument response of the associated method blank then the data must be

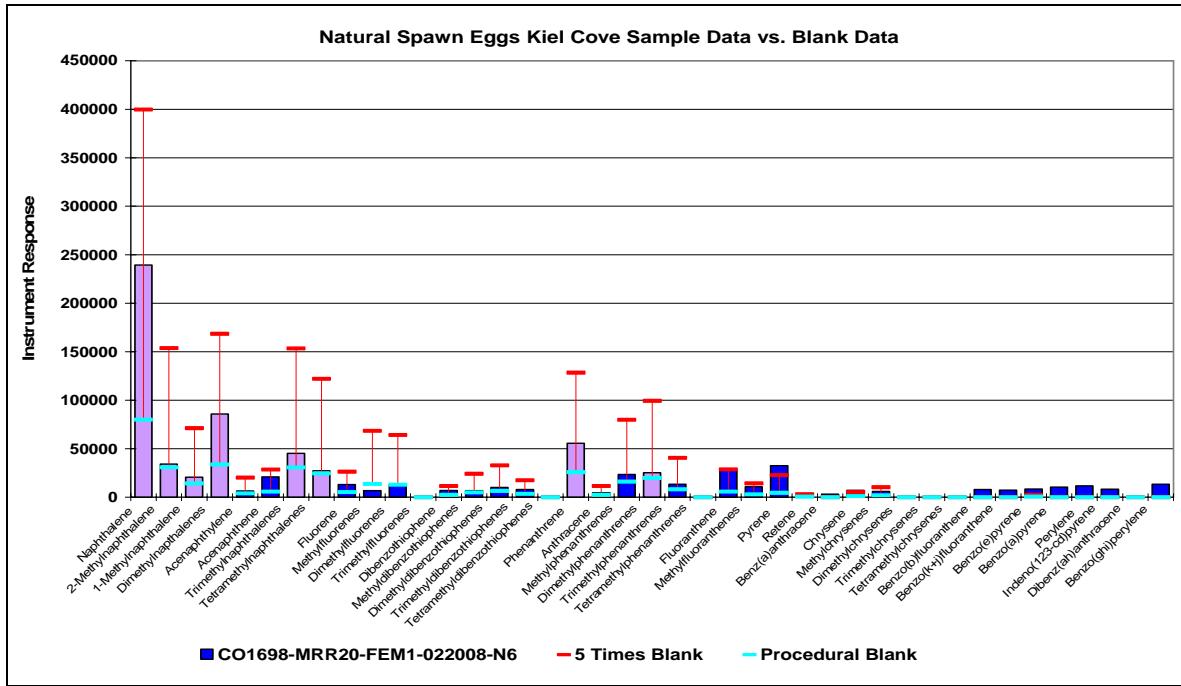
qualified with a “B” (qualified data) and treated as a suspect value^{3,4}. This way the reviewer can consider the variability associated with blank issues when interpreting the results. The closer the field sample response is to the method blank, the less reliable the numerical result. Figure 2 is an example of the PAH instrument responses for a Kiel Cove (oiled beach) natural spawned egg sample versus the associated blank. The pink bars represent the area response of PAH reported in the document, the blue bars represent PAHs with detectable concentrations that are present in the sample but not reported because they are below the laboratory reporting limit. Clearly most of the PAHs reported in this sample are impacted by the blank. PAHs are defined in the report as petrogenic alkylated PAHs (e.g., C1-naphthalenes, C2-phenanthrenes) and pyrogenic PAHs (e.g., fluoranthene, pyrene) associated with urban runoff. All of the reported PAHs in this sample fail the EPA 5X blank criteria and most fail the NOAA 4X blank criteria which means the chemical data are not as useful from an interpretation perspective. Yet, the embryo sample PAHs were averaged as follows:

“Sum “low molecular weight PAHs” (LMWAHs) will include summing the concentrations of naphthalene, C1- through C4-naphthalenes, biphenyl, acenaphthylene, acenaphthene, fluorene, C1- through C3-fluorenes, phenanthrene, C1- through C4-phenanthrenes, dibenzothiophene, C1- through C3-dibenzothiophenes and anthracene. Sum “high molecular weight PAHs” (HMWAHs) will include adding the levels of fluoranthene, pyrene, C1-fluoranthenes/pyrenes, benz[a]anthracene, chrysene/ triphenylene, C1- through C4-chrysenes/ benz[a]anthracenes, benzo[b]fluoranthene, benzo[j]fluoranthenes/ benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, idenopyrene, dibenz[a,h+a,c]anthracene, benzo[ghi]perylene. Total PAHs will be calculated by summing the concentrations of LMWAHs and HMWAHs.” The final figures in the report (e.g., Figure 3-17) are averages (e.g, Total PAH = LAH plus HAH) of averages (average of samples collected at each site). This type of figure obscures the base data and the relationships between individual samples and oiled versus un-oiled sites.

³ USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review. October 1999.

⁴ NOAA 2004. Extraction Cleanup and Gas Chromatography/Mass Spectrometry Analysis of Sediments and Tissues for Organic Contaminants. NOAA Technical Memorandum NMFS-NWFSC-59. March 2004. Page 42.

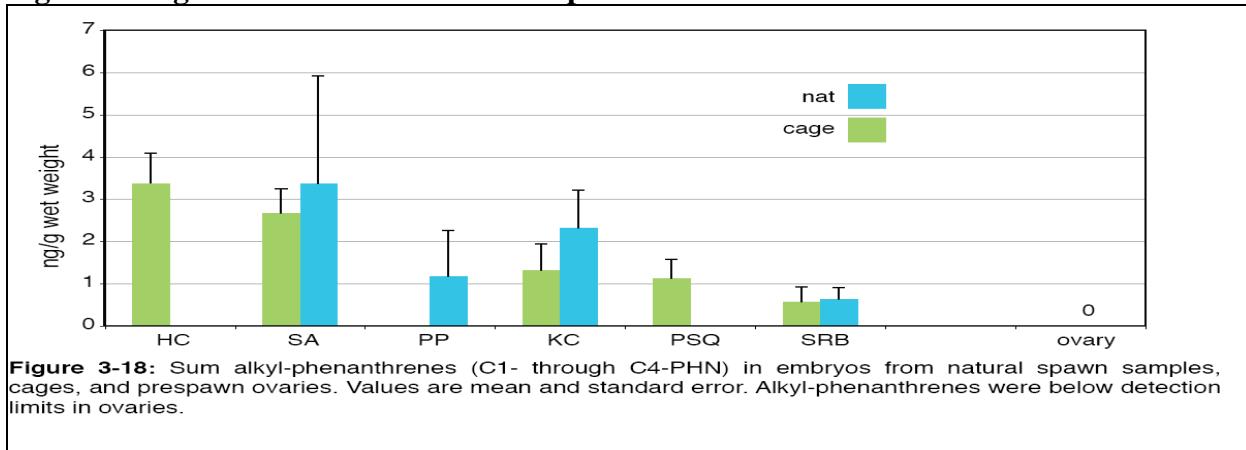
Figure 2. PAH instrument response plot for natural spawned egg sample from Kiel Cove versus the method blank data.



All of the individual sample PAH instrument response and concentration plots prepared by NewFields and used to evaluate the sample/blank data are provided in Attachment 1 and Attachment 2. The conclusion based on this analysis is that the high blank/sample ratio significantly reduces the interpretive value of the chemical data.

Finding #2: The mean embryo total alkyl-phenanthrenes concentration trends between oiled and un-oiled sites as presented in Figure 3-18 of the report are not useful because the supporting embryo data are impacted by method blank contamination.

Figure 3. Figure 3-18 from the NOAA report



Proof: Figure 3-18 is confusing because the lower error bars are omitted from the plot that would show the concentration overlap at each site. Second, the individual herring egg PAH analyses used to construct this plot contain field data results that are the same magnitude as the concentrations detected in the method blank yet were included in the mean values.

In Figure 4 (Keil Cove herring egg sample), the green box highlights the C1-C4 alkylated phenanthrenes that the report states are the toxic components in Cosco Busan oil and are responsible for biological damage to the herring embryos. Note that the two highest alkyl-phenanthrenes, C1-phenanthrenes and C2-phenanthrenes, are only slightly greater than the method blank response (e.g., the blank response represents more than half of the field sample).

Finding #3: The frequency of method blank problems was somewhat lower in the PEMD samples (e.g., Horseshoe Cove) than the tissue samples although several PEMD samples were impacted. Once the impact of the method blanks is identified, some source diagnostic information can be derived from the analytical data (e.g., fluoranthene/pyrene ratio).

Figure 4. PAH instrument response plot for natural spawned egg sample from Kiel Cove versus the instrument response for the associated method blank.

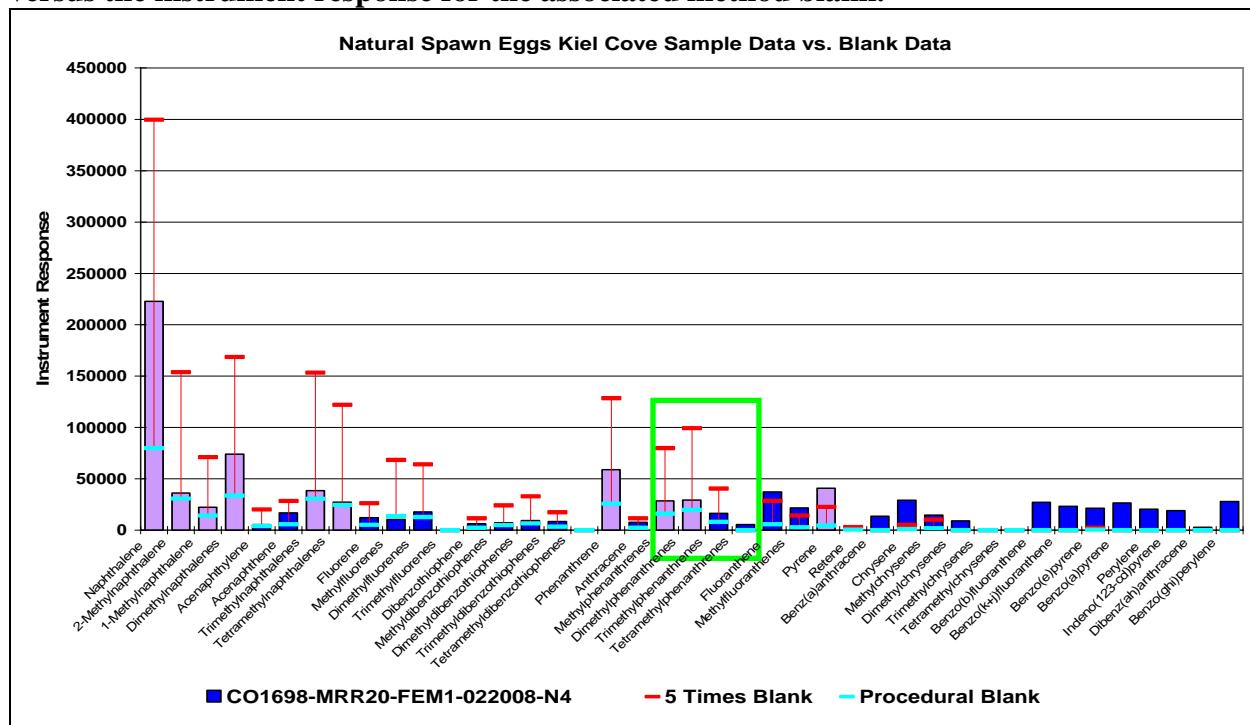
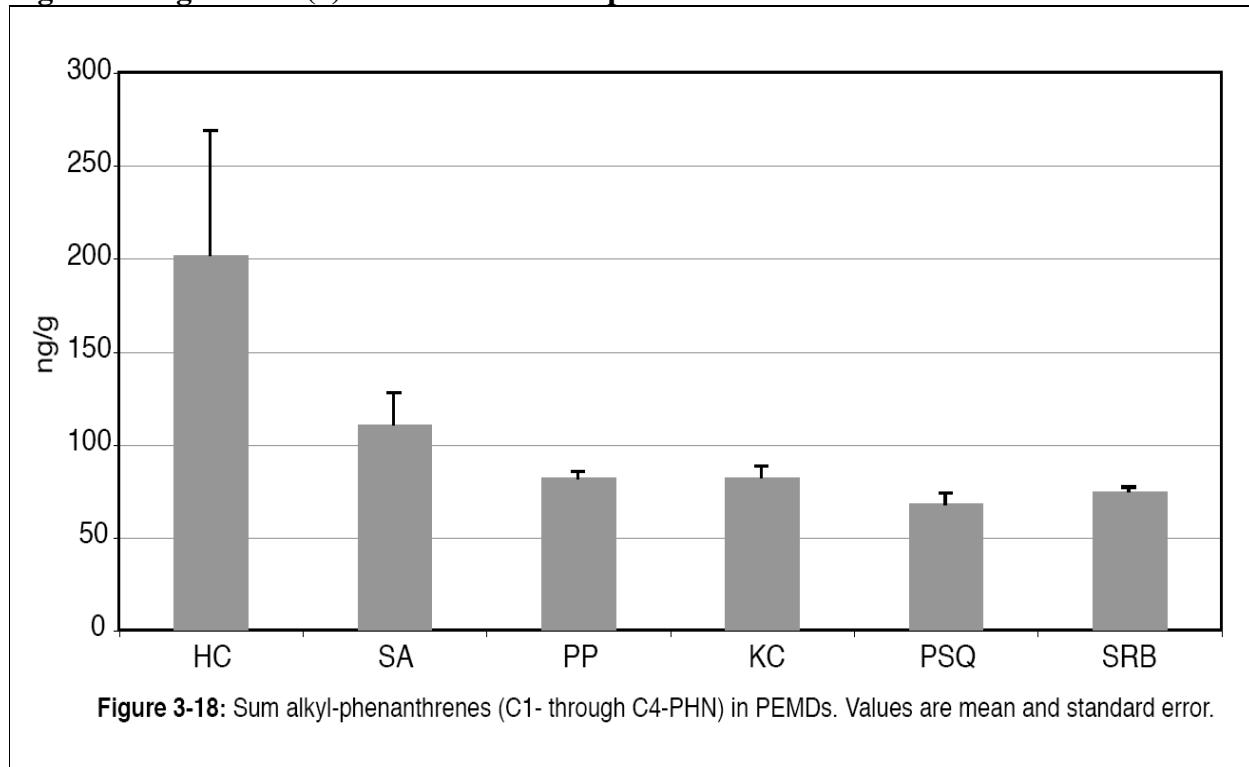
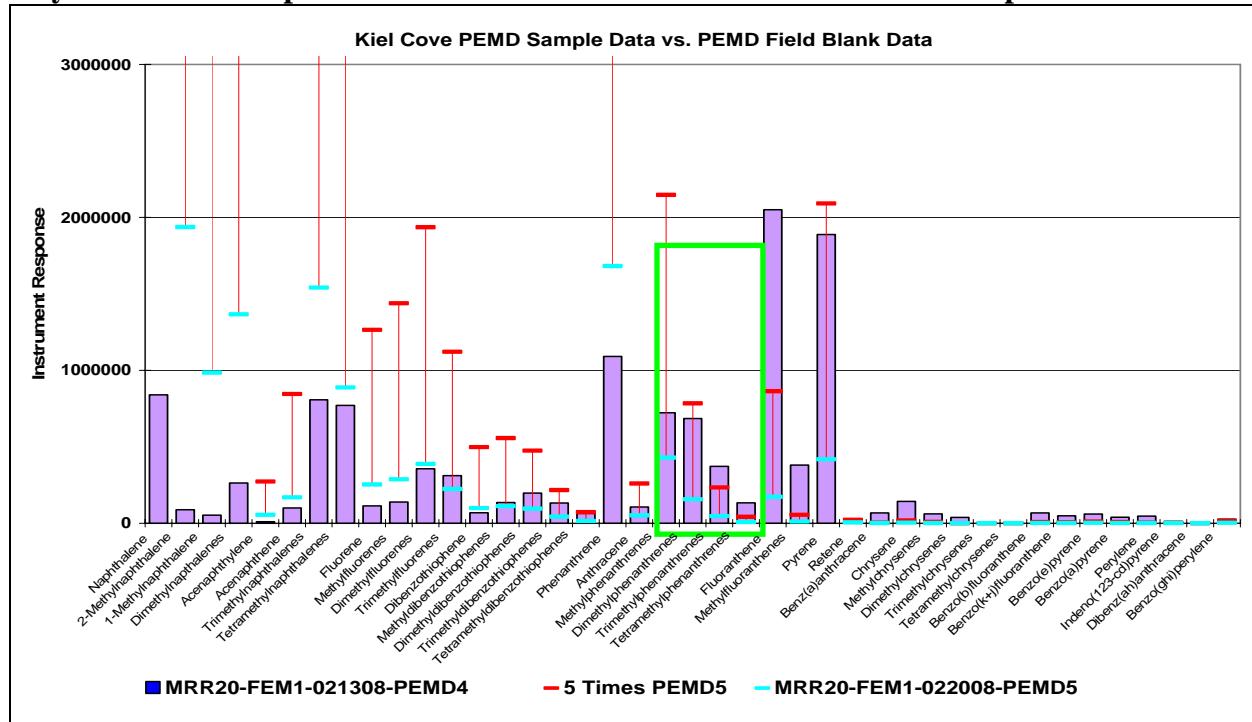


Figure 5. Figure 3-18(a) from the NOAA report¹



Proof: Figure 5 is the plot of the sum of alkyl-phenanthrenes (C1-C4-PHN) in the PEMDs. The figure in the report suggests that there are substantive differences between oiled and un-oiled sites and that the differences are related to Cosco Busan oil. Figure 6 is a plot of the instrument response for one of the PEMD samples used to prepare Figure 3-18 (Kiel Cove) sample where the dominant alkyl-phenanthrenes (C1, C2- phenanthrenes) exceed the EPA and NOAA blank criteria. This demonstrates that for this sample, the petrogenic alkyl-phenanthrenes are influenced by the PEMD field blank and may not be representative of field conditions. It should be noted that urban runoff diagnostic PAHs such as phenanthrene, fluoranthene and pyrene are generally less impacted by blank contamination and therefore may be used to evaluate PAH sources to the water column. Finally, PEMD blank concentrations will measurably influence sample variability associated with PEMD samples with lower PAH concentrations (e.g., Kiel Cove).

Figure 6. PAH instrument response plot for Kiel Cove PEMD 4 field sample versus the instrument response for the associated PEMD 5 field blank. Note that the PEMD C1-C2-phenethrenes exceed the EPA blank criteria and that most of the remaining PEMD alkylated PAHs are present at concentrations below the PEMD blank response.



Finding #4: The C1-C4 phenanthrenes for many of the PEMD samples are greater than 5X the associated method blank response, but less than 5X the associated field blank. When using the raw data without consideration for its validity as in the report, the PAH distributions in the oiled shoreline samples reflect the same PAH distributions observed at the reference sites (e.g., San Quentin, San Rafael) and are characteristic of urban runoff. There is no credible chemical evidence to indicate that the herring embryos were exposed to Cosco Busan oil using both qualified and un-qualified data.

Proof: Figure 7 is a PAH instrument response plot for one of the PEMD samples from Kiel Cove used to estimate mean C1-C4 phenanthrenes concentrations. The field sample response in all four of these alkyl-phenanthrenes is greater than 5X the sample response relative to the laboratory method blank but less than 5X the sample response when compared to the PEMD field blank (e.g. Figure 8, C1, and C2-phenanthrenes). The same problematic blank contamination pattern was also identified in the un-oiled San Rafael samples (Figures 9 and 10) and document that field sample handling of the PEMDs could be the source of blank contamination in the field samples.

Figure 7. PAH instrument response plot for Kiel Cove PEMD 3 versus the instrument response for the associated PEMD laboratory method blank.

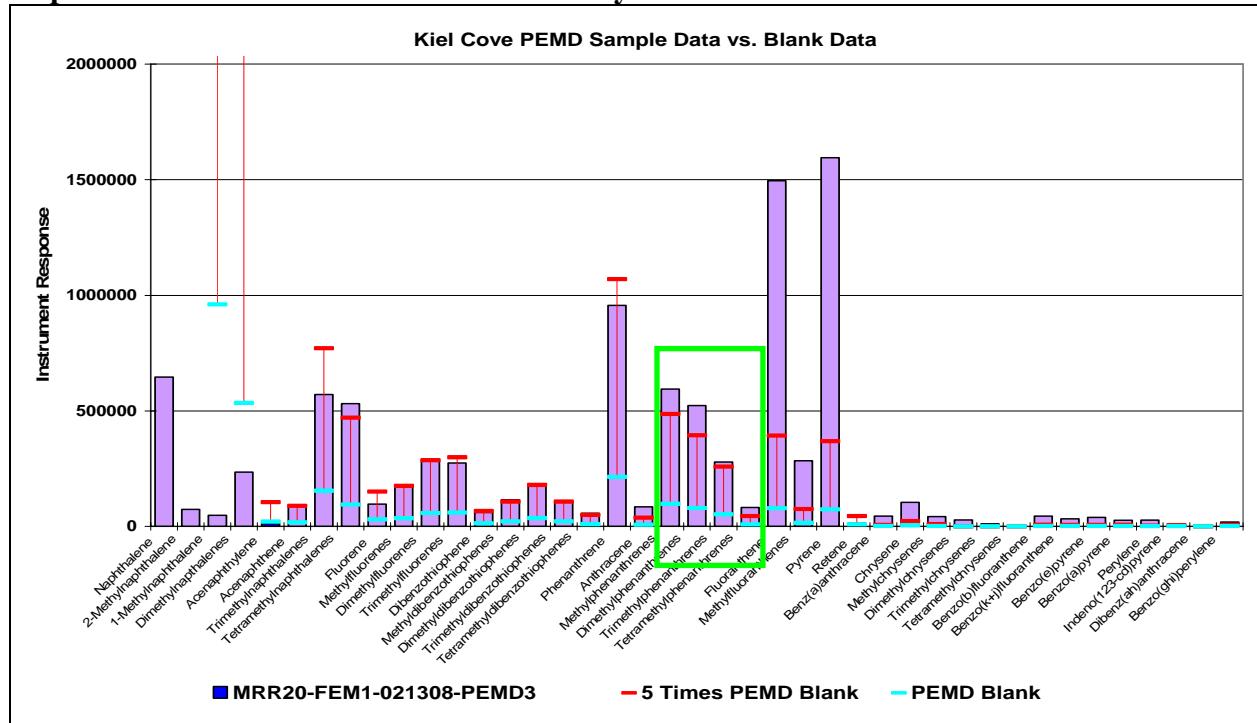


Figure 8 PAH instrument response plot for Kiel Cove PEMD 3 versus the instrument response for the associated PEMD field blank.

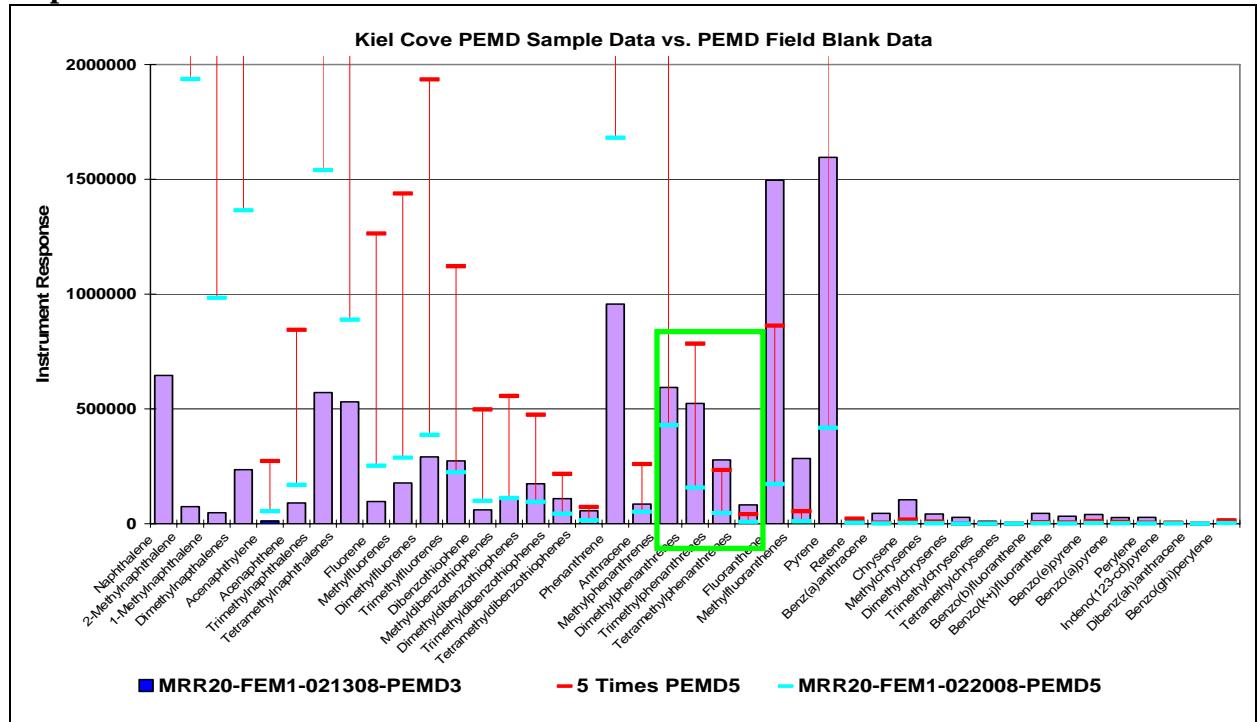


Figure 9. PAH instrument response plot for San Rafael reference site PEMD versus the instrument response for the associated PEMD laboratory method blank.

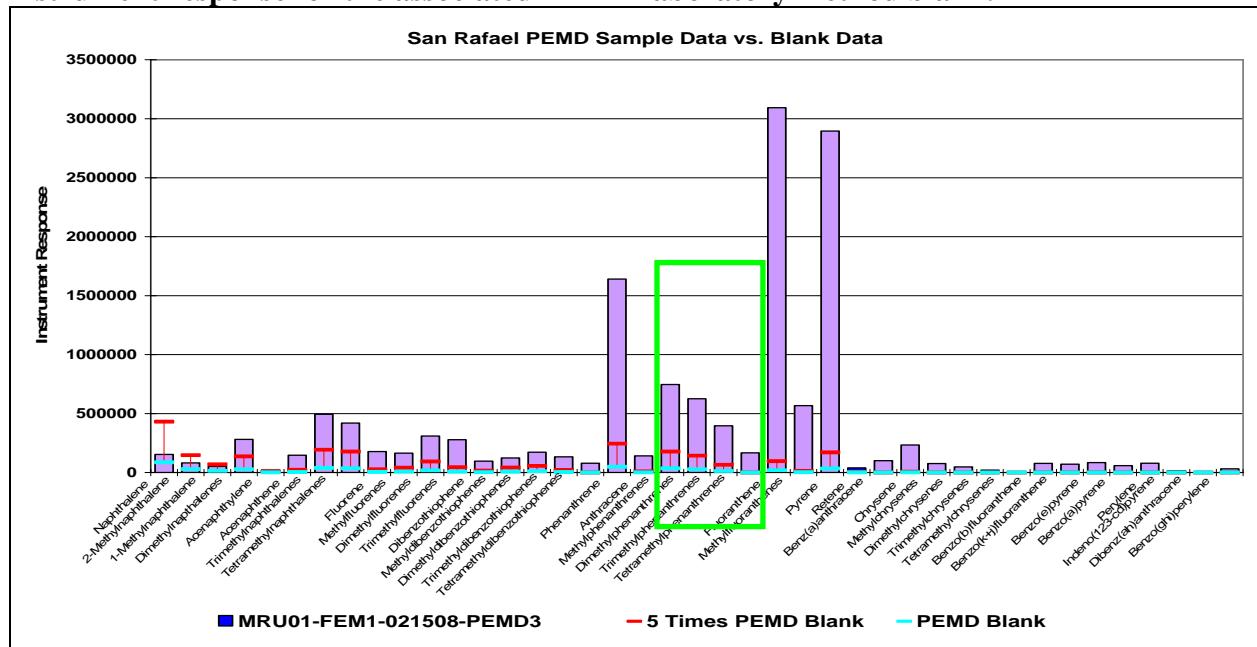
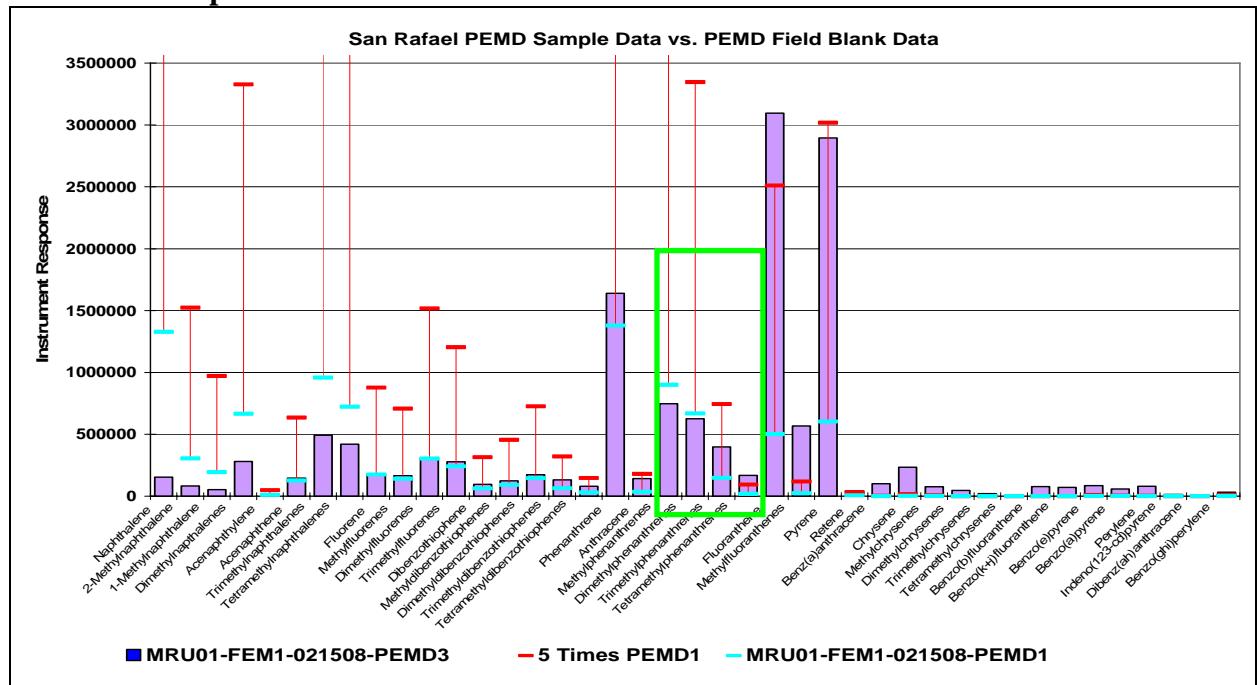


Figure 10. PAH instrument response plot for San Rafael reference site PEMD versus the instrument response for the associated PEMD field blank.



Finding #5: If one assumes as NOAA did, that the field blank contribution to the PEMD results does not significantly impact the validity of the data⁵, then one can only conclude that the PAH distributions at the oiled and reference sites are derived from urban runoff and not the Cosco Busan oil spill.

Proof: When both qualified (sample/blank < 5) and un-qualified (sample/blank > 5) data are used for source identification, the chemical relationships support an urban runoff source and not a Cosco Busan source as indicated in the report. Figures 11 and 12 are plots of the sum C1-C4 phenanthrenes versus fluoranthene and pyrene respectively for all of the data. The high correlations observed in both plots indicate that the PEMD alkyl-phenanthrenes are derived from an urban runoff source not a petrogenic source (oil related) such as Cosco Busan. The high correlation between fluoranthene and pyrene (mostly un-qualified data, Figure 13) and the characteristic slope of the relationship also indicates that the PAHs are derived from urban runoff⁶.

Figure 11. PEMD results plot C1-C4 phenanthrenes versus fluoranthene (all data).

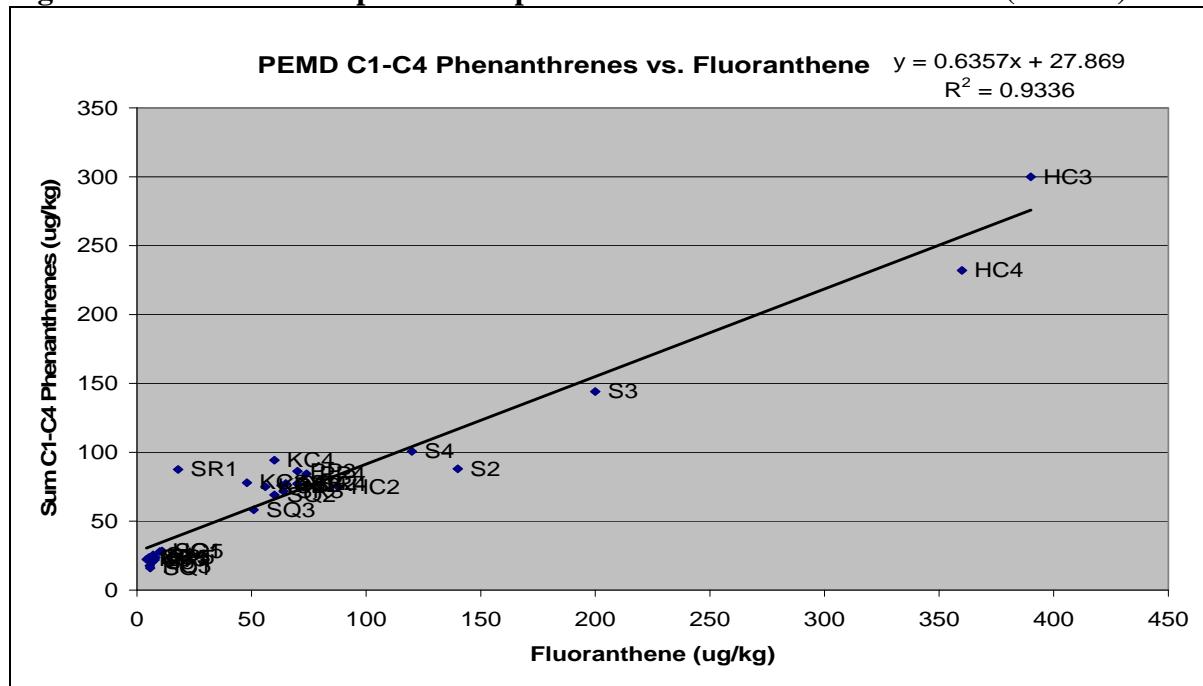


Figure 11 and Figure 12 represent the qualified and un-qualified data for all sites using the specific C1-C4-phenanthrenes PAH groupings presented in Figure 3-18 of the report. They selected this approach because the C1-C4-phenanthrenes are “*the most abundant of the toxicologically relevant tricyclic PAHs in Cosco Busan bunker oil*”. The variability within the PEMD sample cluster (Figure 14, expanded scale) in part reflects the proximity of the sample PAH concentrations to the blank PAH concentrations. As the sum of C1-C4 –phenanthrenes decreases in the PEMD sample, the blank concentrations impact the measured concentrations to

⁵ For the sake of argument one may assume that the method blank, not the field blank more accurately reflects the blank contribution to the PEMD samples.

⁶ Stout, S.A., Uhler, A.D., Emsbo-Mattingly, S.D. 2004. Comparative Evaluation of Background Anthropogenic Hydrocarbons in Surficial Sediments from Nine Urban Waterways. *Environ. Sci. Technol.* 2004. **38**. pp 2987-2994.

a greater degree. For example, all of the field samples in Figure 14 exceed the EPA blank criteria, and **PEMD field blank SR1 is greater than all of the field samples with the exception of KC4 and PP3.** This variability does not indicate a petrogenic source, simply that the lower concentration samples have a higher blank/sample ratio. The sample variability and concentration range is virtually undistinguishable from the un-oiled reference sites.

Figure 12. PEMD results plot C1-C4 phenanthrenes versus pyrene (all data).

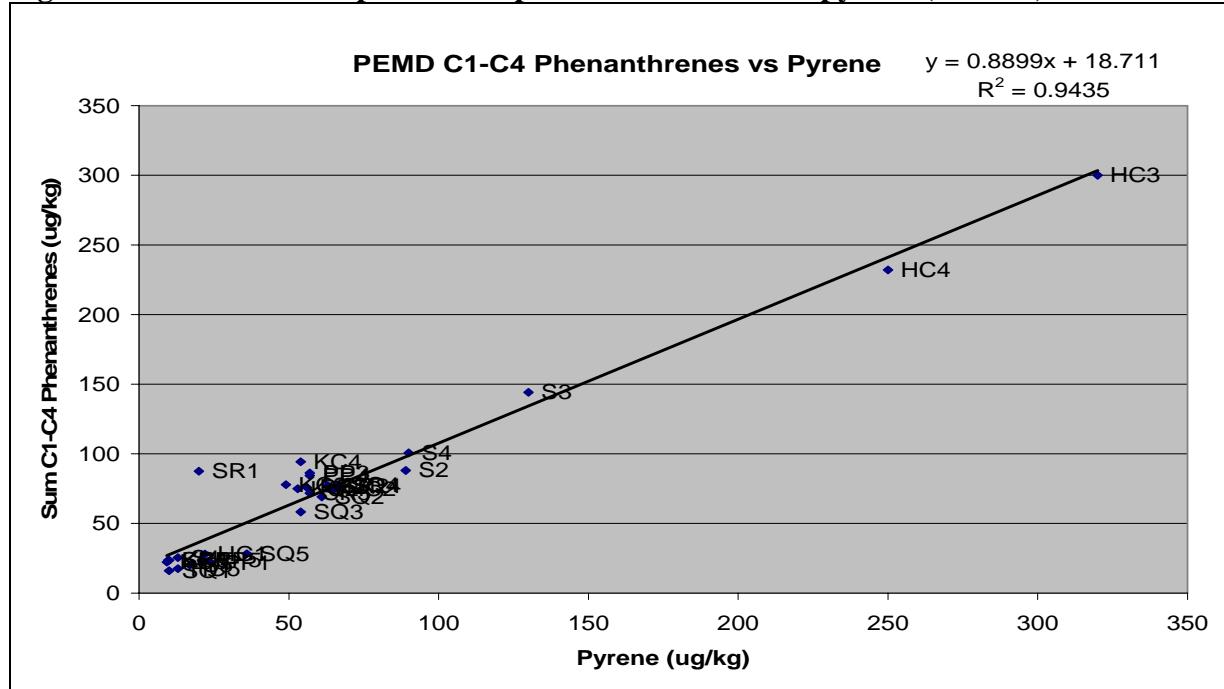


Figure 13. Plot of combustion/urban runoff related PEMD PAH; pyrene versus fluoranthene. All samples all sites. ($R^2 = 0.98$).

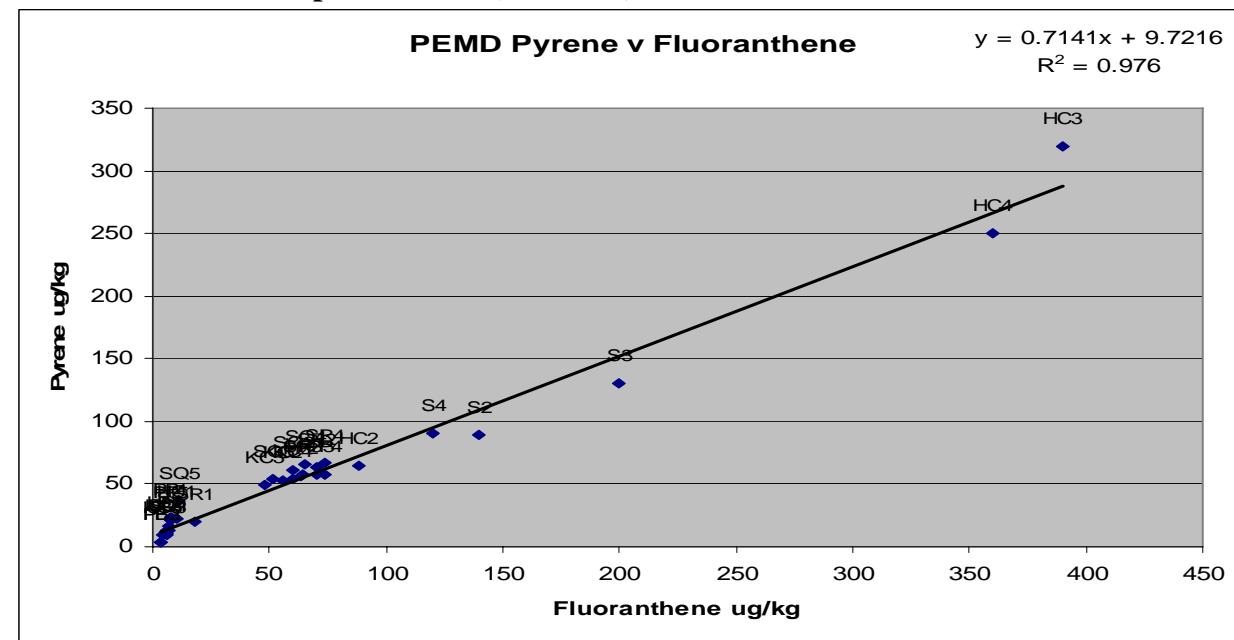
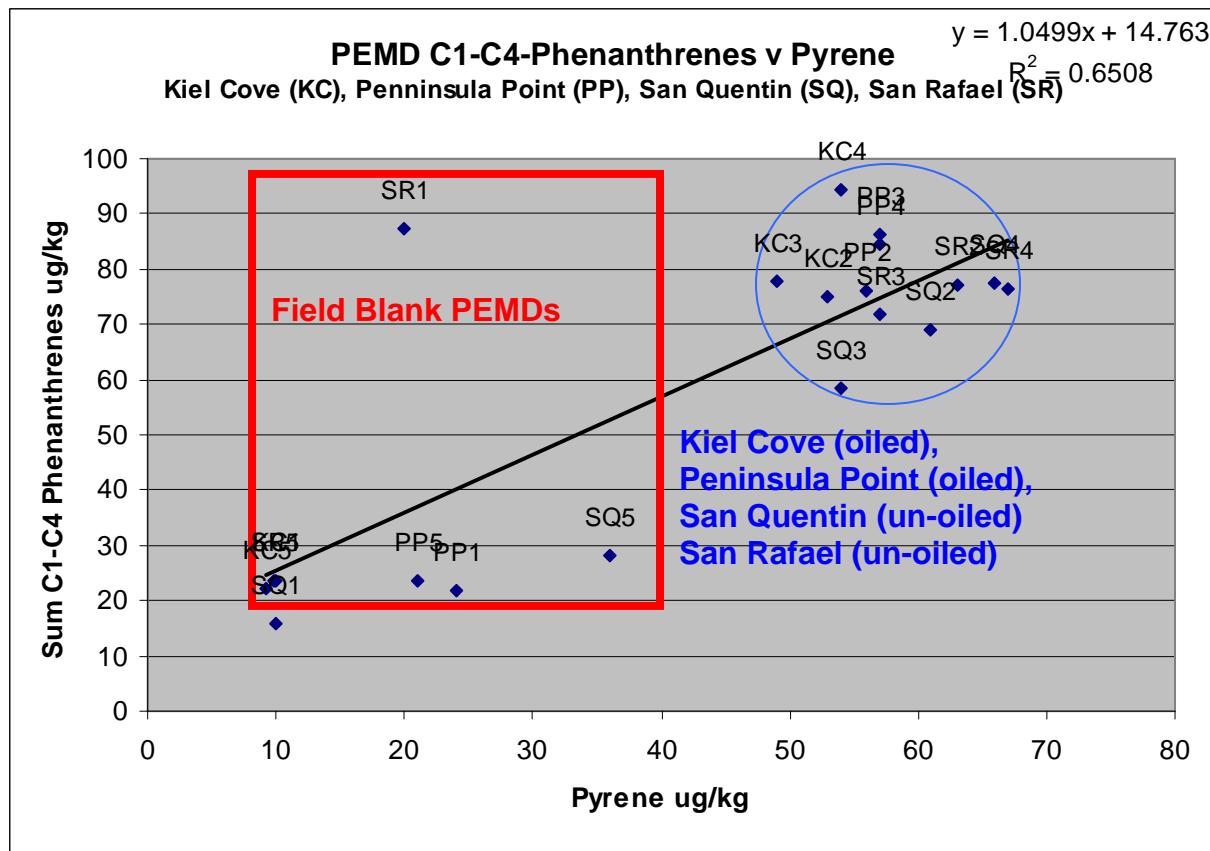


Figure 14. Sum of PEMD C1-C4 phenanthrenes versus fluoranthene for Peninsula Point, Kiel Cove, San Quentin (reference) and San Rafael (reference). Samples with a 1 or 5 suffix represent PEMD field blanks, samples with 2, 3, 4 suffix are field samples.



The same PEMD TPAH blank issue applies to the total PAH results for the Kiel Cove and Peninsula Point PEMD samples (Figure 15). The basic principle as discussed above is that the PEMD devices have an inherent and substantial blank problem. NOAA excluded naphthalene and C1-naphthalene because of poor naphthalene-d8 recoveries but did not exclude C2-naphthalenes, C3-naphthalenes, and C4-naphthalenes, target PAHs that would also be impacted by poor naphthalene-d8 recoveries. As documented in Figure 8 and Figure 10, and Attachment 1, many of these PAHs should be considered suspect simply because the PEMD blank response is close to or greater than the sample response.

Figure 17 confirms the observation that there are no measurable differences between the mean Kiel Cove PEMD C1, C2, C3, C4 –phenanthrenes and the San Quentin PEMD reference sample mean. The distribution of PAHs in these samples is strong evidence that the source of PAHs is urban runoff and not Cosco Busan oil.

Figure 15. Plot of PEMD C1-C4-phenanthrenes for the reduced data set evaluated by NOAA including oiled Stations Kiel Cove (KC), Peninsula Point (PP), and un-oiled reference stations San Quentin (SQ) and San Rafael (SR). The red bars represent the station associated PEMD field blanks; the blue bars represent the field sample results.

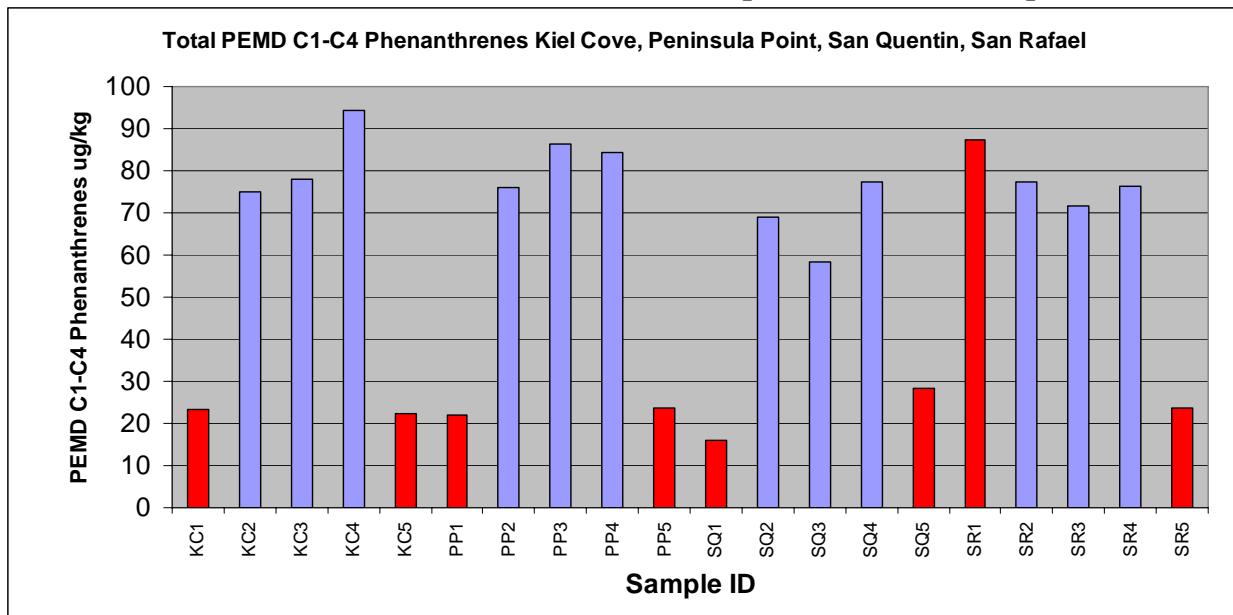


Figure 16. Plot of PEMD TPAH for the reduced data set evaluated by NOAA including oiled Stations Kiel Cove (KC), Peninsula Point (PP), and un-oiled reference stations San Quentin (SQ) and San Rafael (SR). The red bars represent the station associated PEMD field blanks; the blue bars represent the field results. (naphthalene and C1-naphthalene are exclude)

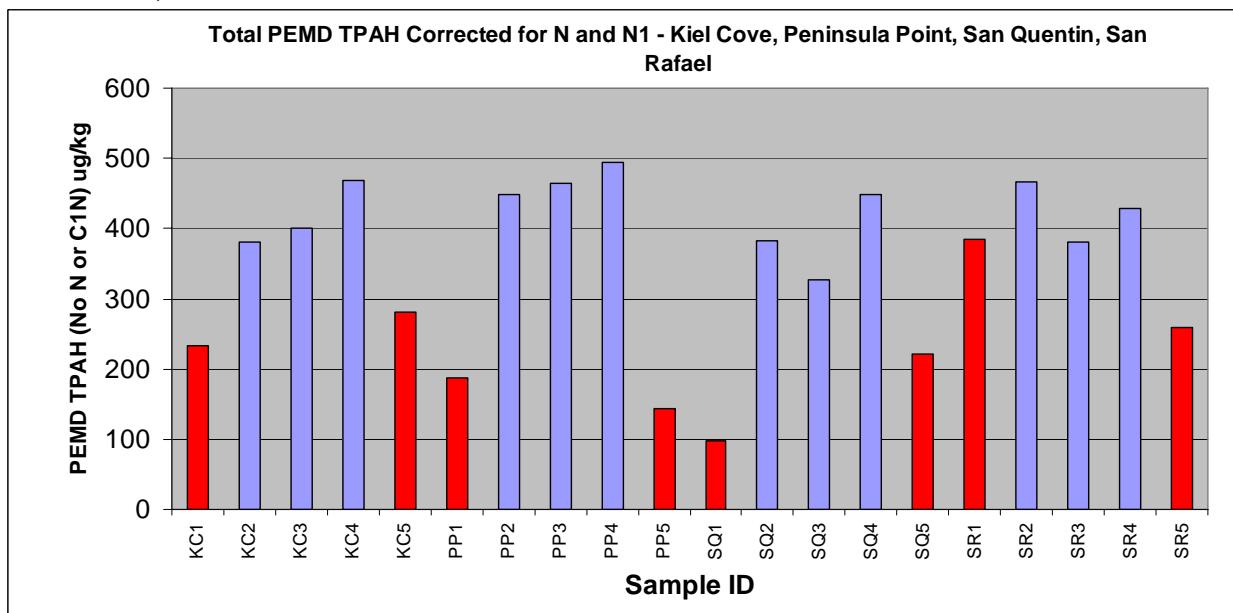
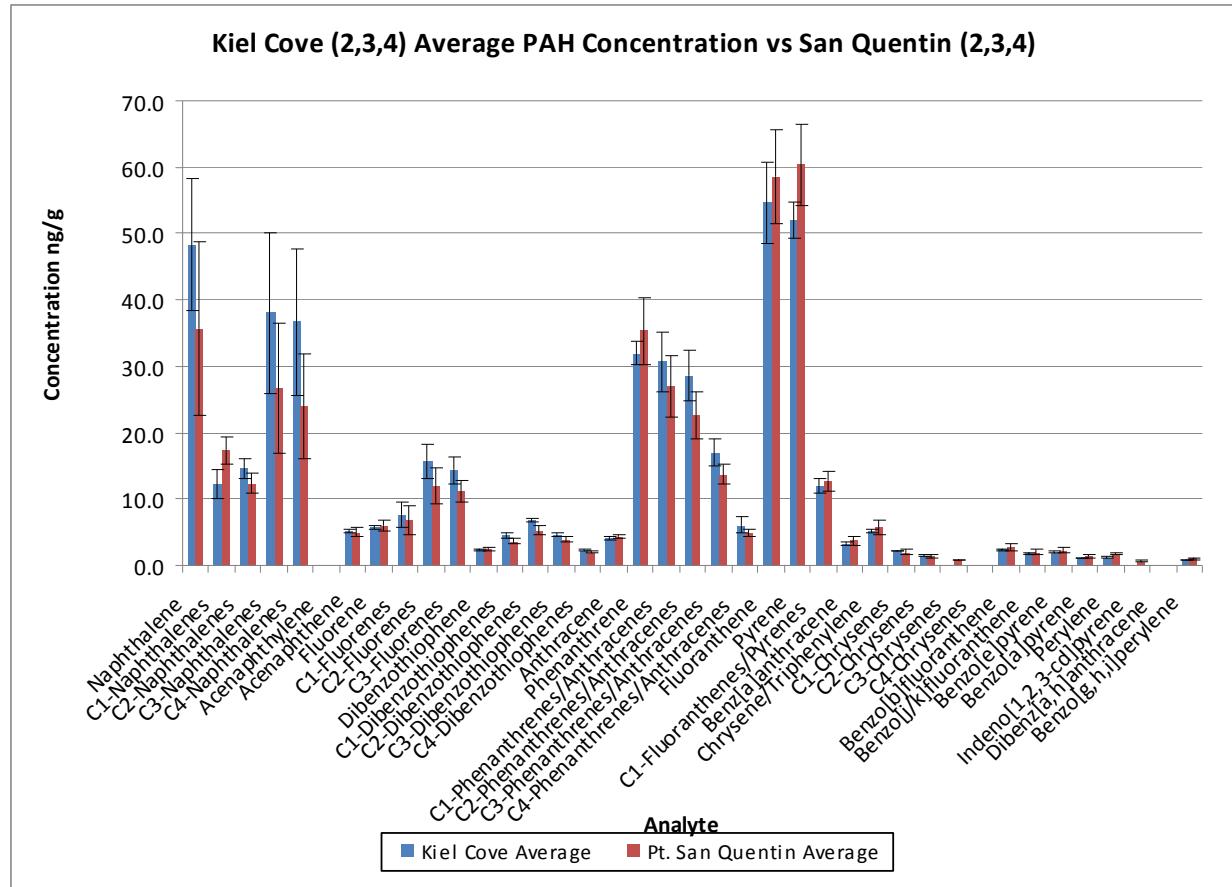


Figure 17. Comparison of mean PEMD PAH concentrations from Kiel Cove (n=3) versus the San Quentin reference site (n=3). These data demonstrate that the PEMD PAH distributions at the oiled site are derived from urban runoff and not Cosco Busan oil. Error bars = \pm 1SD.



The simple statistics using all of the data and presented in Figure 17 demonstrate that the mean PAH concentrations are indistinguishable between Kiel Cove (oiled site) and the Pt. San Quentin un-oiled reference site. In fact these data shows that the individual C1-C4-phenanthrenes, are approximately the same in the reference samples and the Kiel Cove oiled shoreline samples. Second, Dr. Shahrokh Rouhani⁷ performed the detailed statistical analysis of the data. The comprehensive parametric and non-parametric tests were implemented in order to detect statistically significant differences among reported values at background and potentially impacted sites.

Among the investigated analytes, PEMD values of certain PAHs resulted in the rejection of the null hypothesis, *i.e.*, statistically significant differences were detected. These analytes were referred to as “PEMD distinguishing analytes,” which were subjected to further analyses. Among PEMD distinguishing analytes were C1-Phenanthrenes/Anthracenes and C2-

⁷ Dr. Shahrokh Rouhani is recognized expert in the field of environmental statistics with more than 30 years of experience.

Phenanthrenes/Anthracenes. As noted above, upon detection of statistically significant differences, a series of thorough data evaluations were conducted to assess the nature and extent of these detected differences. For this purpose, reported PEMD data of distinguishing analytes were plotted. Figures 18 and 19 display the plots for C1-Phenanthrenes/Anthracenes and C2-Phenanthrenes/Anthracenes PEMD results at various investigated sites, respectively. In these plots, the sites are positioned from left to right in accordance of their reported visible oiling. The left-most site is Keil Cove with heavy oiling, followed by Horseshoe Cove with moderate oiling, Sausalito with light oiling, and Peninsula Point with light/very light oiling. Data from San Rafael and San Quentin, both with no oiling, are positioned along the right side of each plot. In case of direct relationship between the observed oiling, the plots should show a discernable declining trend from left to right.

Figure 18. Plot of Site-specific PEMD C1-phenanthrenes

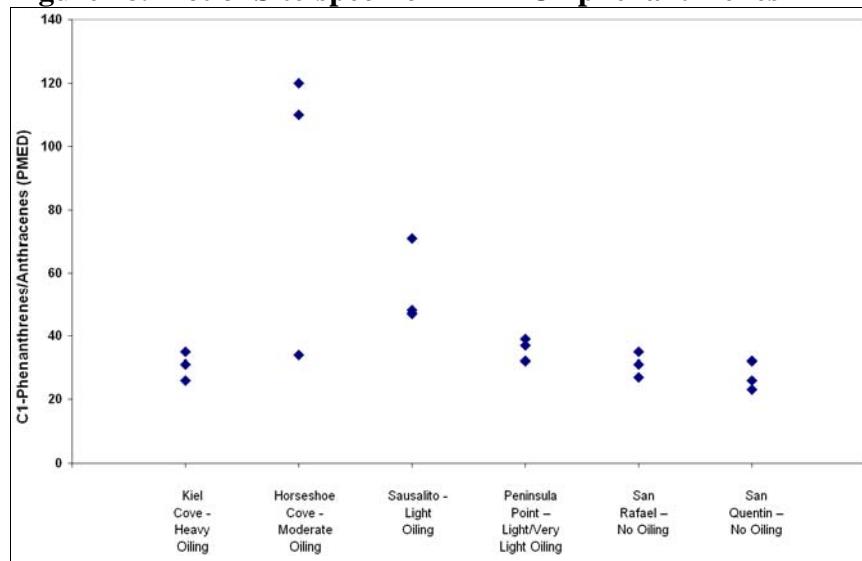
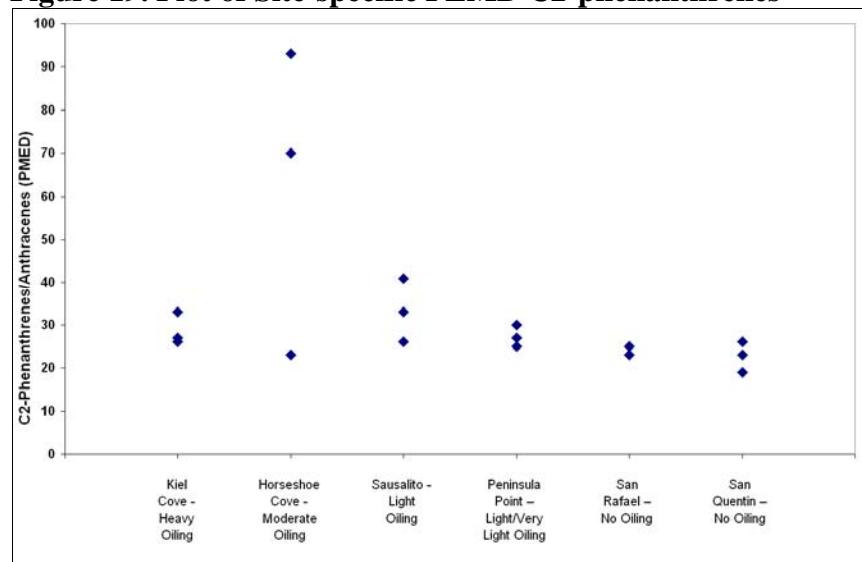


Figure 19. Plot of Site-specific PEMD C2-phenanthrenes



An inspection of Figures 18 and 19 indicates that detected differences in C1-Phenanthrenes/Anthracenes and C2-Phenanthrenes/Anthracenes PEMD results do not display a discernable trend associated with the observed oiling condition at the investigated sites. This is clearly demonstrated by the fact that PMED results at the site with most visible heavy oiling, *i.e.*, Kiel Cove, are fully consistent with those reported at the reference sites with no oiling (also shown in Figure 17). Such spatial patterns lead to the following findings: (a) the detected statistically significant differences among C1-Phenanthrenes/Anthracenes and C2-Phenanthrenes/Anthracenes PEMD results cannot be attributed to the oiling conditions at various sites; and (b) the detected differences among C1-Phenanthrenes/Anthracenes and C2-Phenanthrenes/Anthracenes PEMD results are most likely attributable to local sources, which are independent of observed oiling conditions at those investigated sites.

Conclusion:

Based on my analysis of the NOAA report and associated data I conclude the following:

1. There is a significant blank contamination of the egg samples which severely impacts the usability of the data.
2. The frequency of blank problems was somewhat lower in the PEMD samples although several samples were impacted.
3. If one assumes as NOAA did, that the PEMD data is valid, then the PAH distributions in the field samples support the conclusion that the source of PAHs observed at the oiled shoreline sites are derived from the same urban runoff material identified at the reference sites and that there is no chemical evidence to indicate that the field samples were exposed to Cosco Busan oil.
4. Finally, there is no statistical difference in PAH distribution between the oiled and un-oiled (reference) sites.

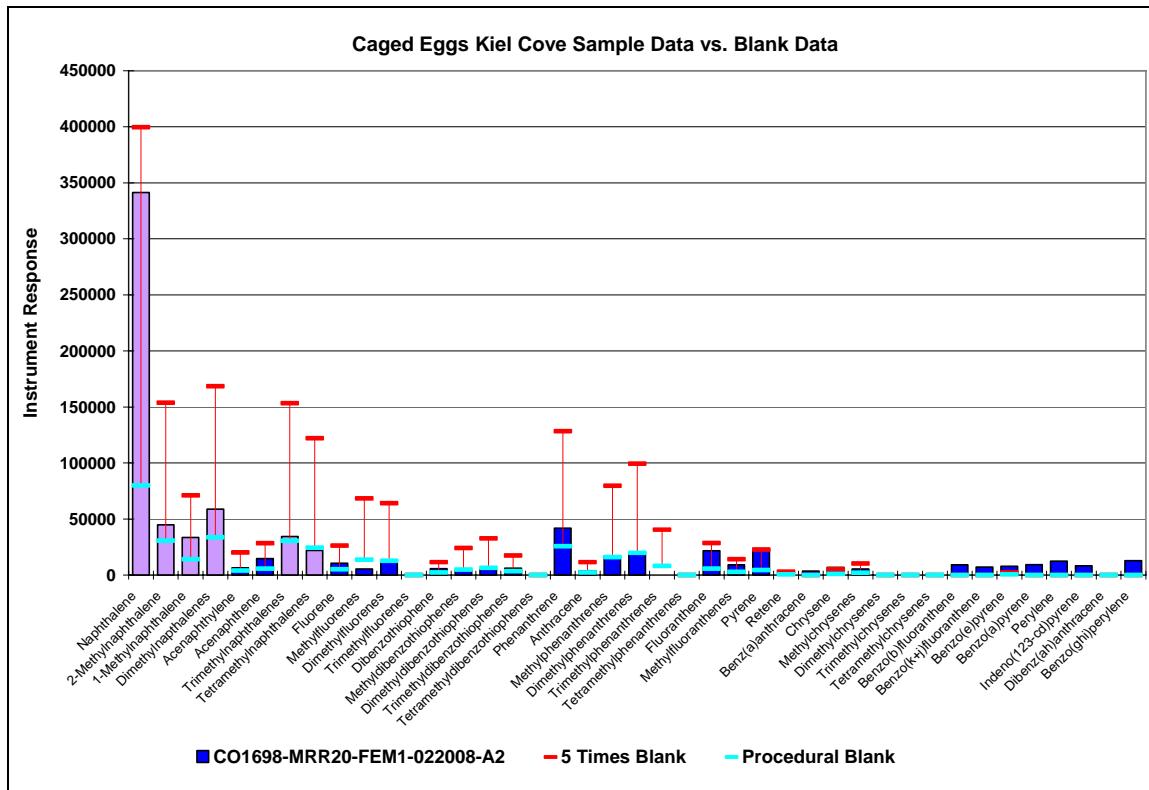
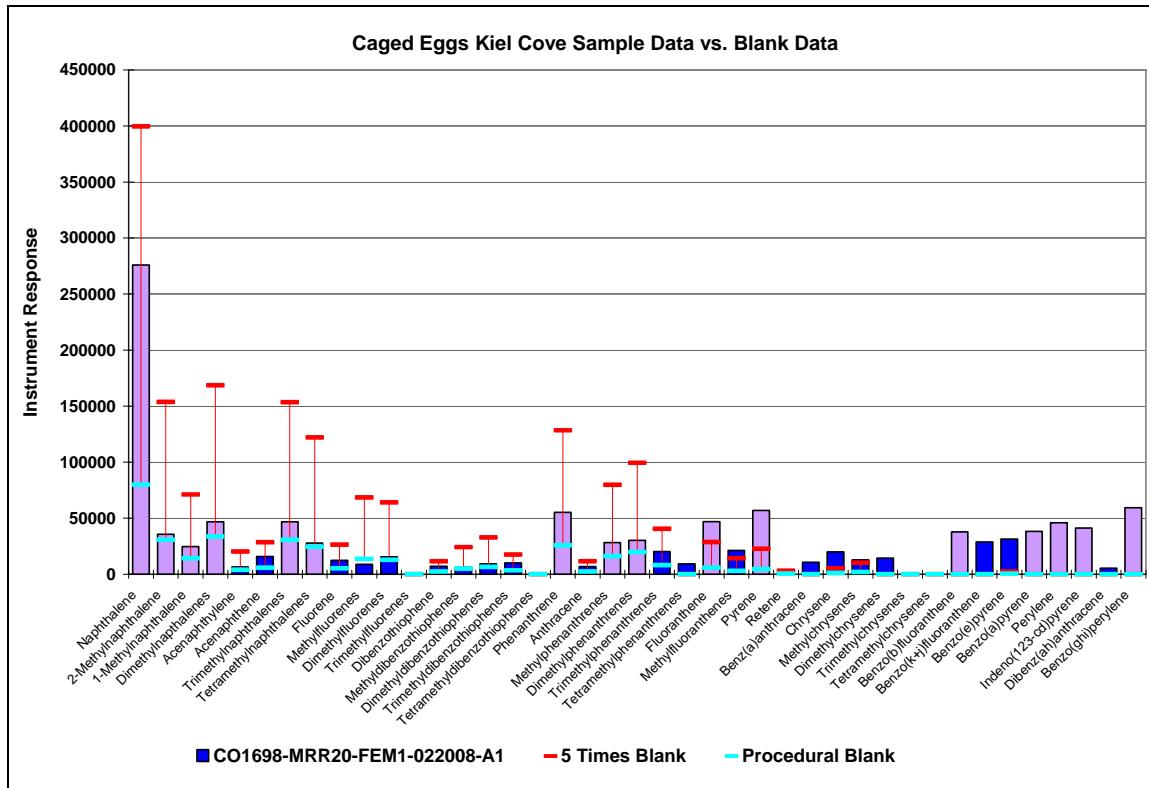
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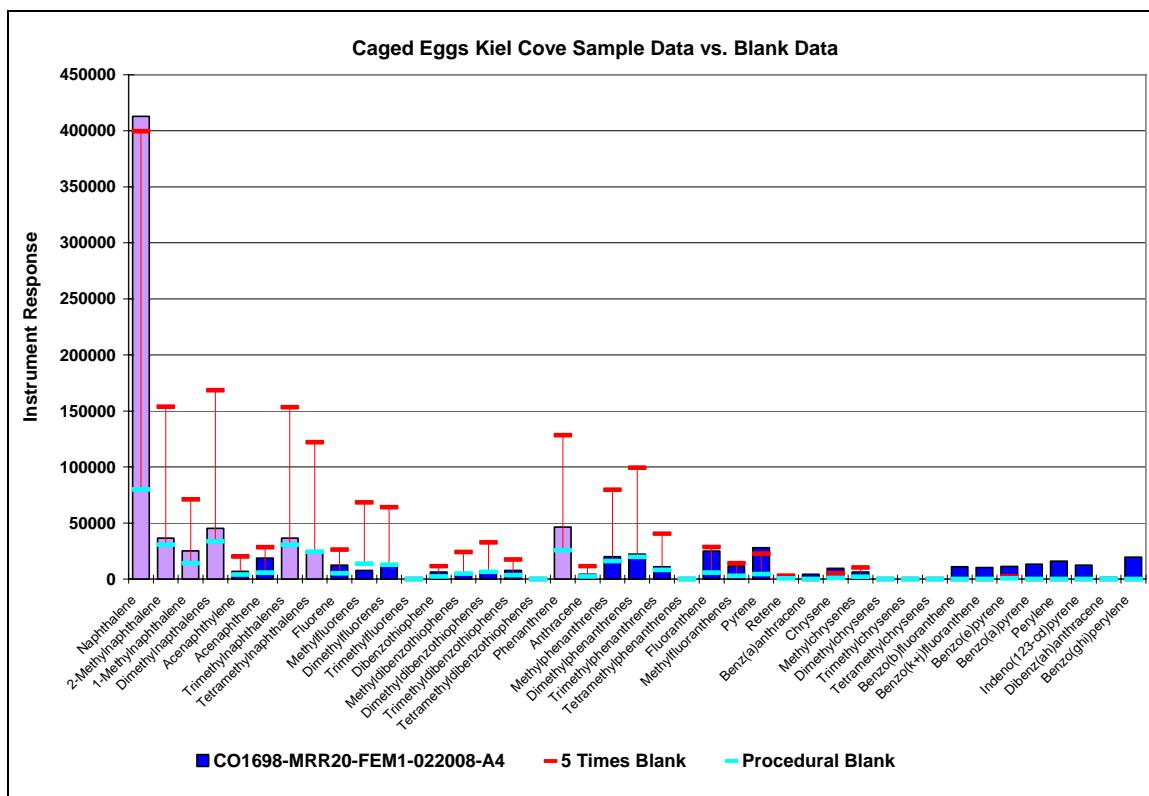
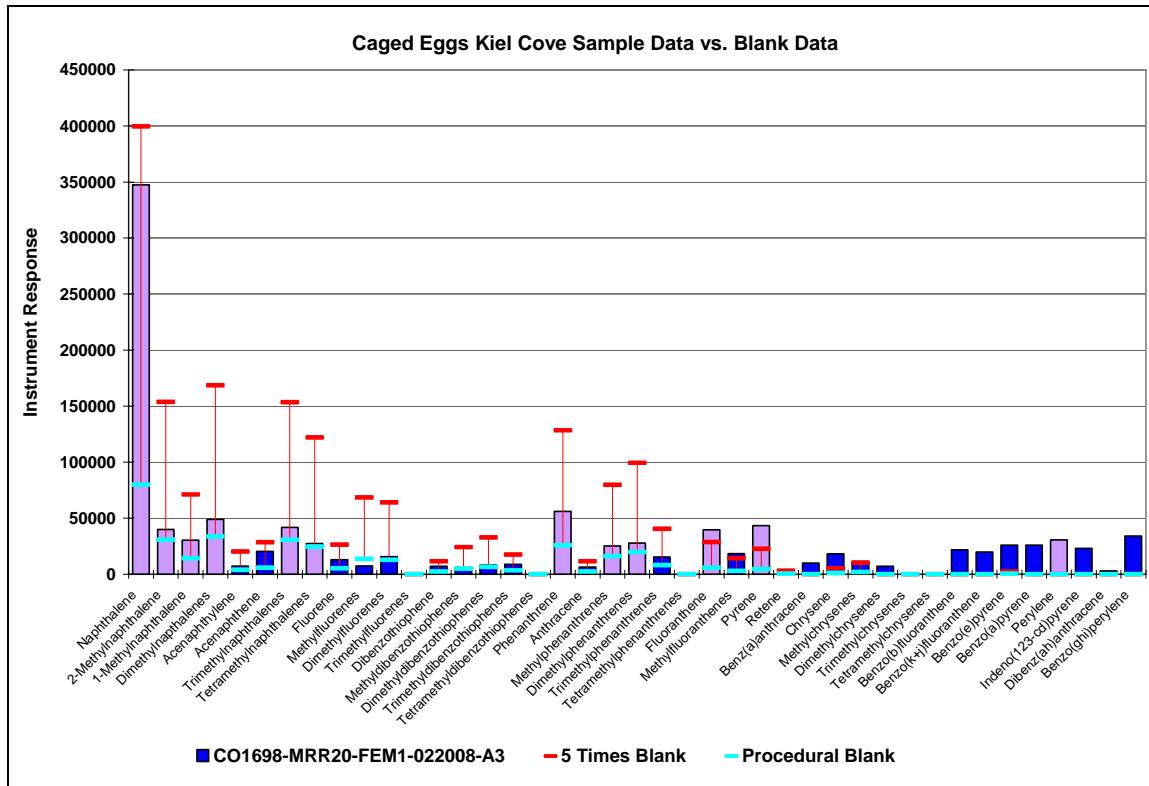
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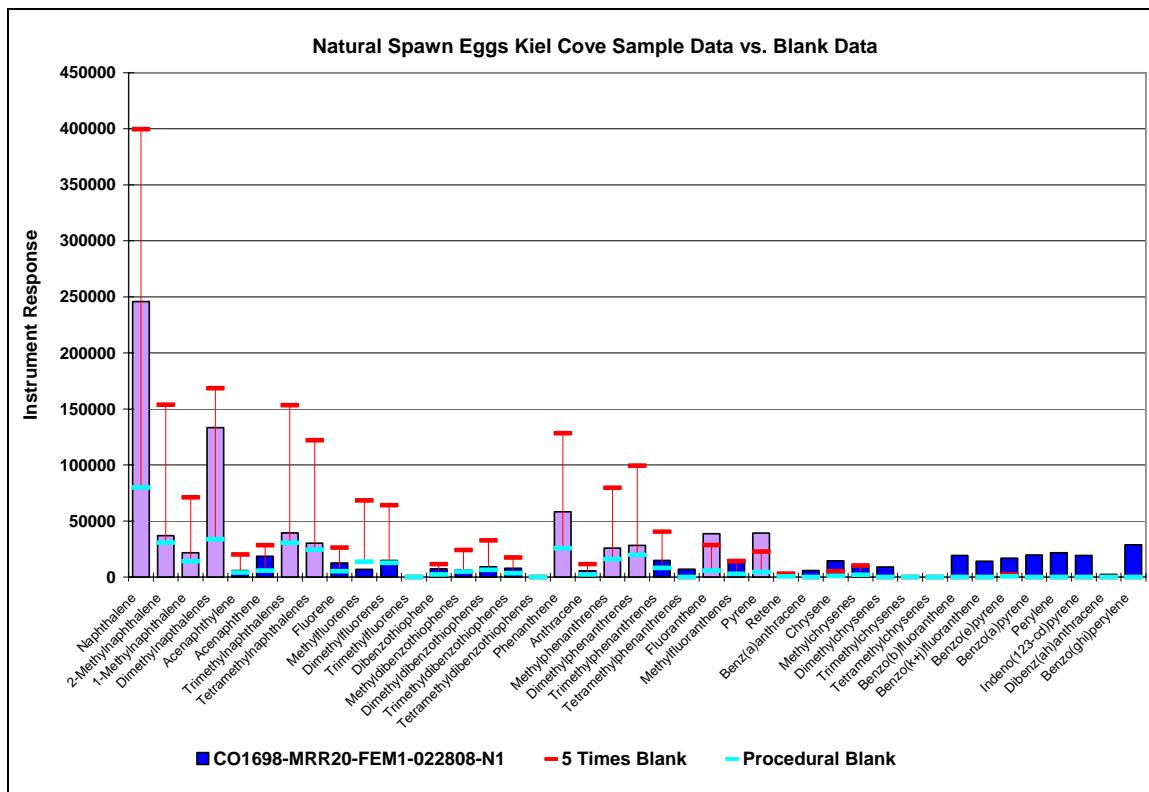
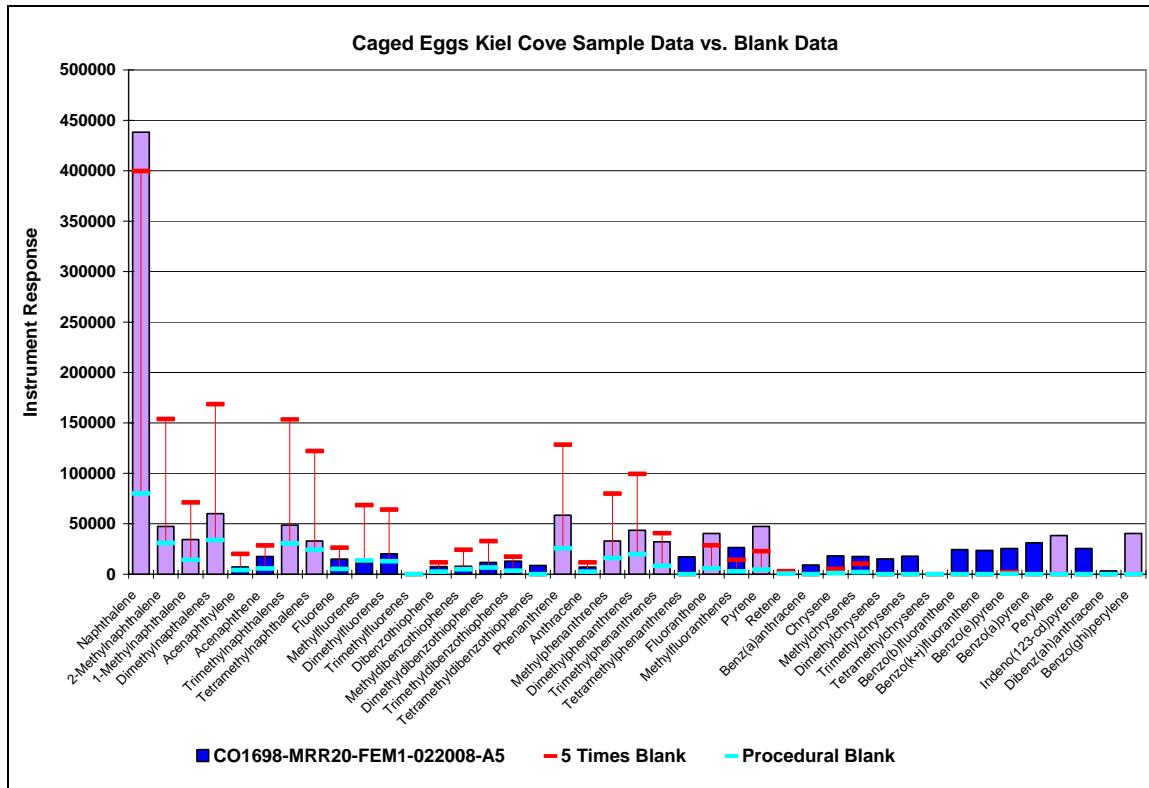


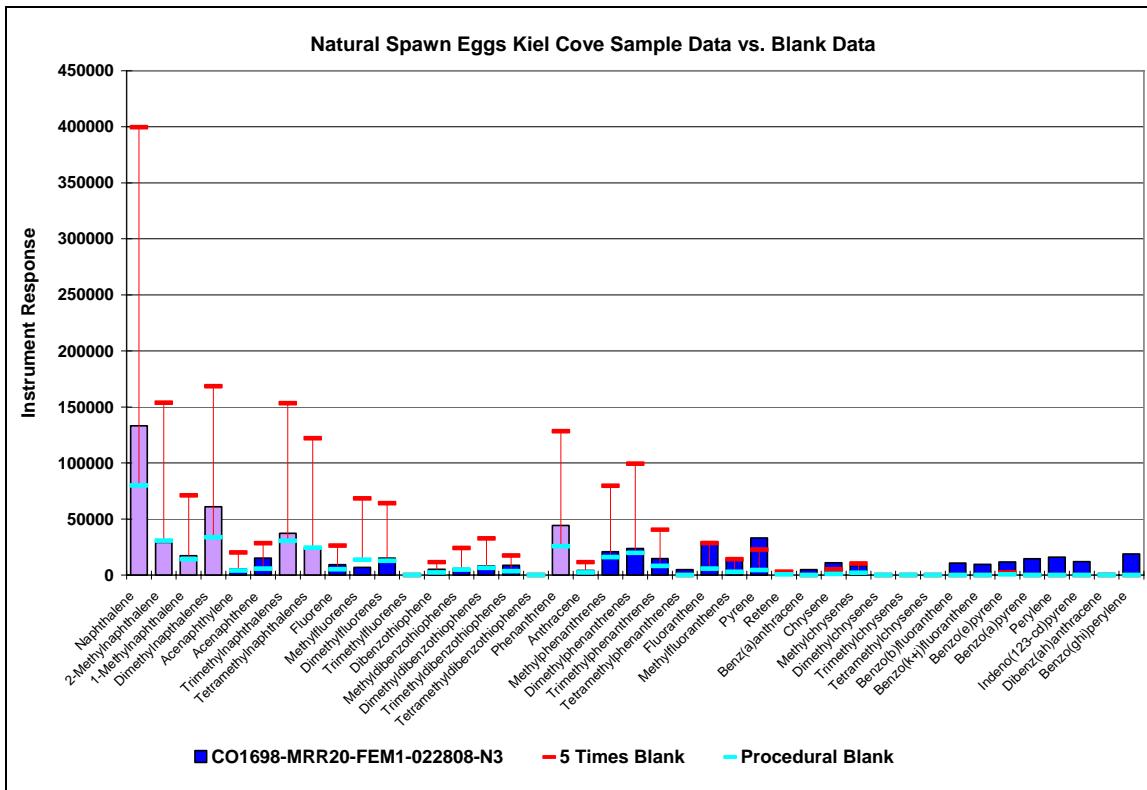
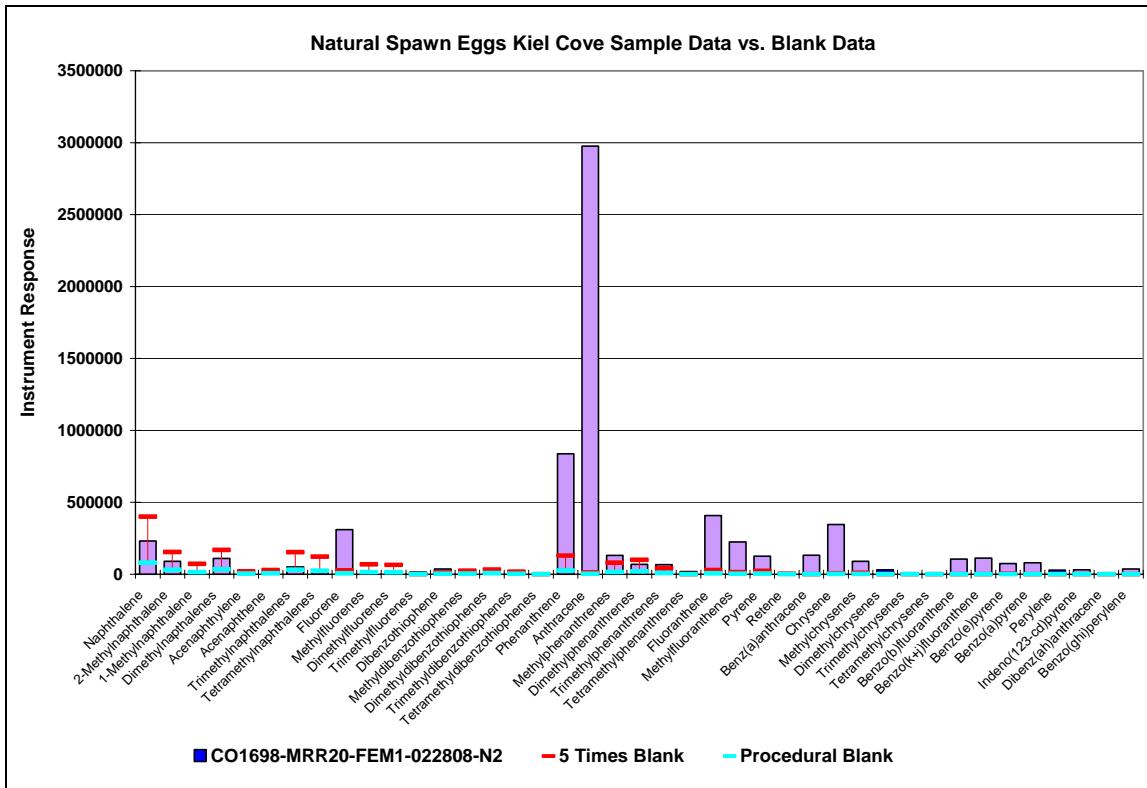
Gregory S. Douglas, Ph.D
NewFields Environmental Forensics Practice.

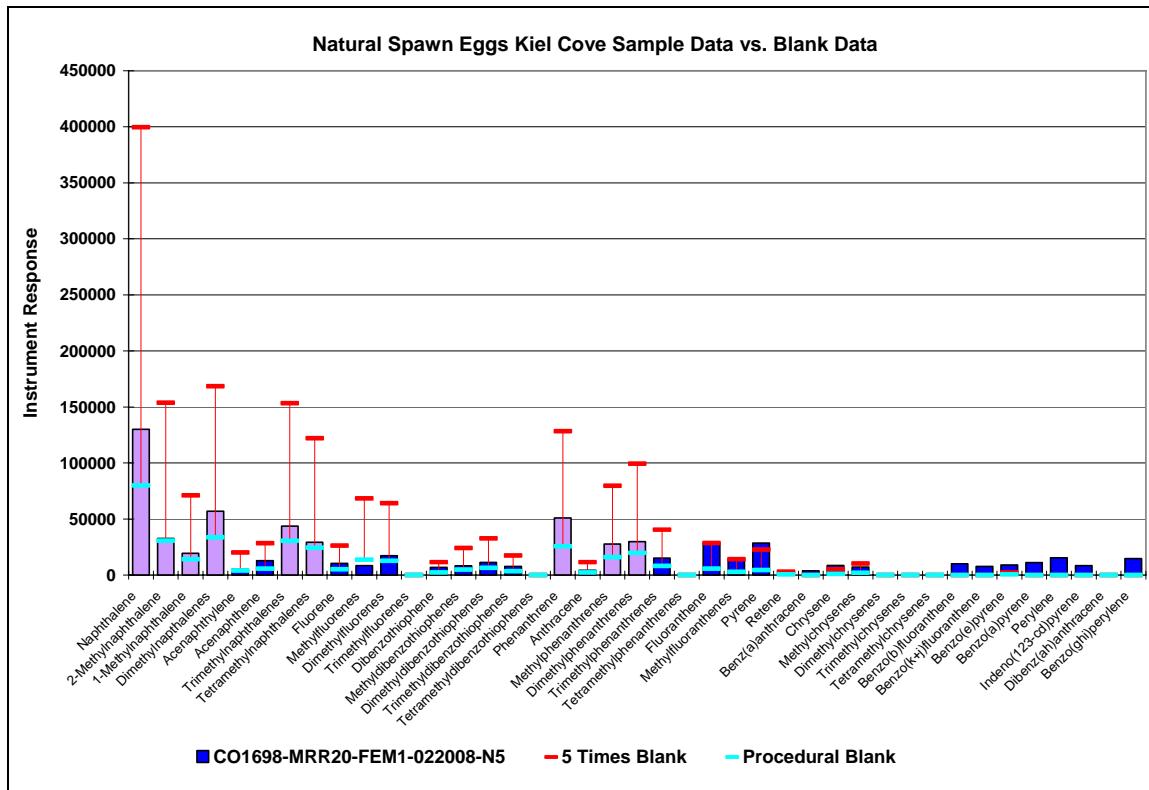
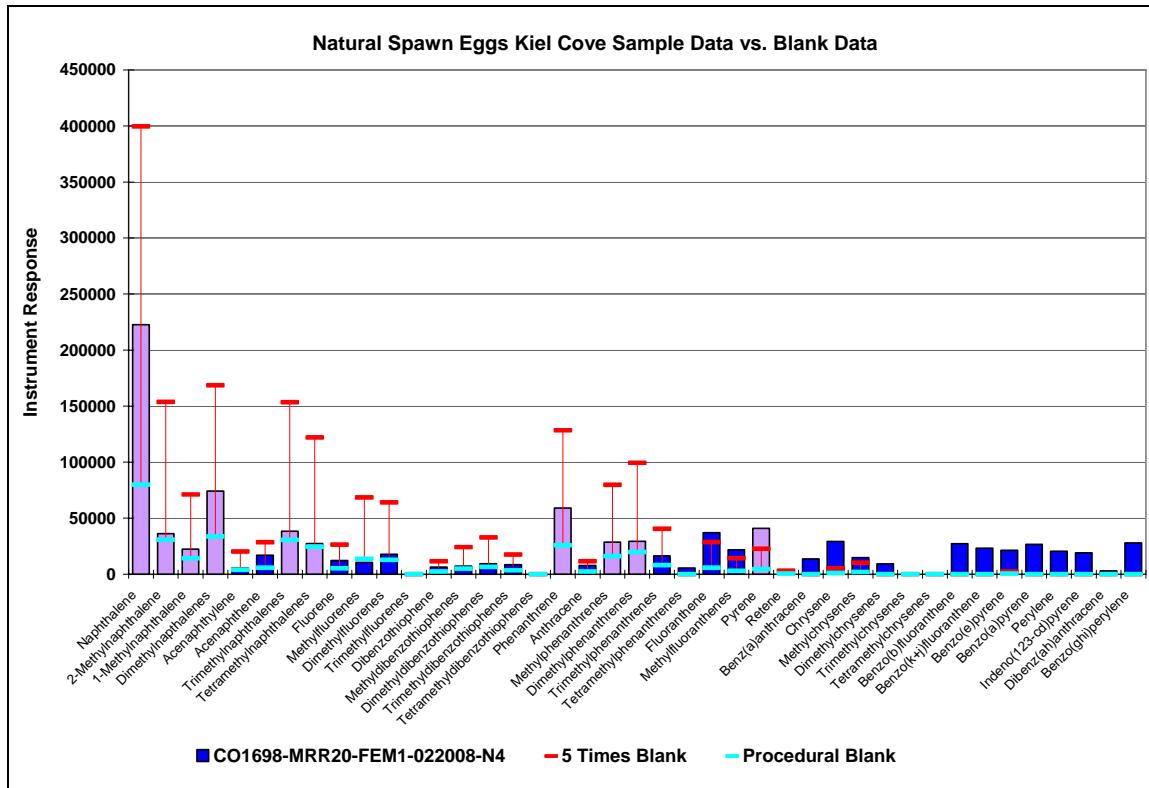
Attachment 1
**Comparison Of PAH Instrument Responses in Herring Egg
and PEMD Field Sample Versus Representative Blank
Samples**

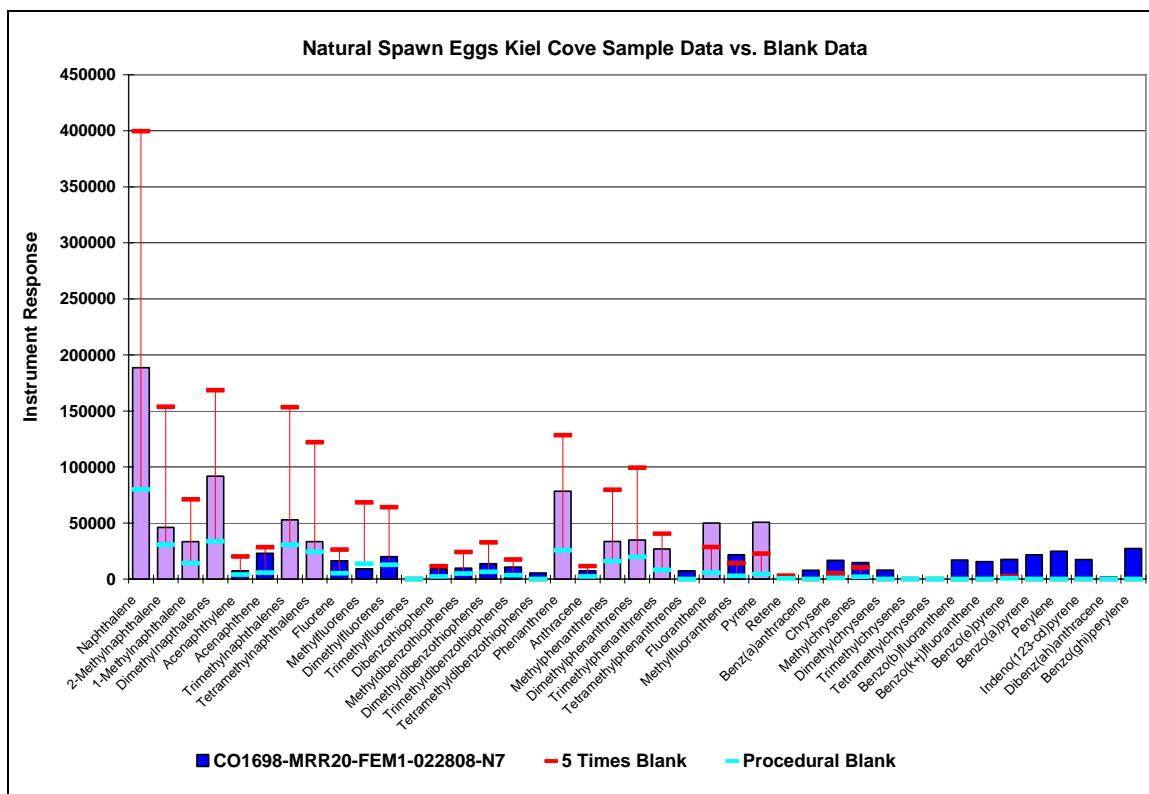
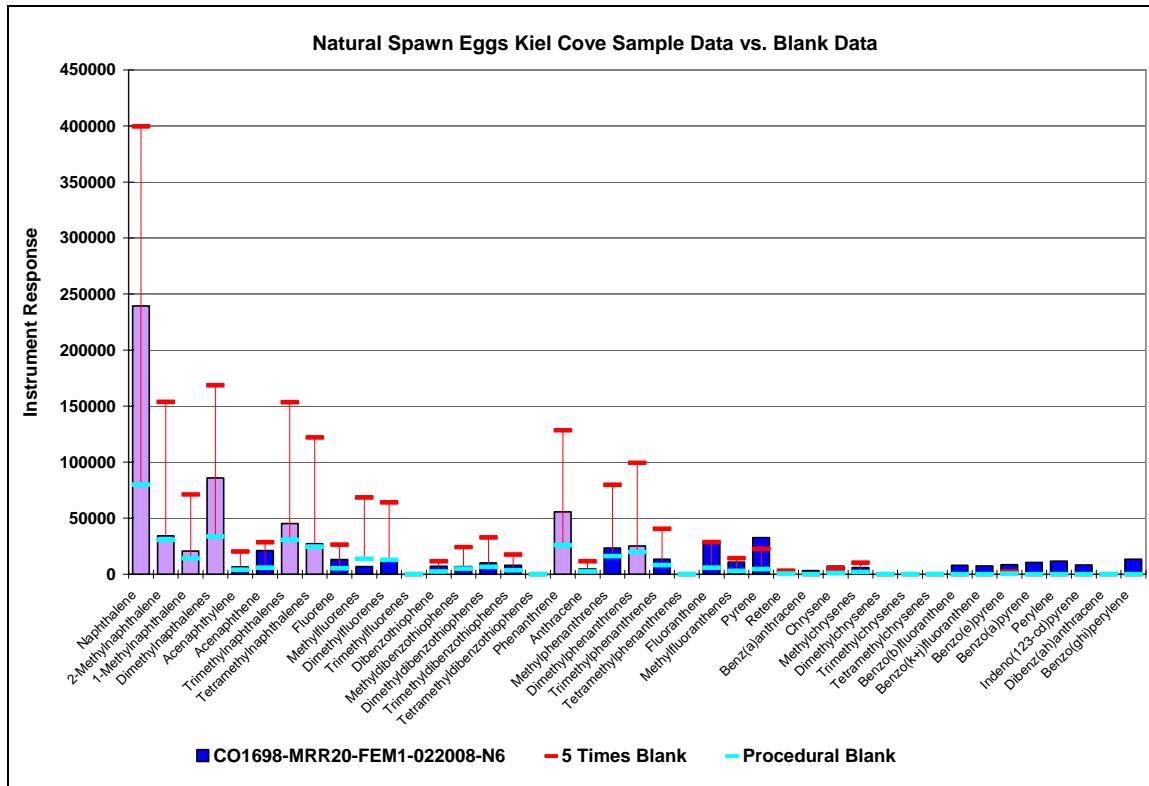


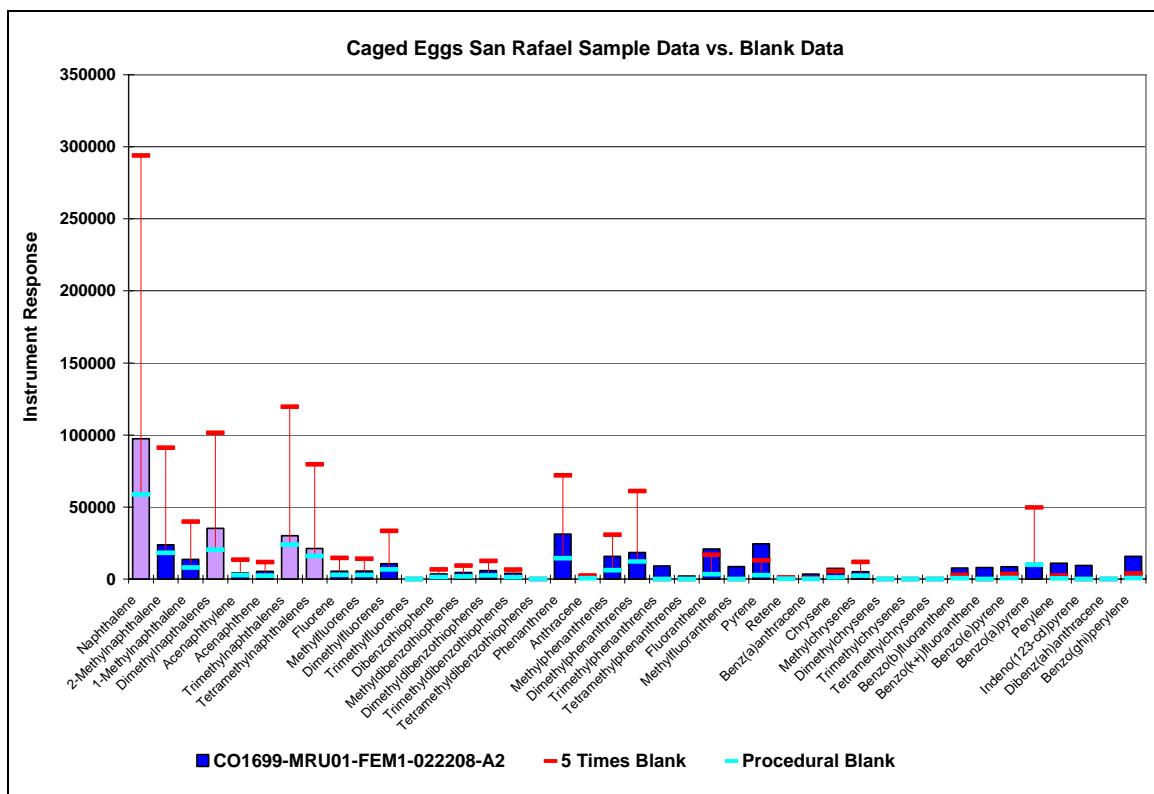
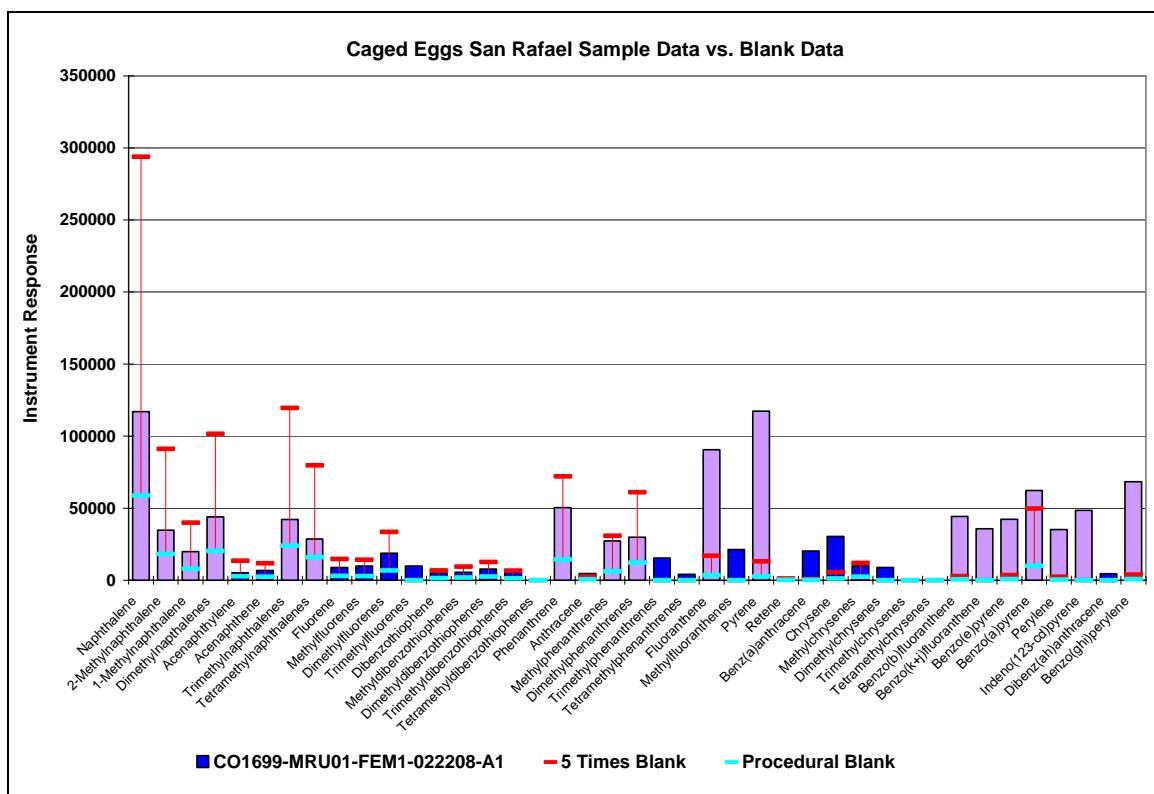


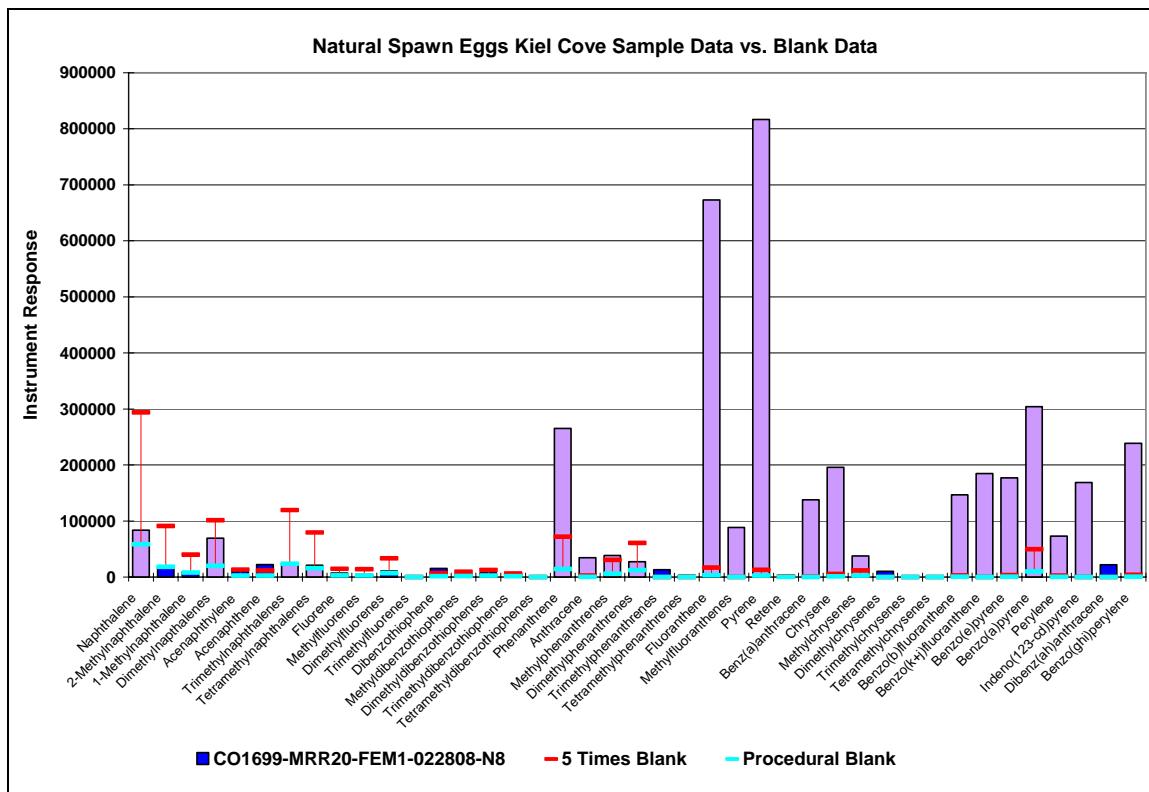
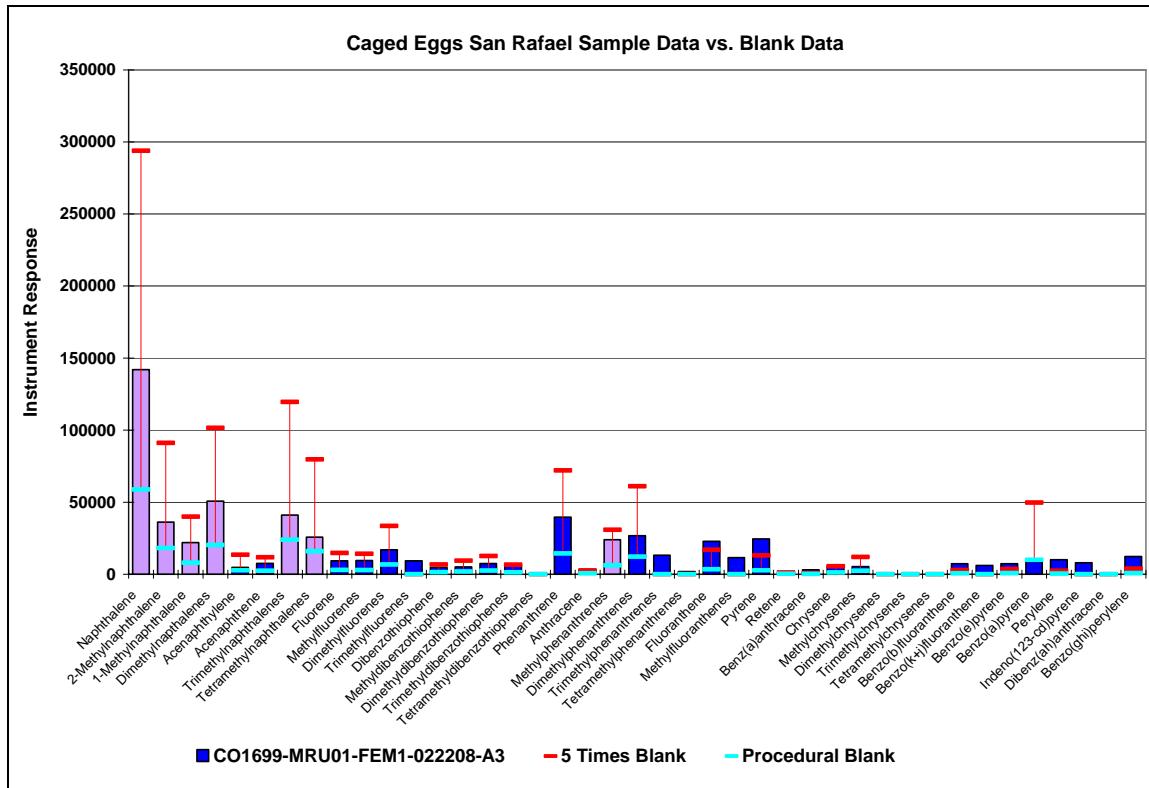


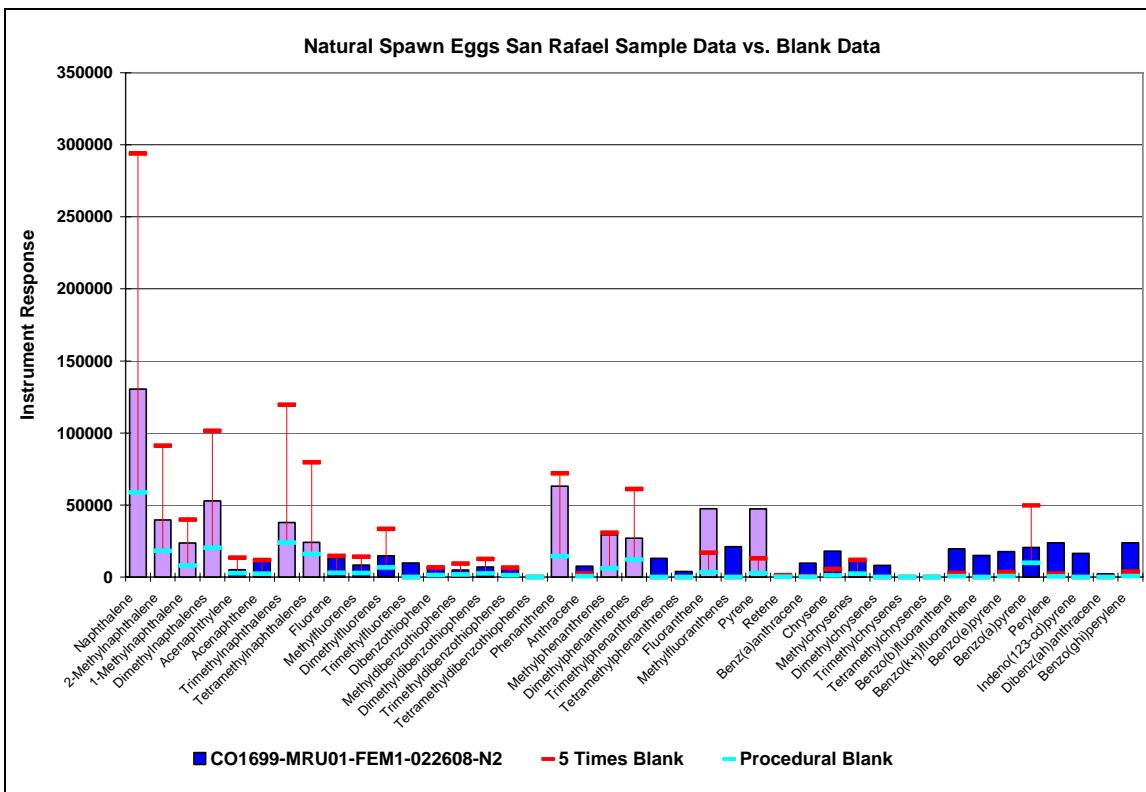
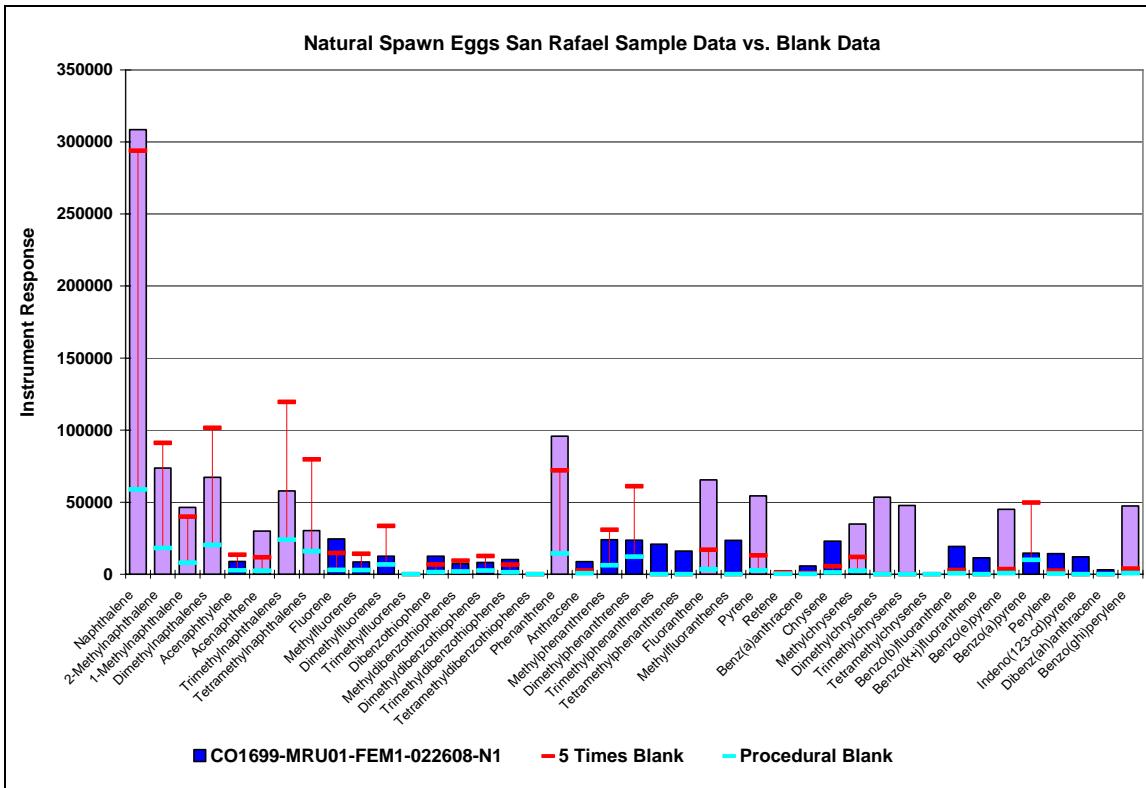


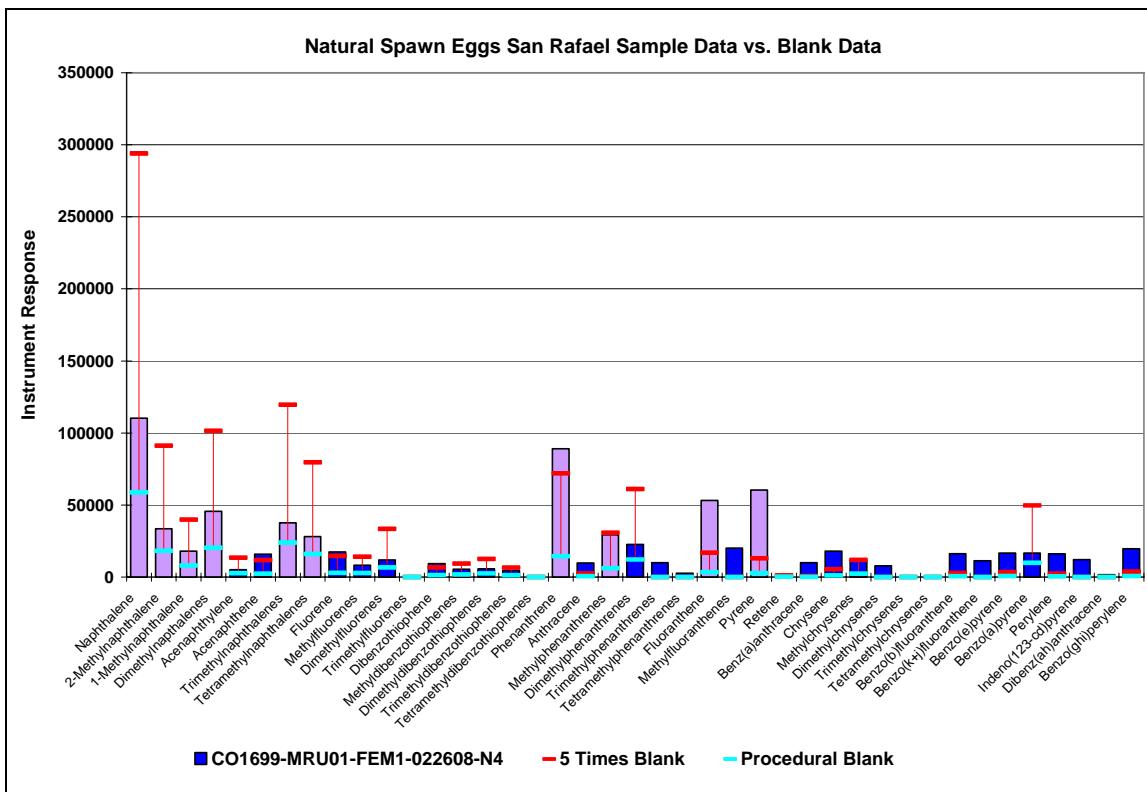
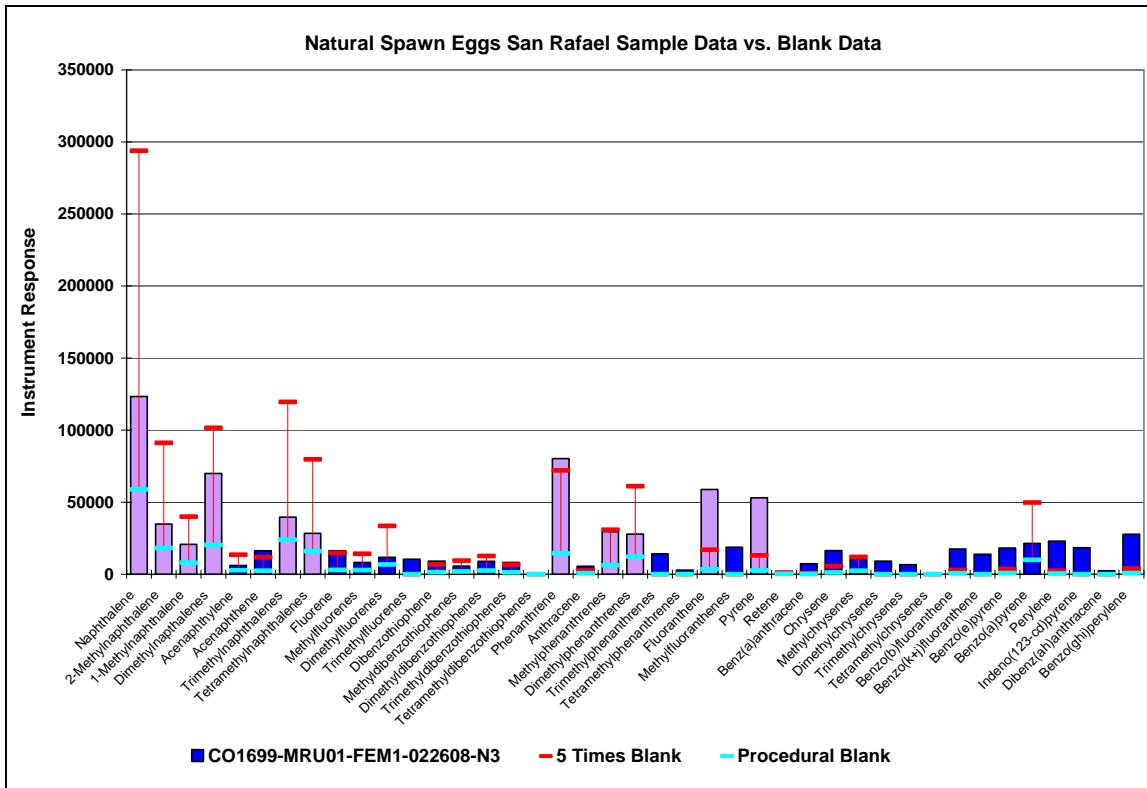


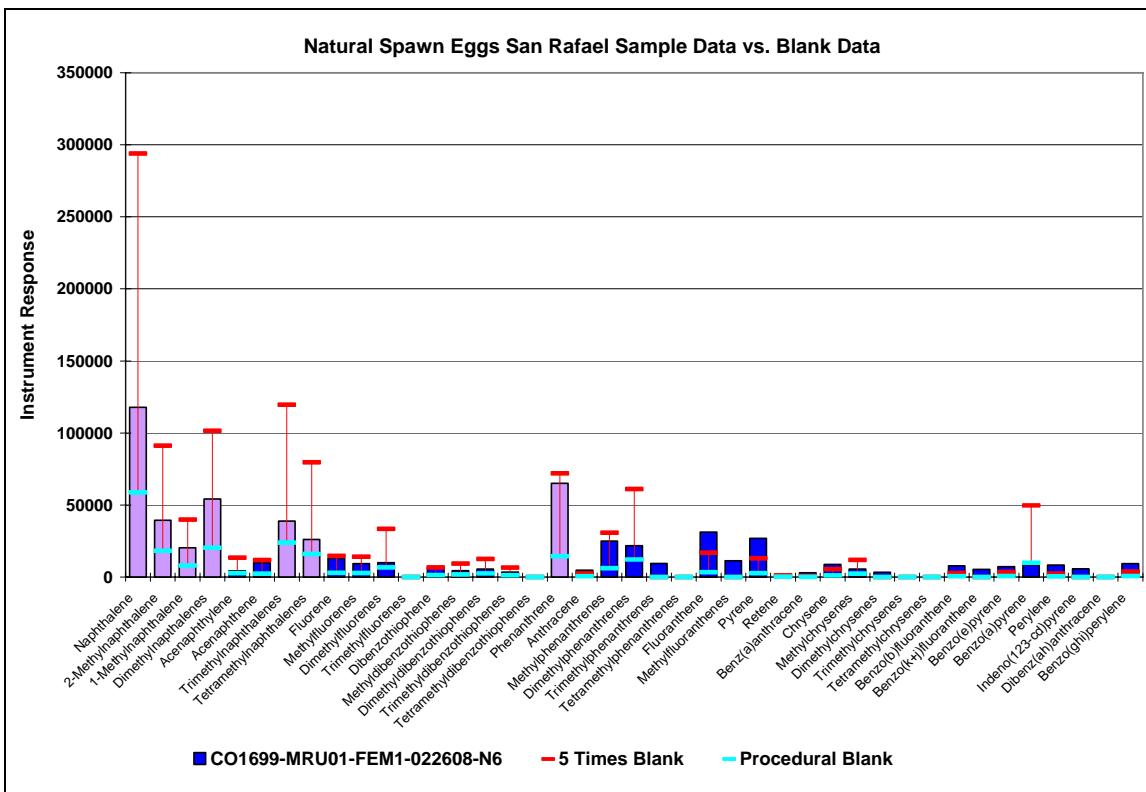
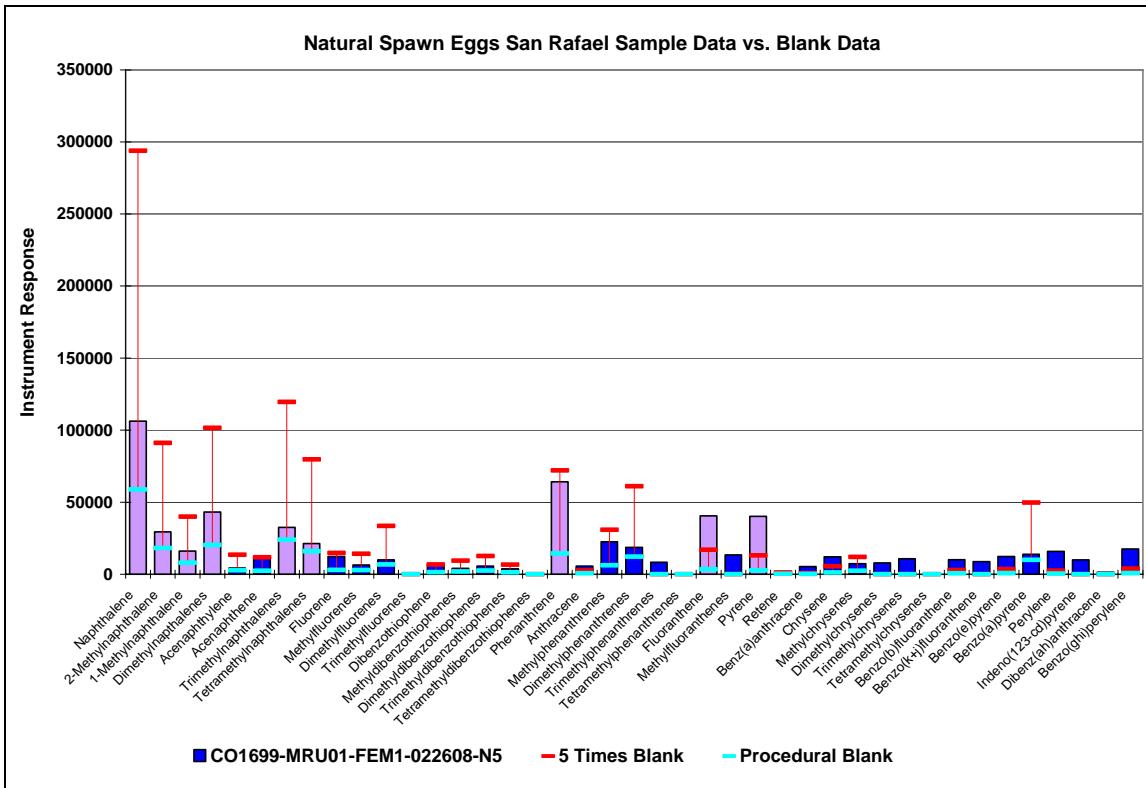


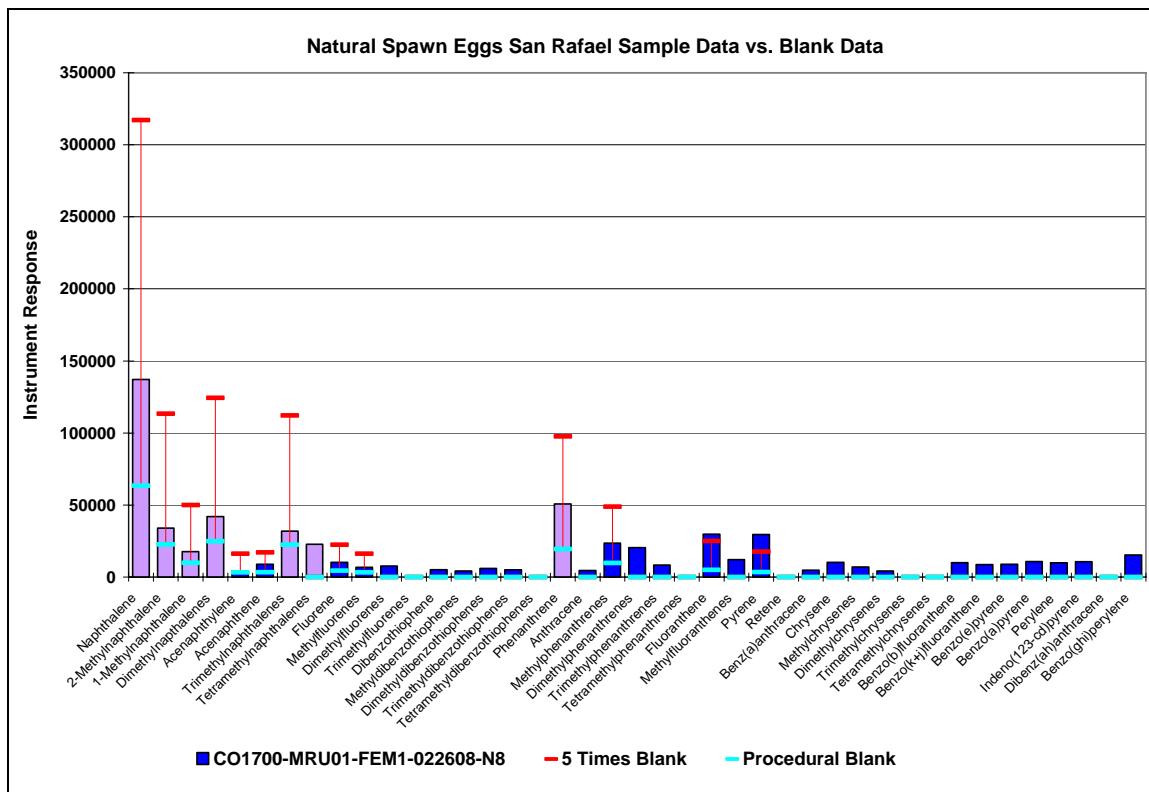
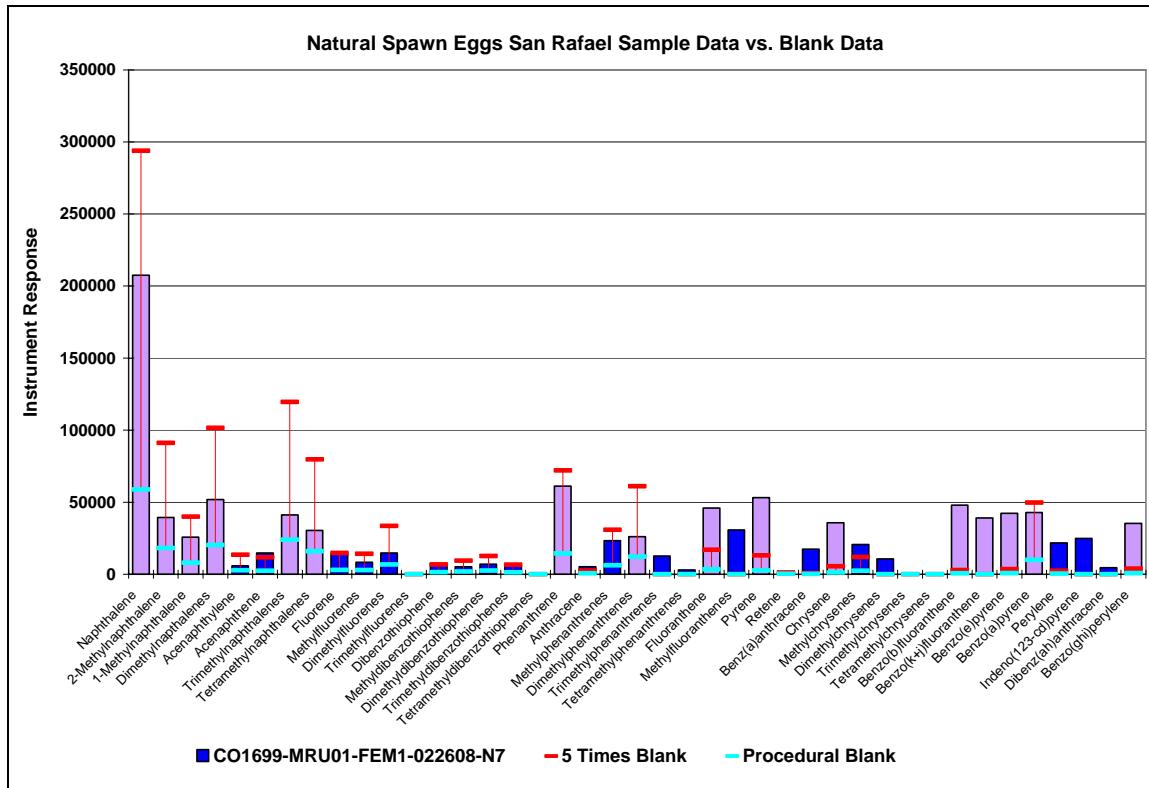


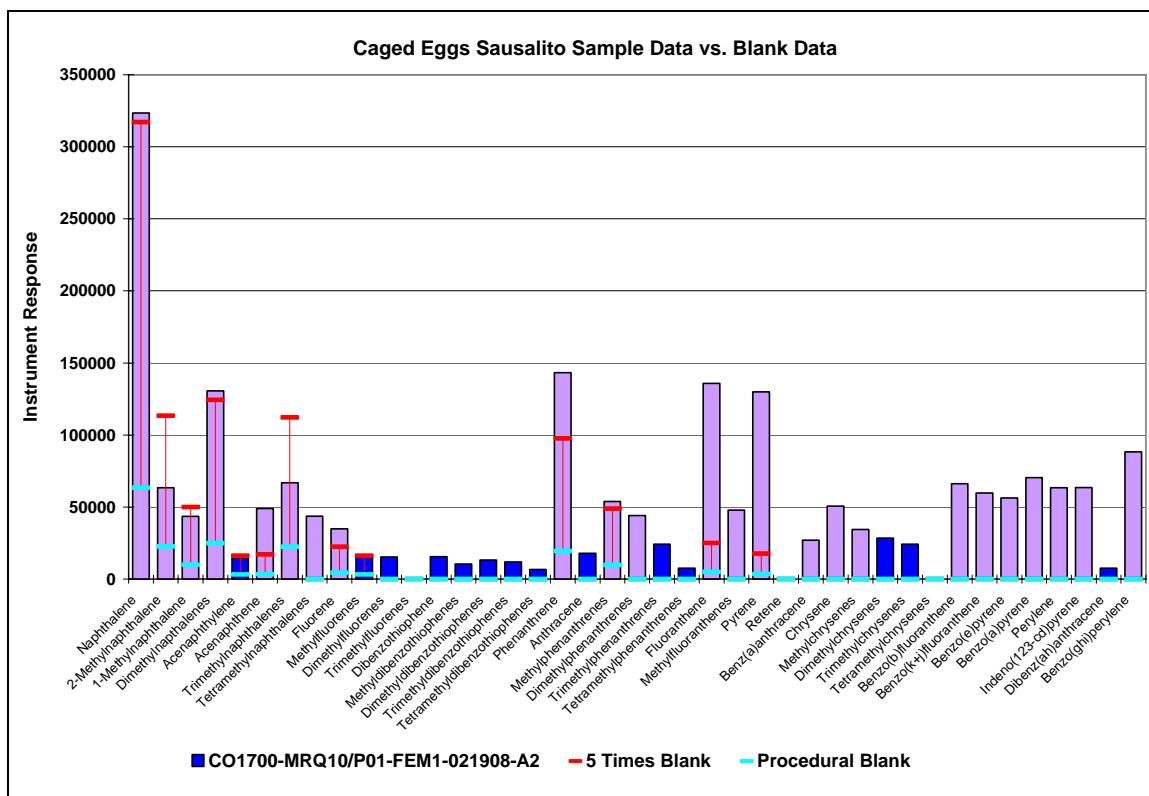
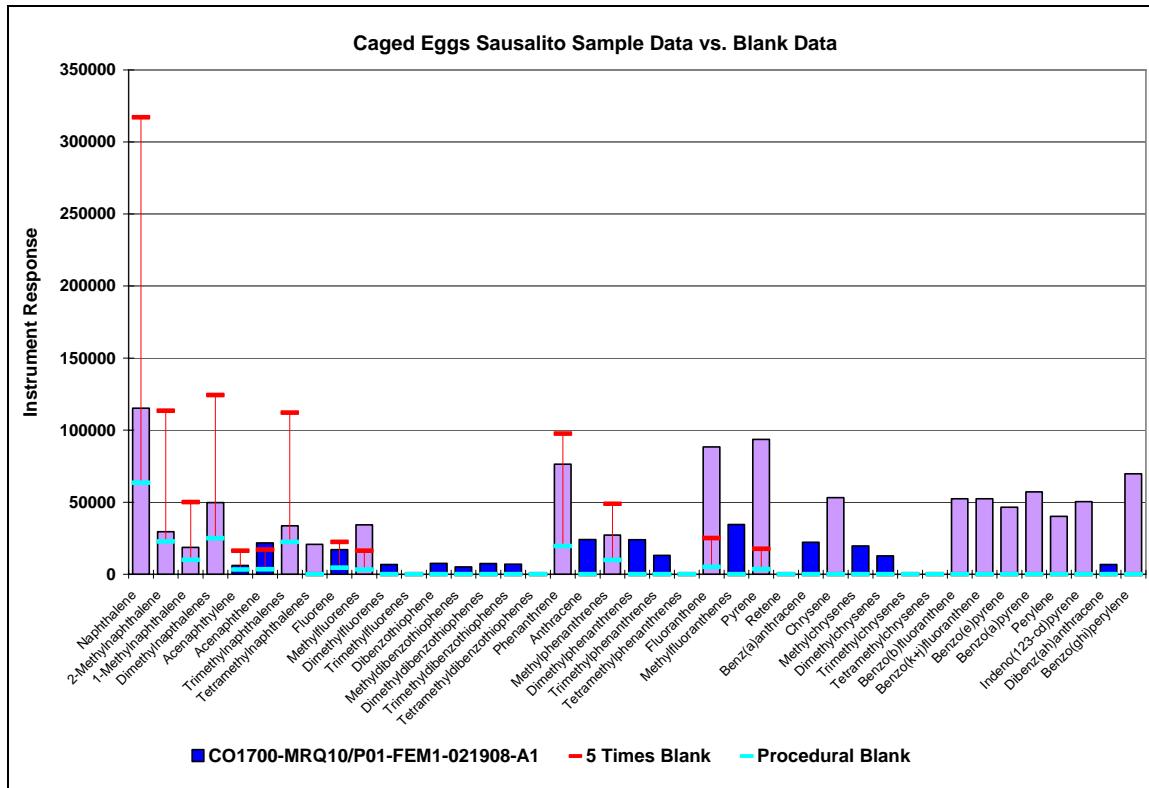


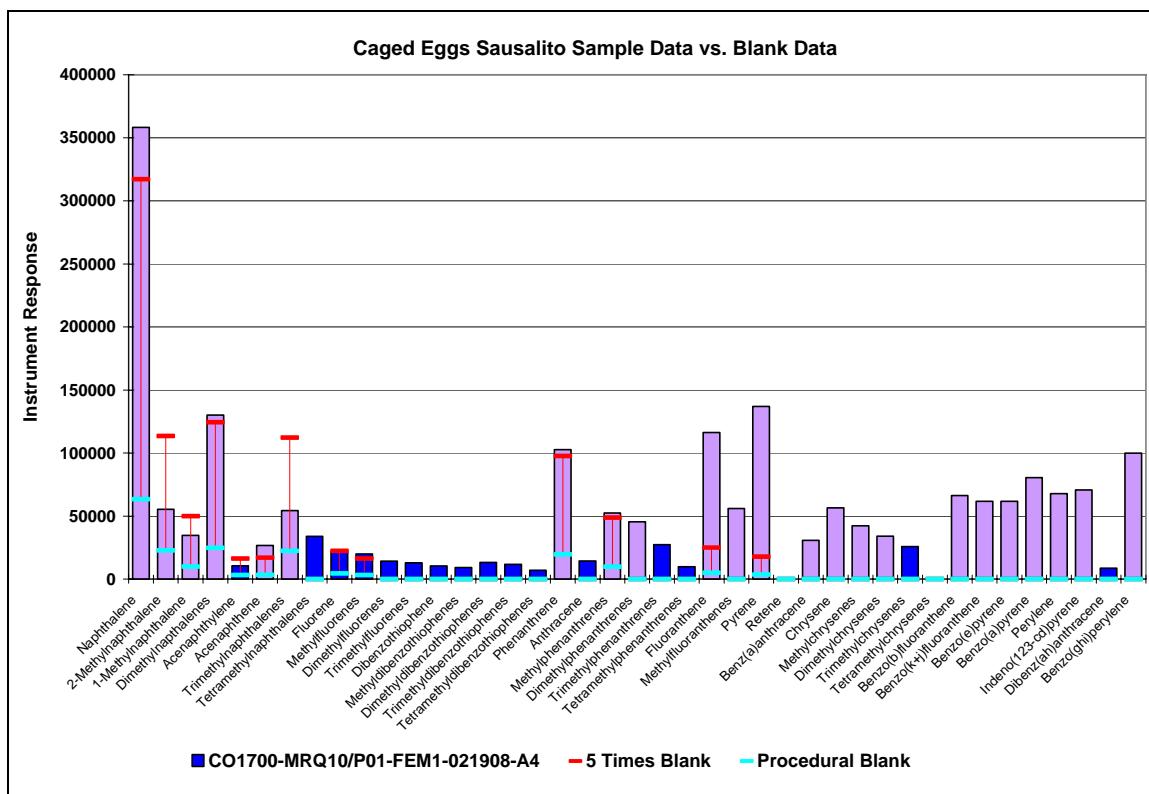
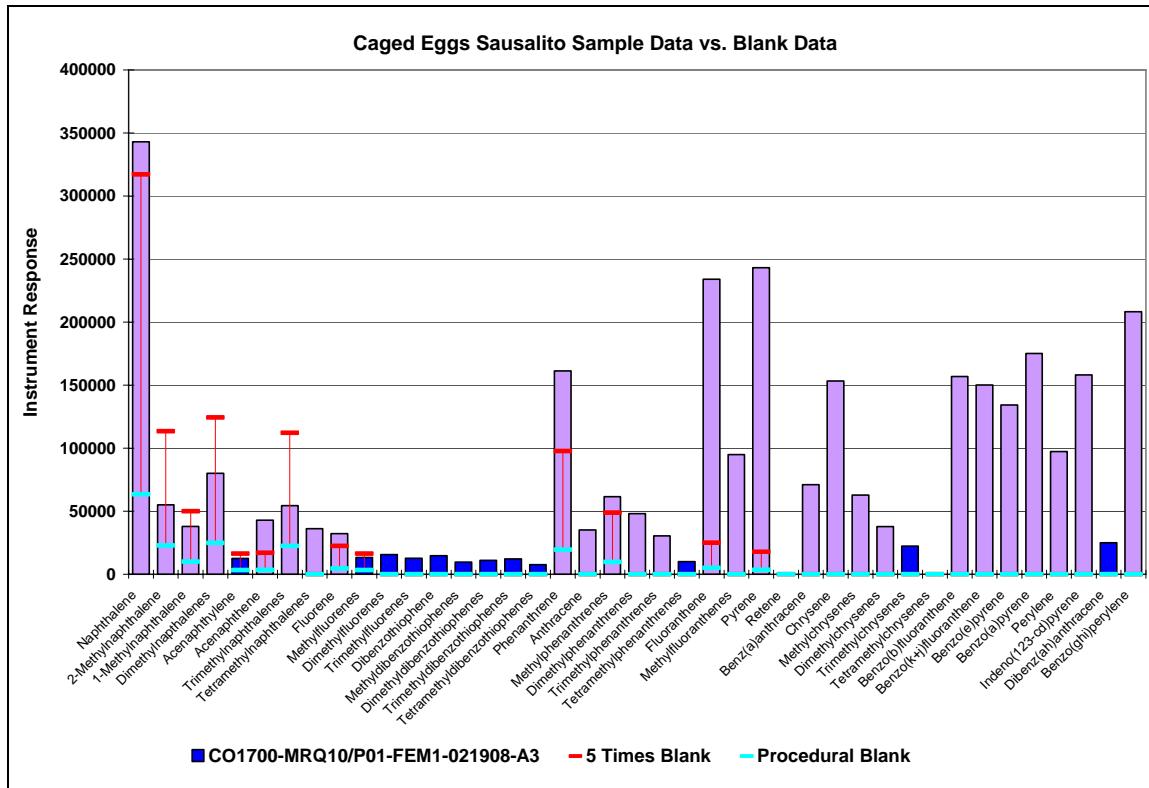


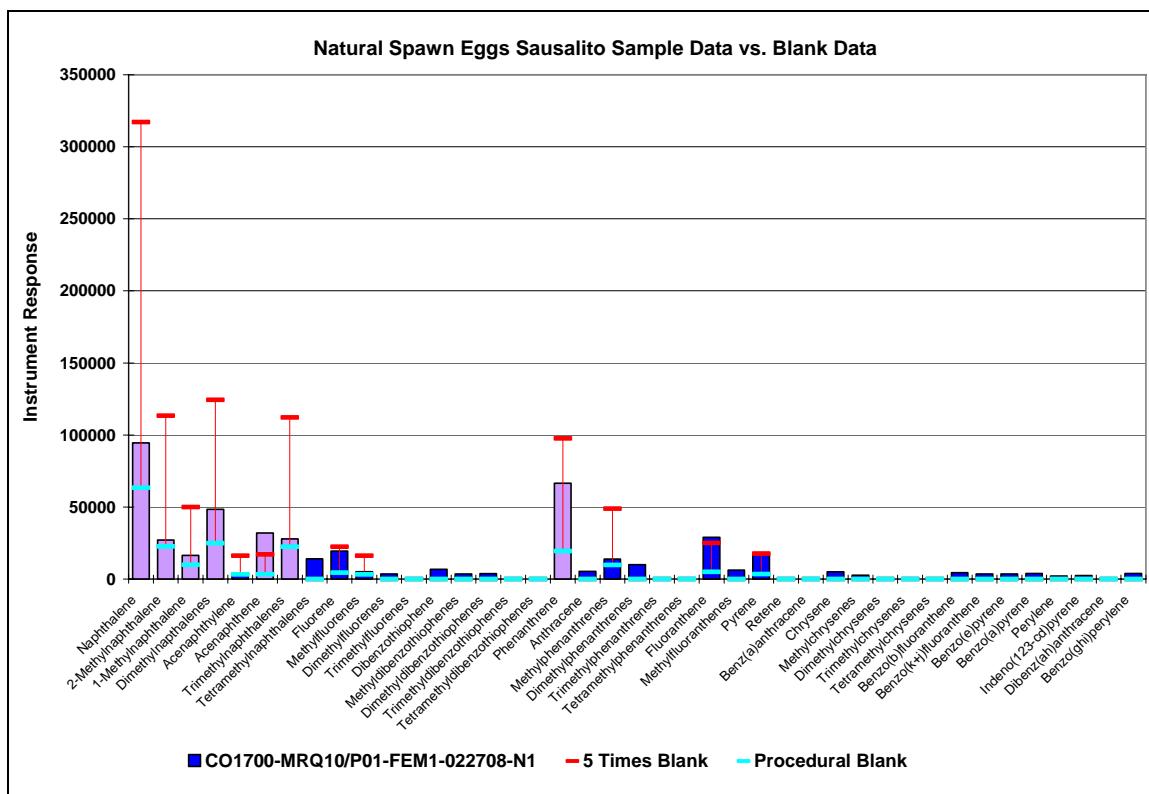
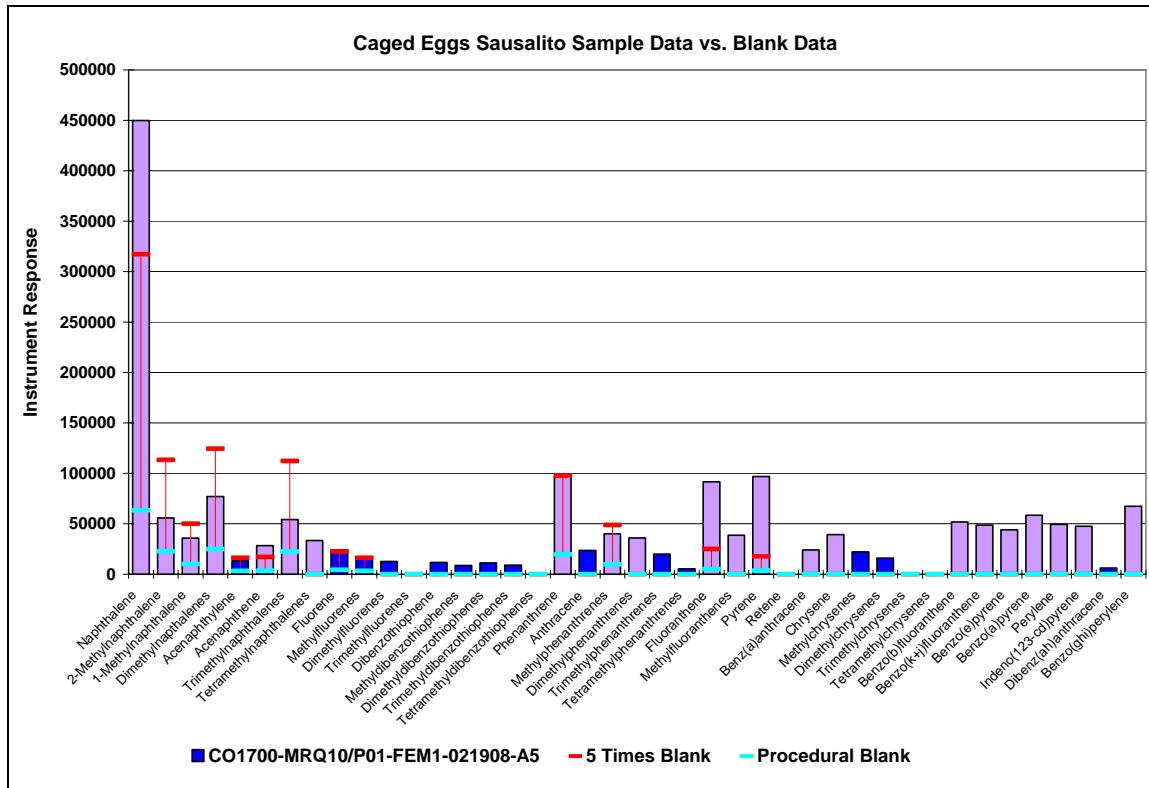


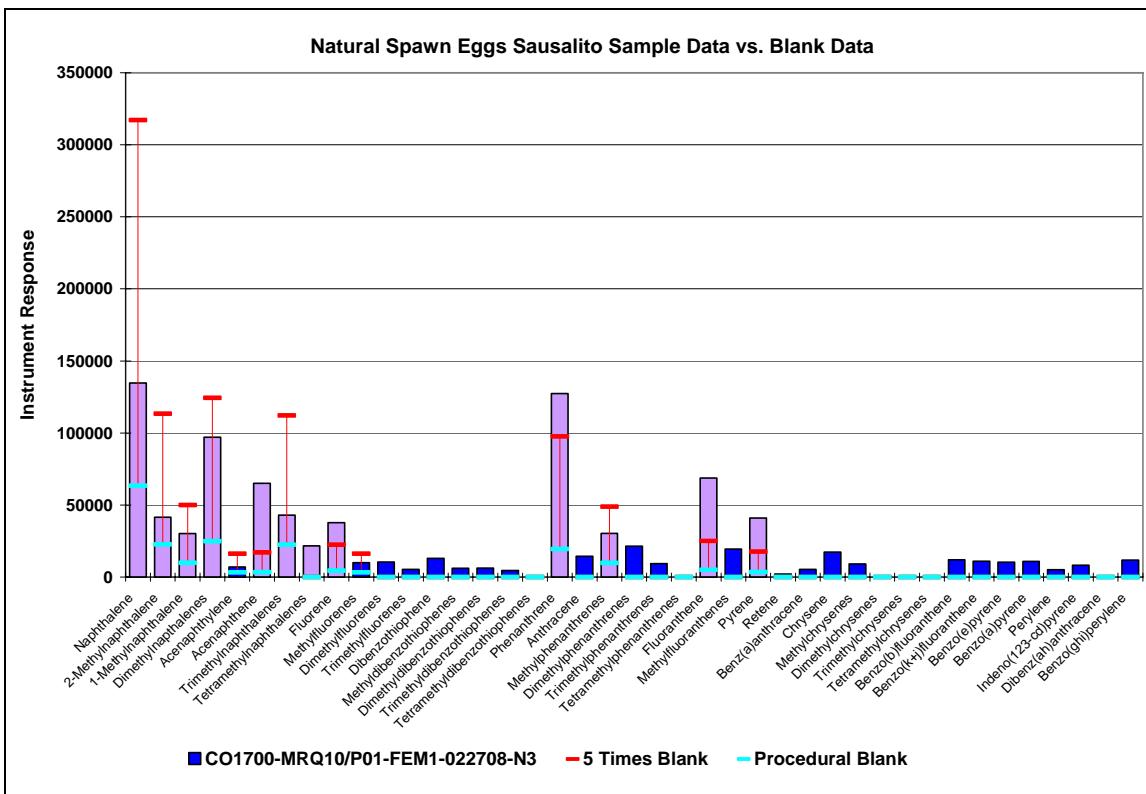
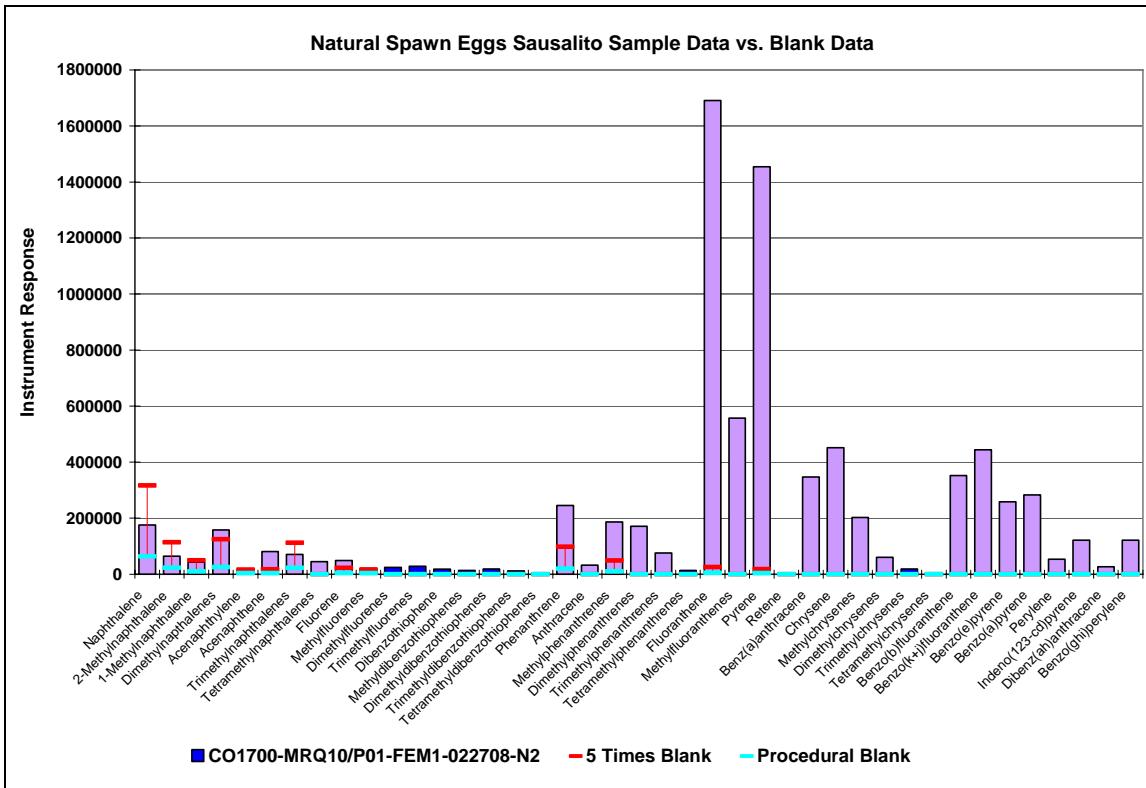


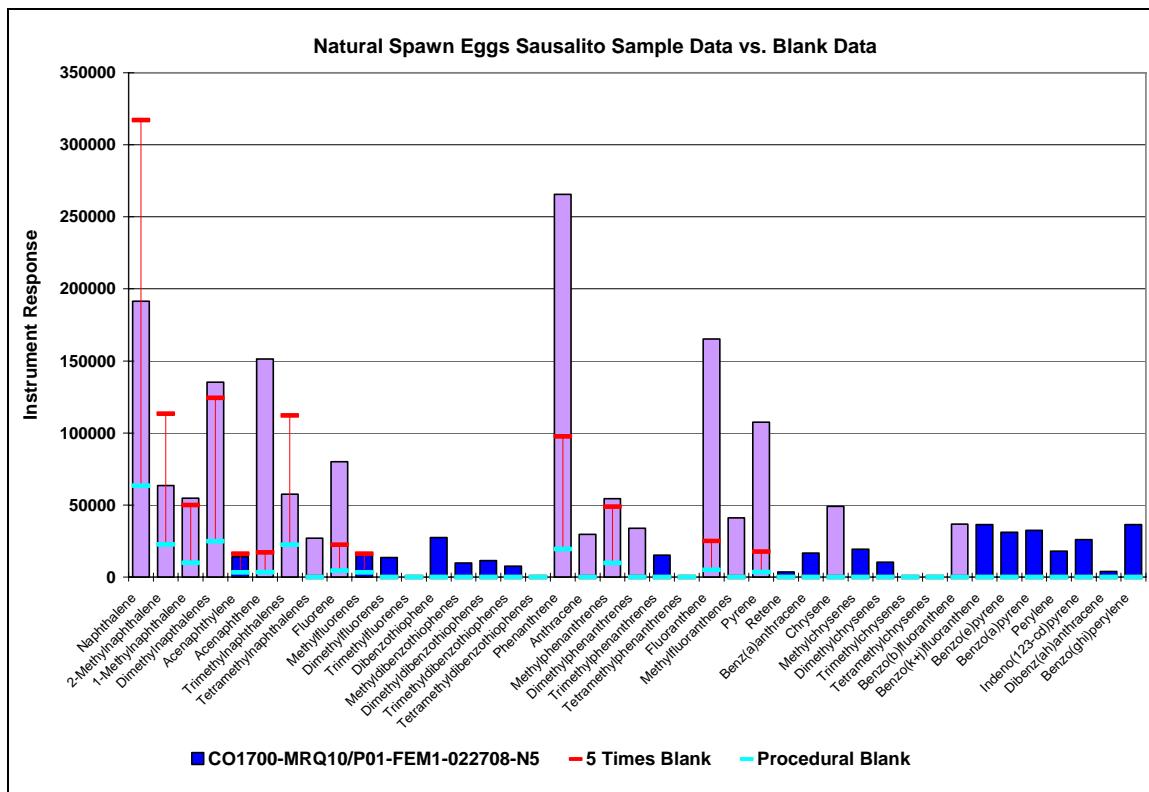
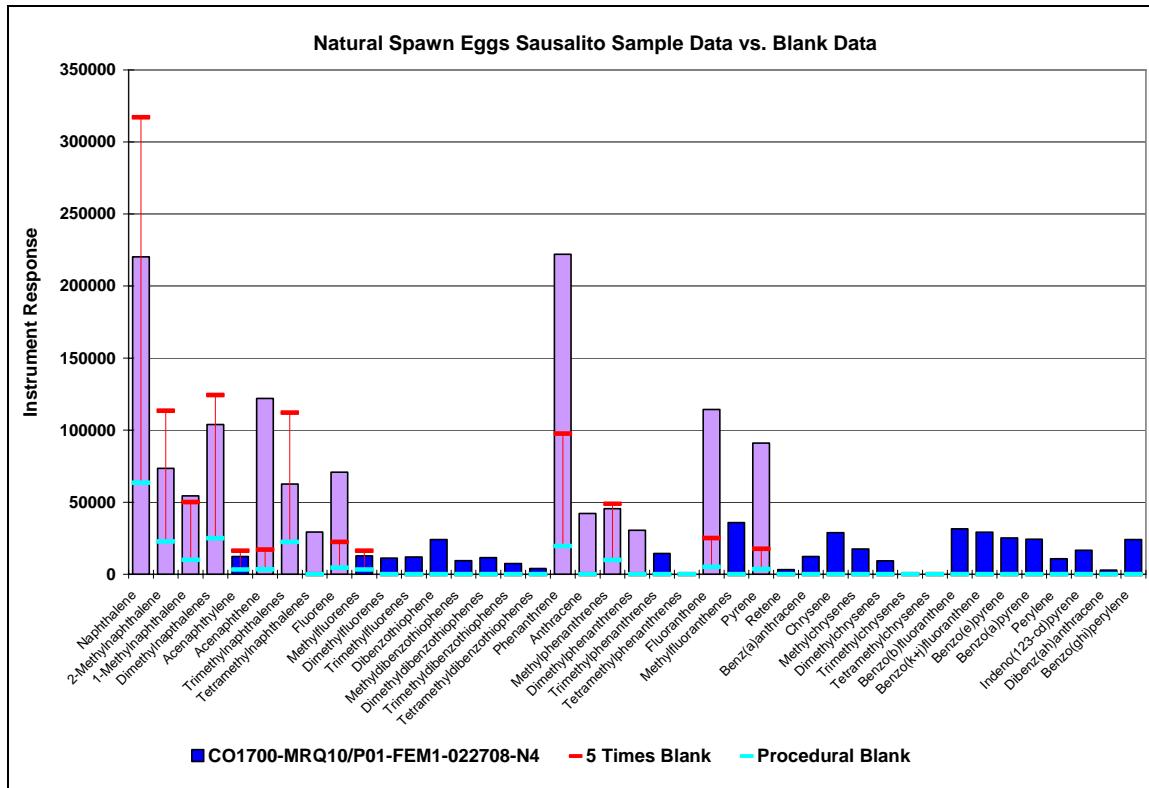


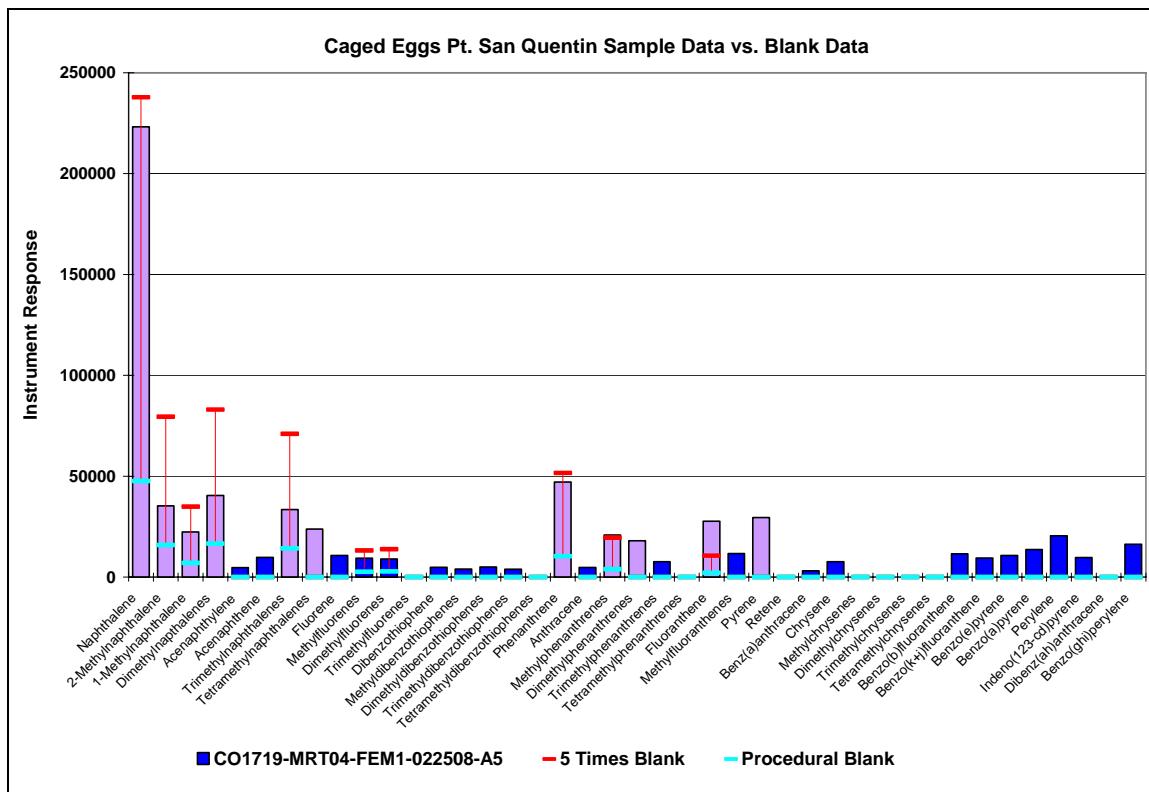
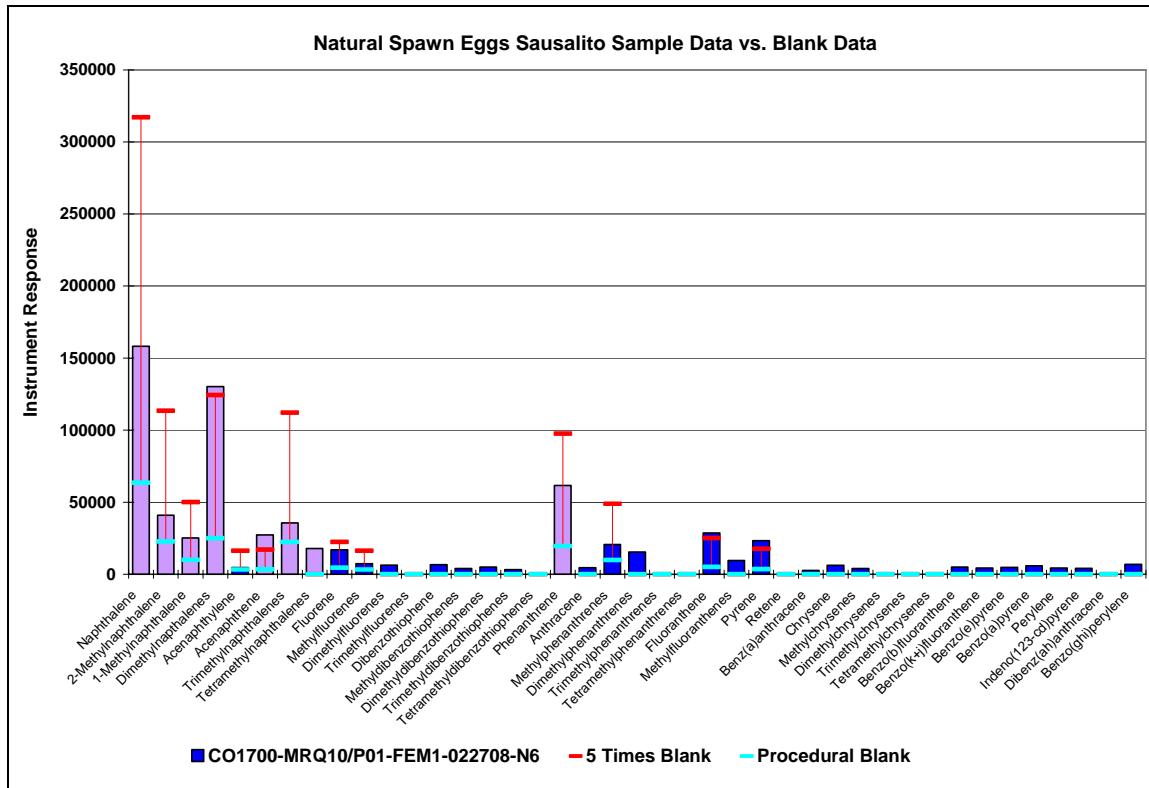


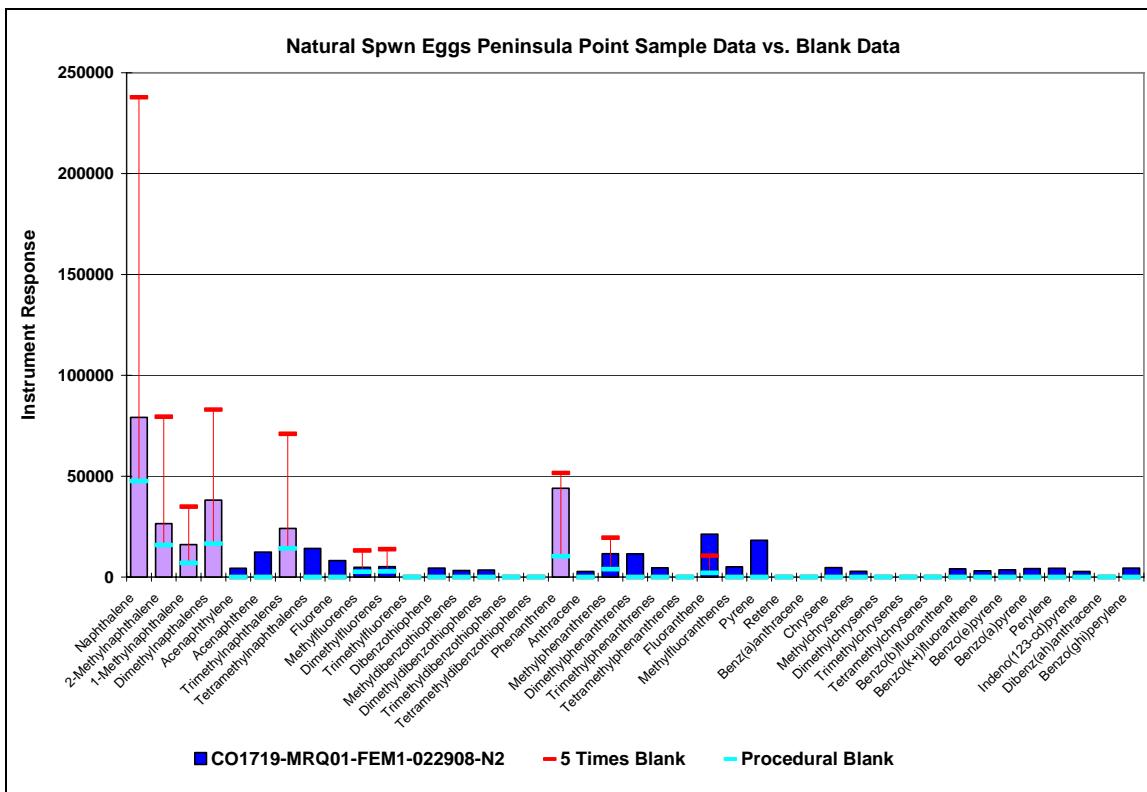
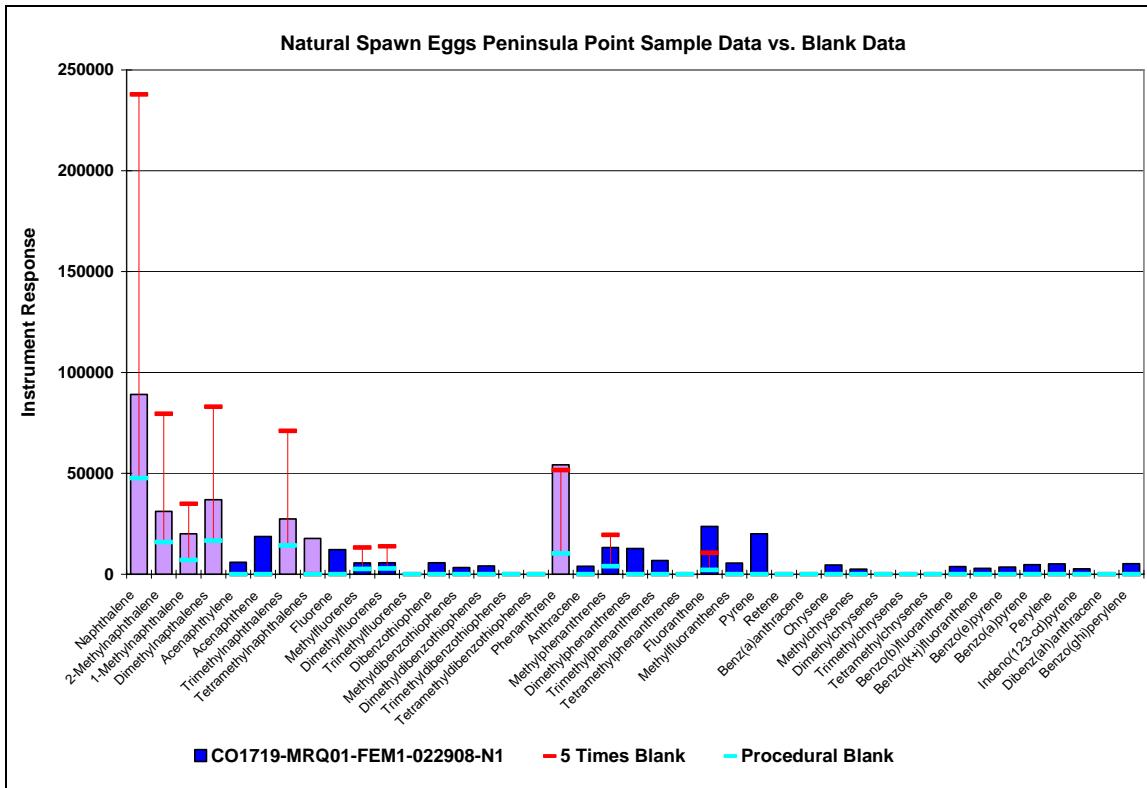


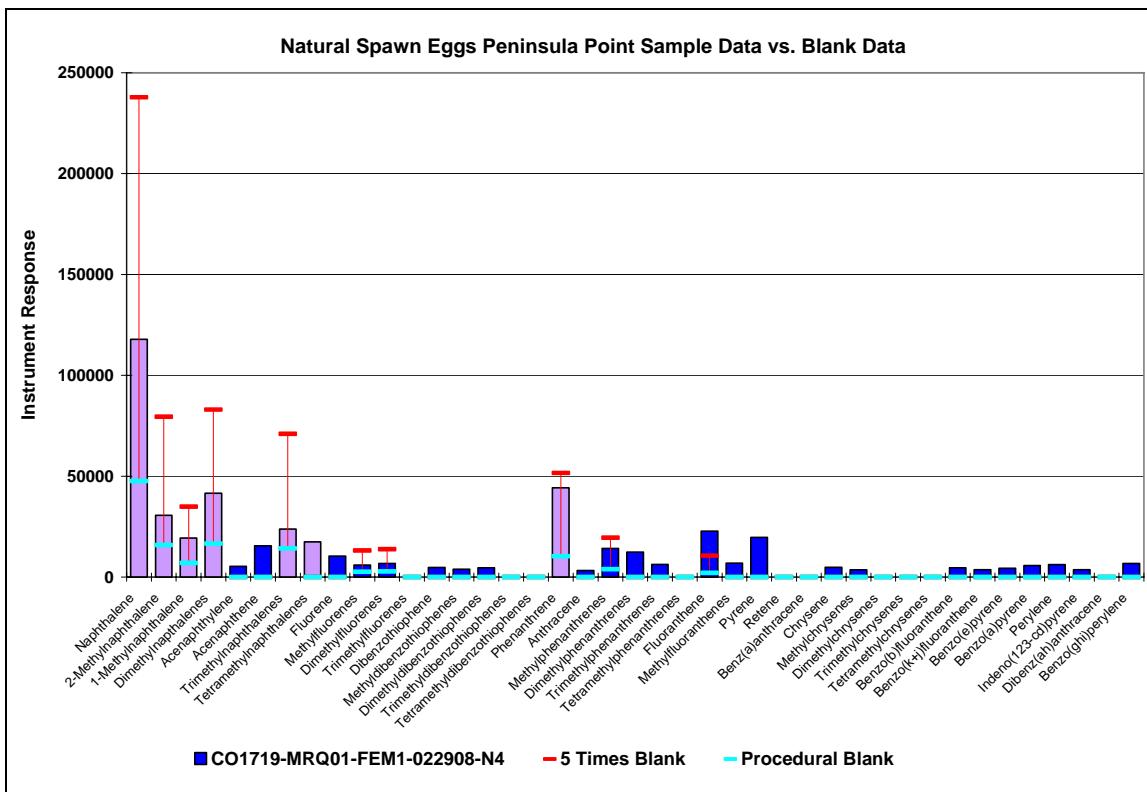
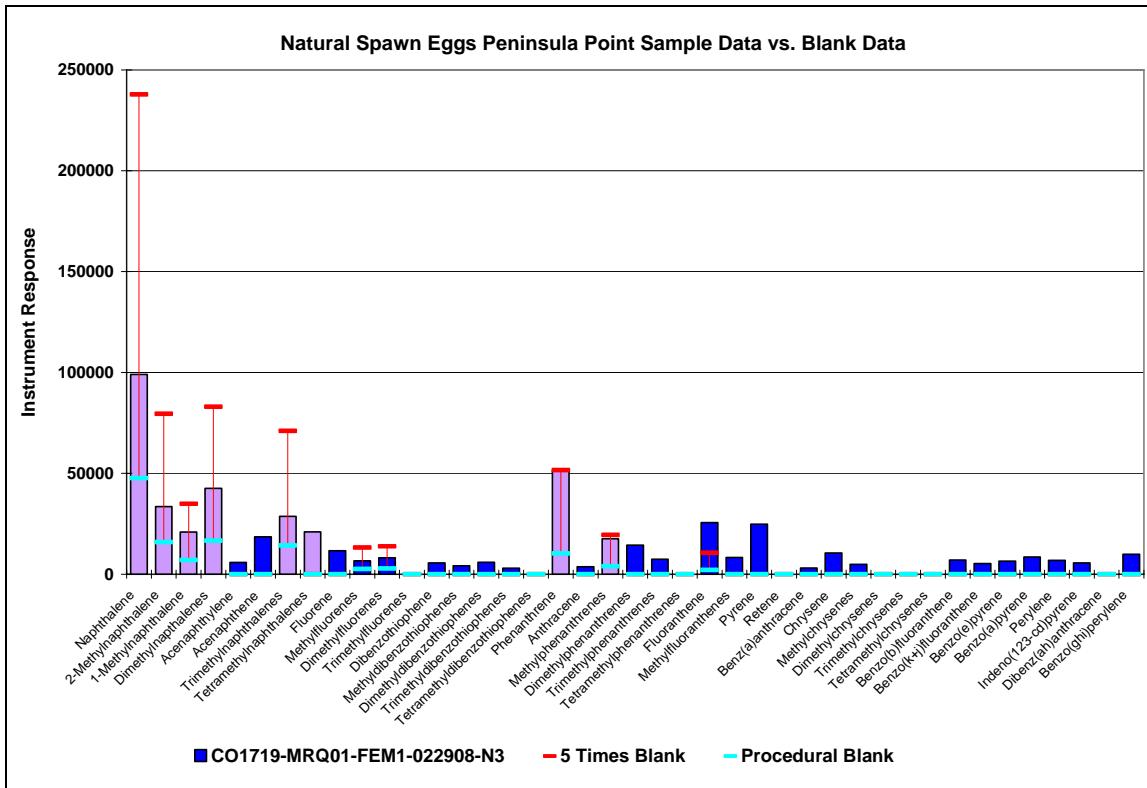


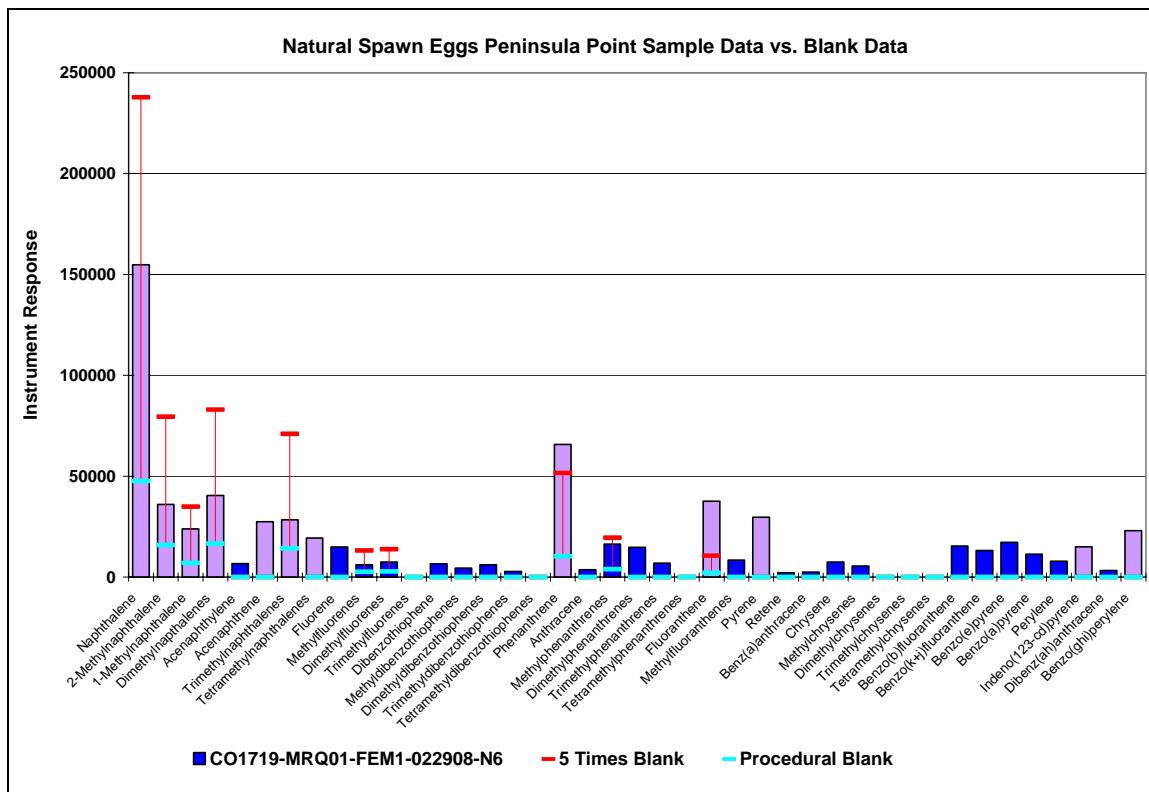
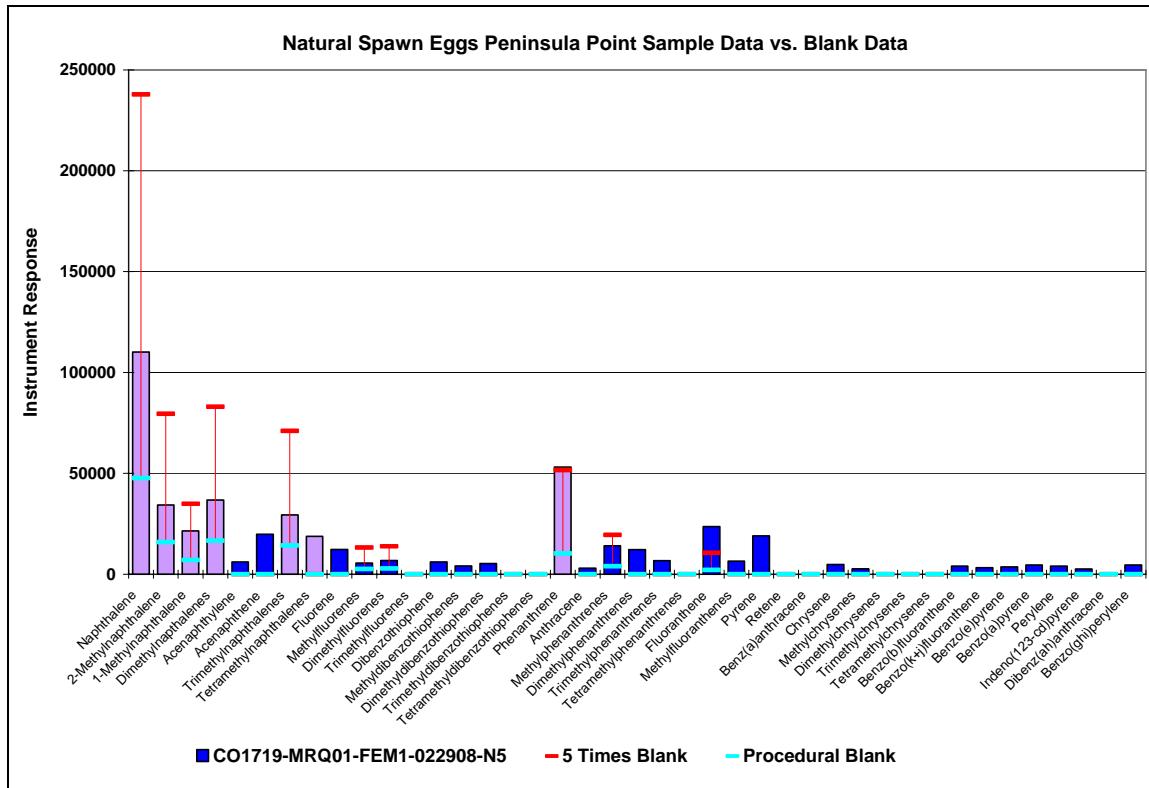


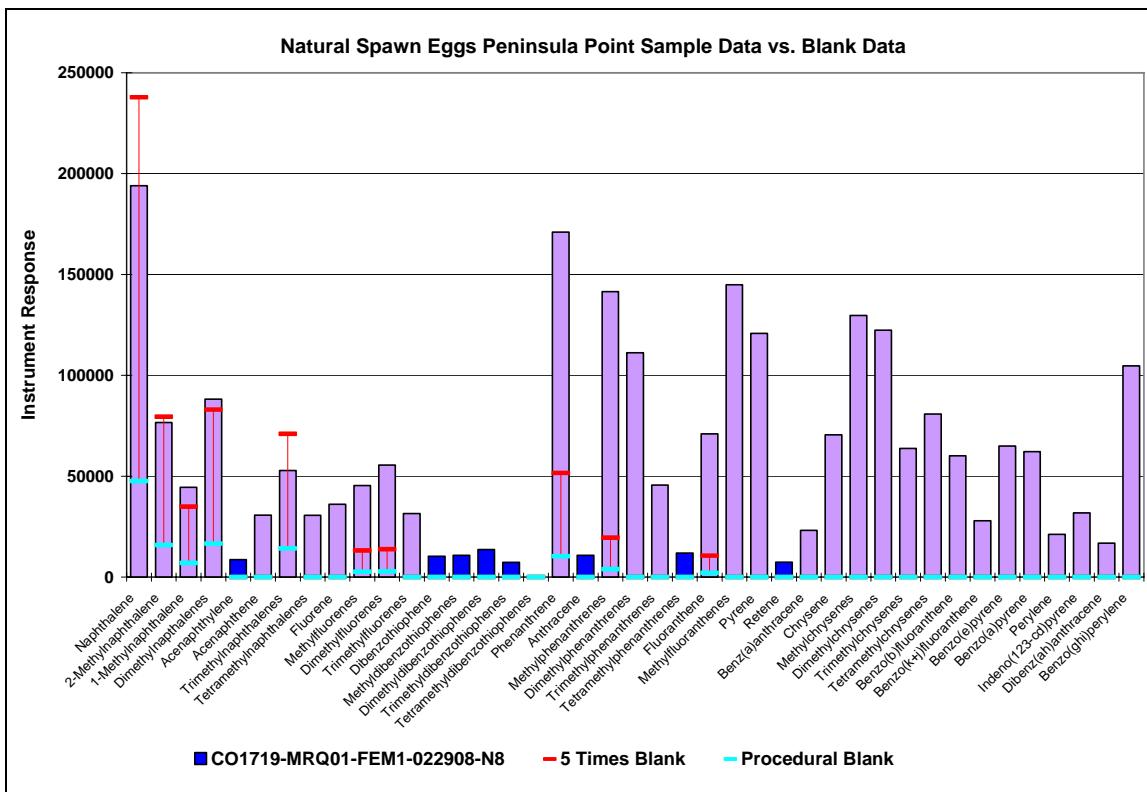
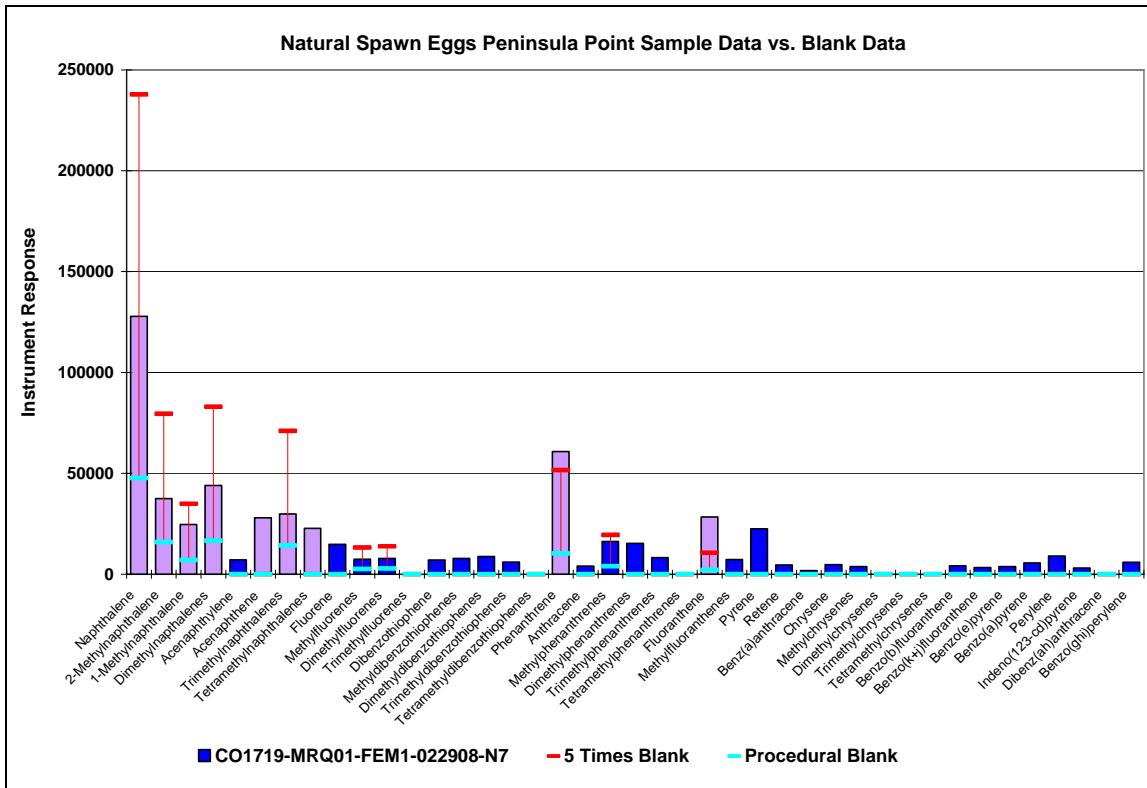


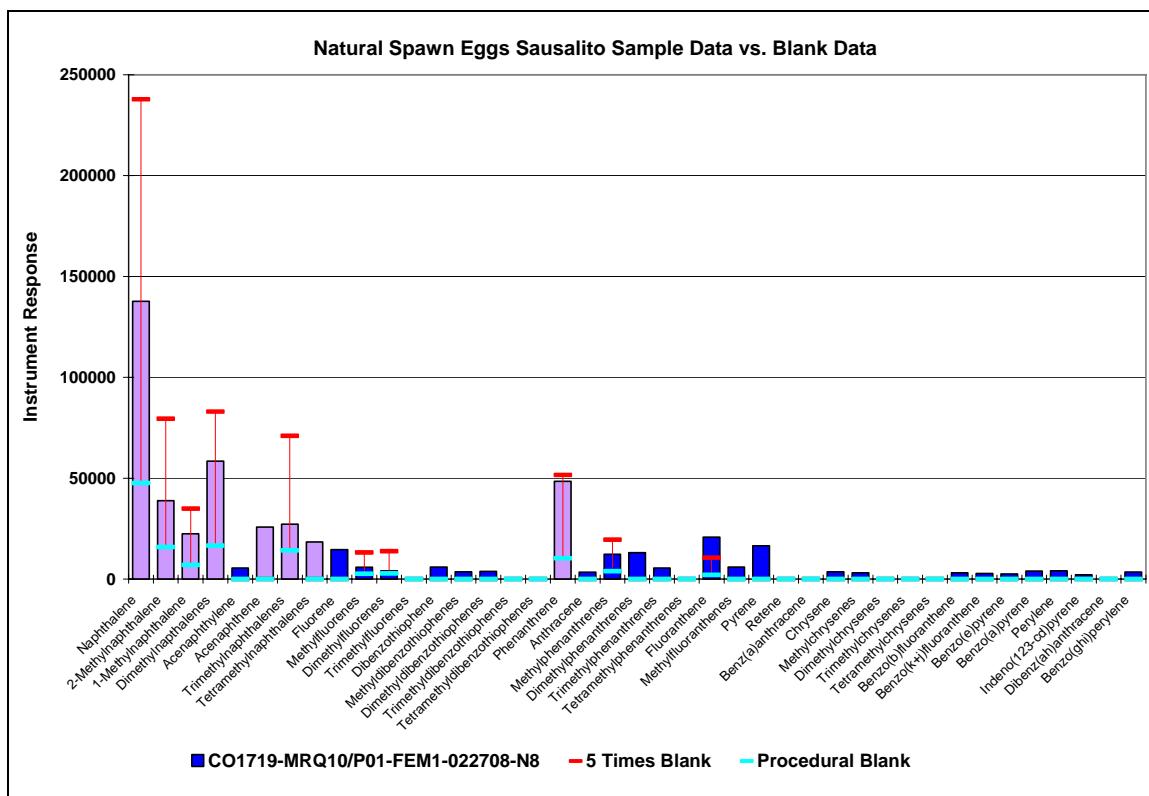
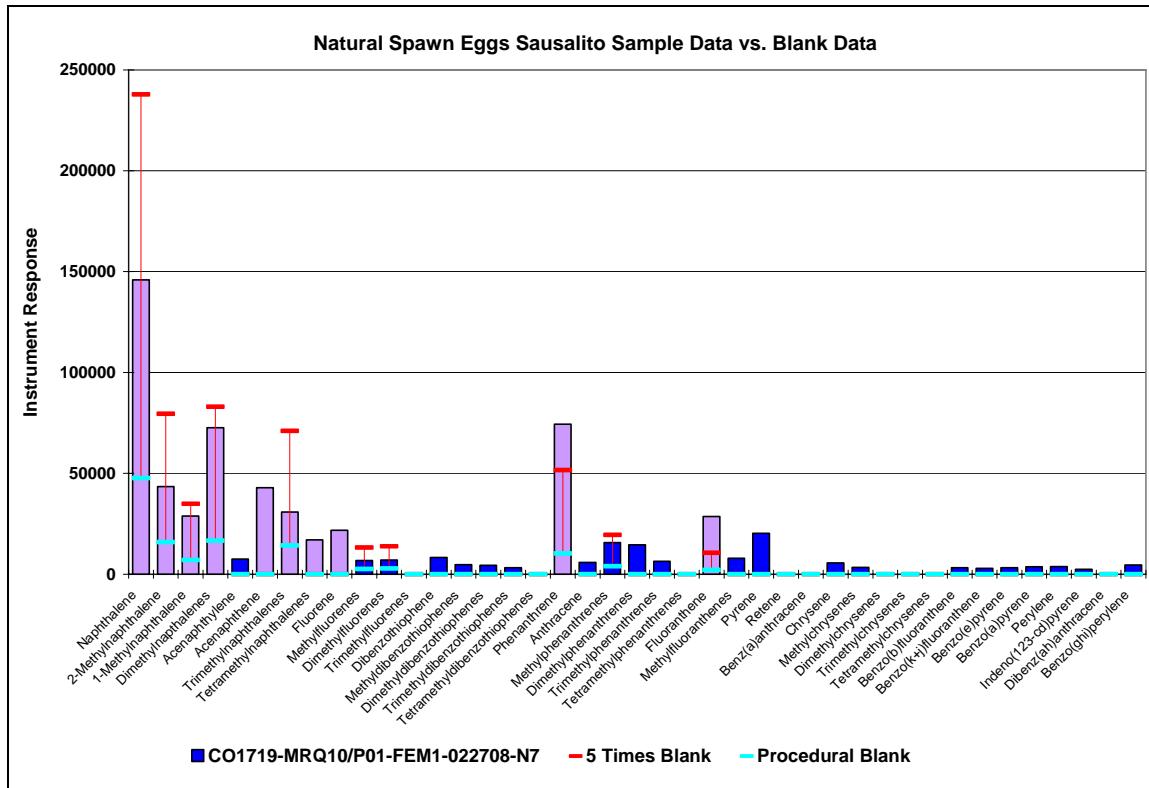


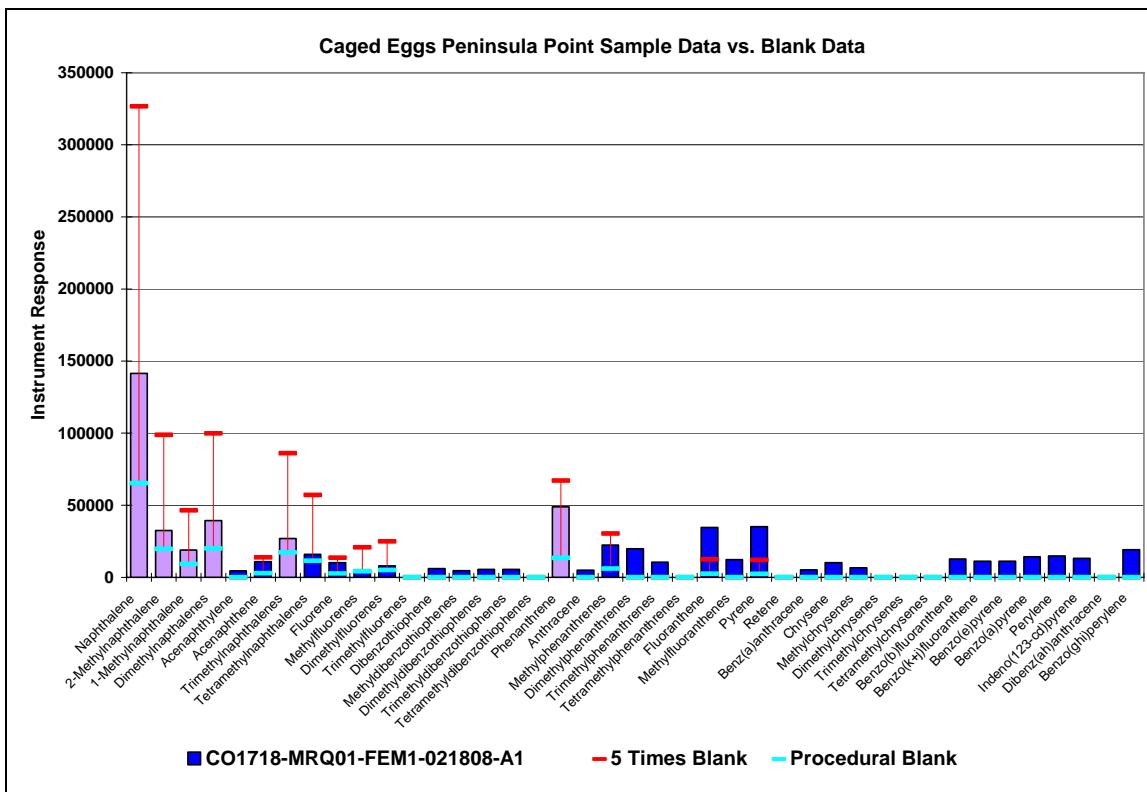
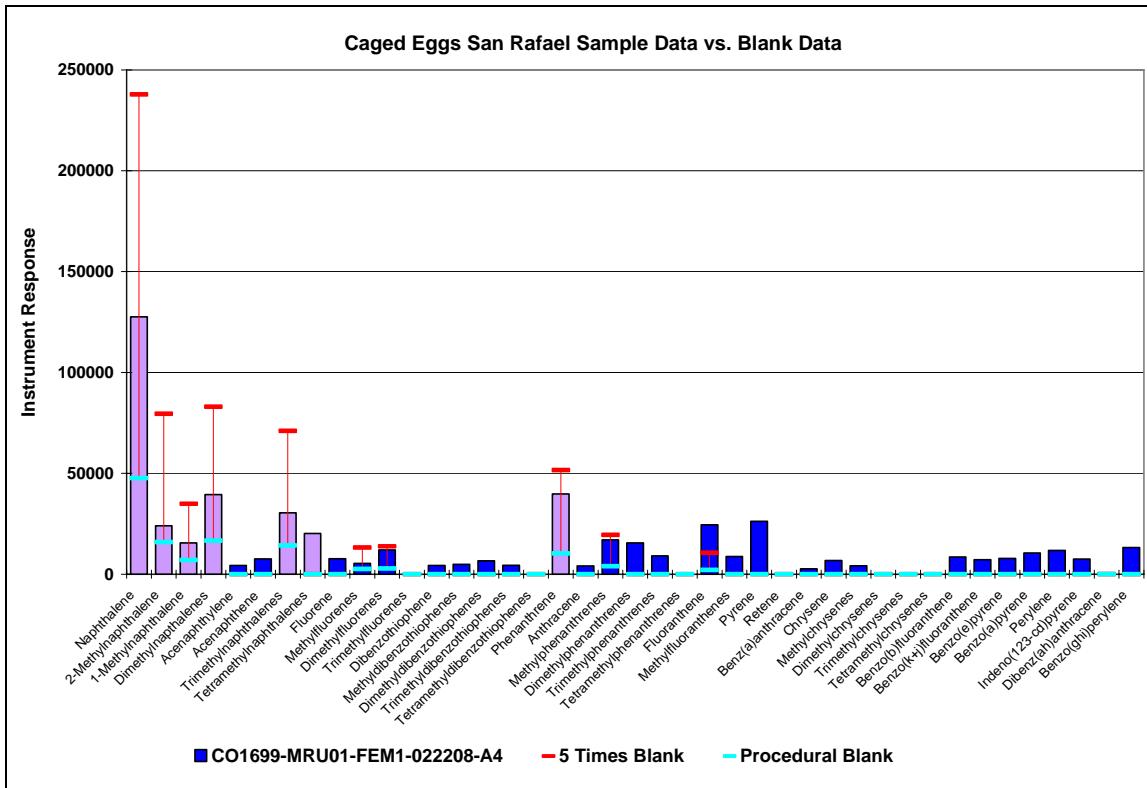


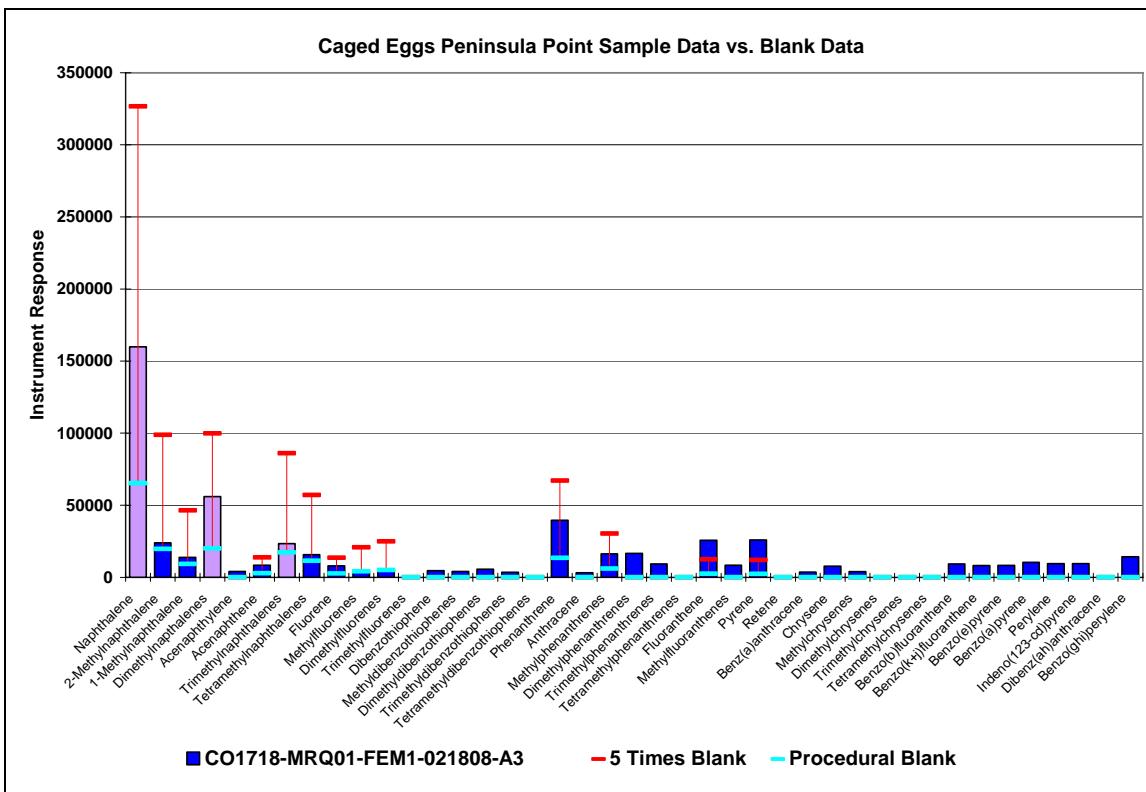
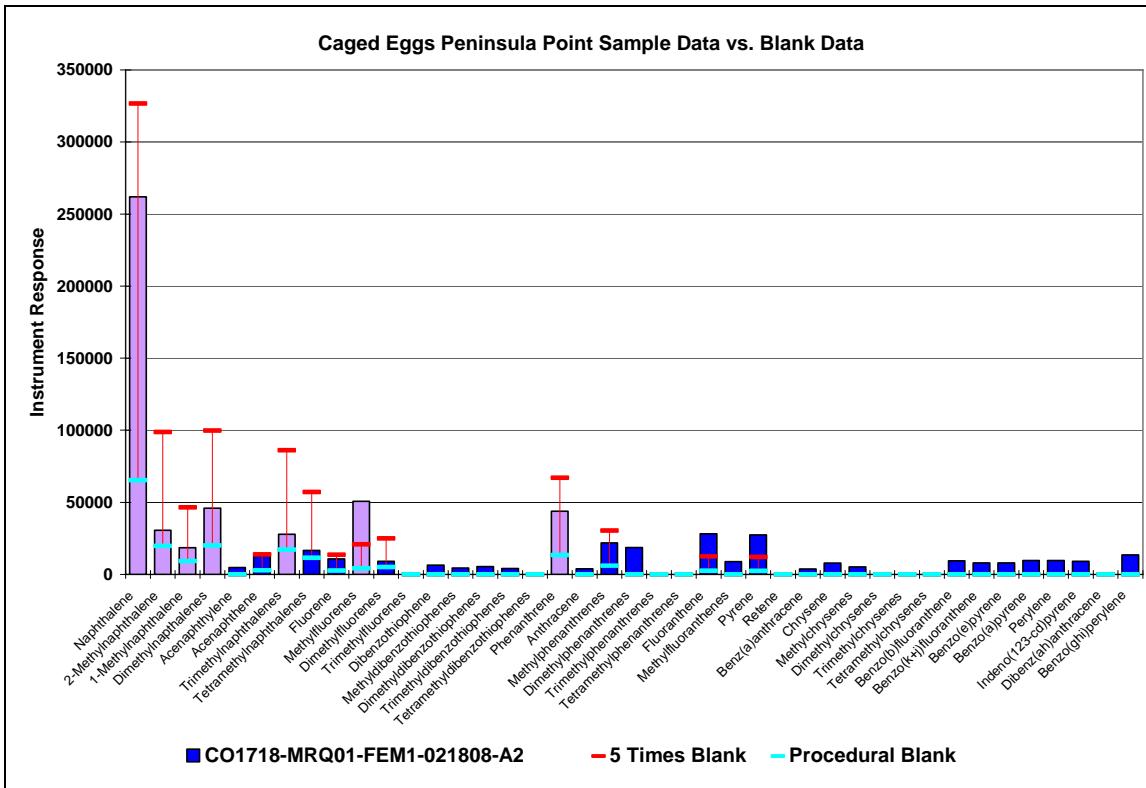


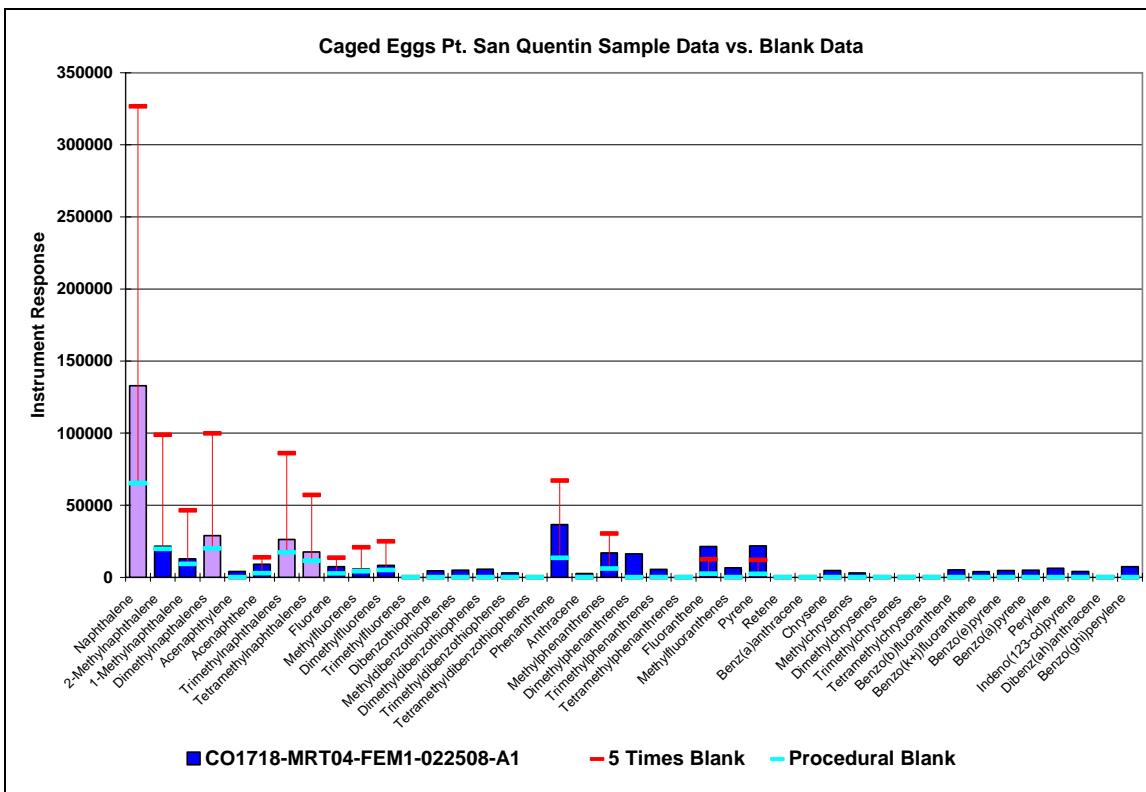
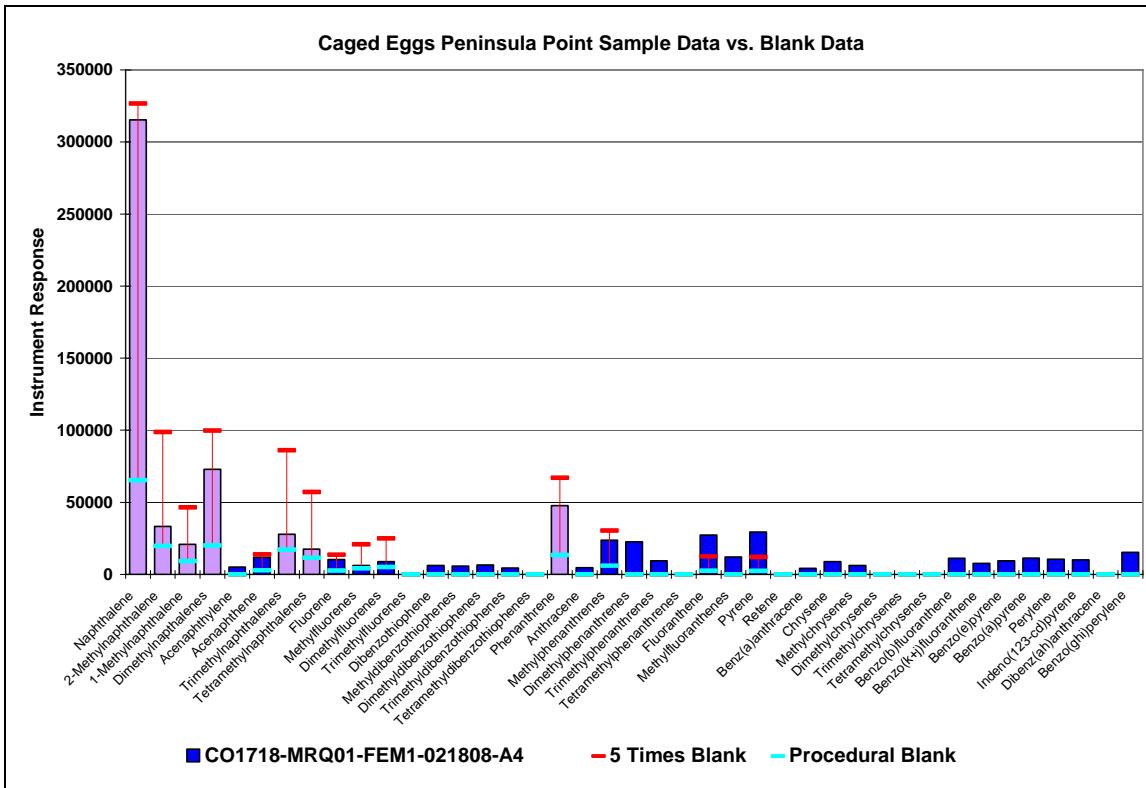


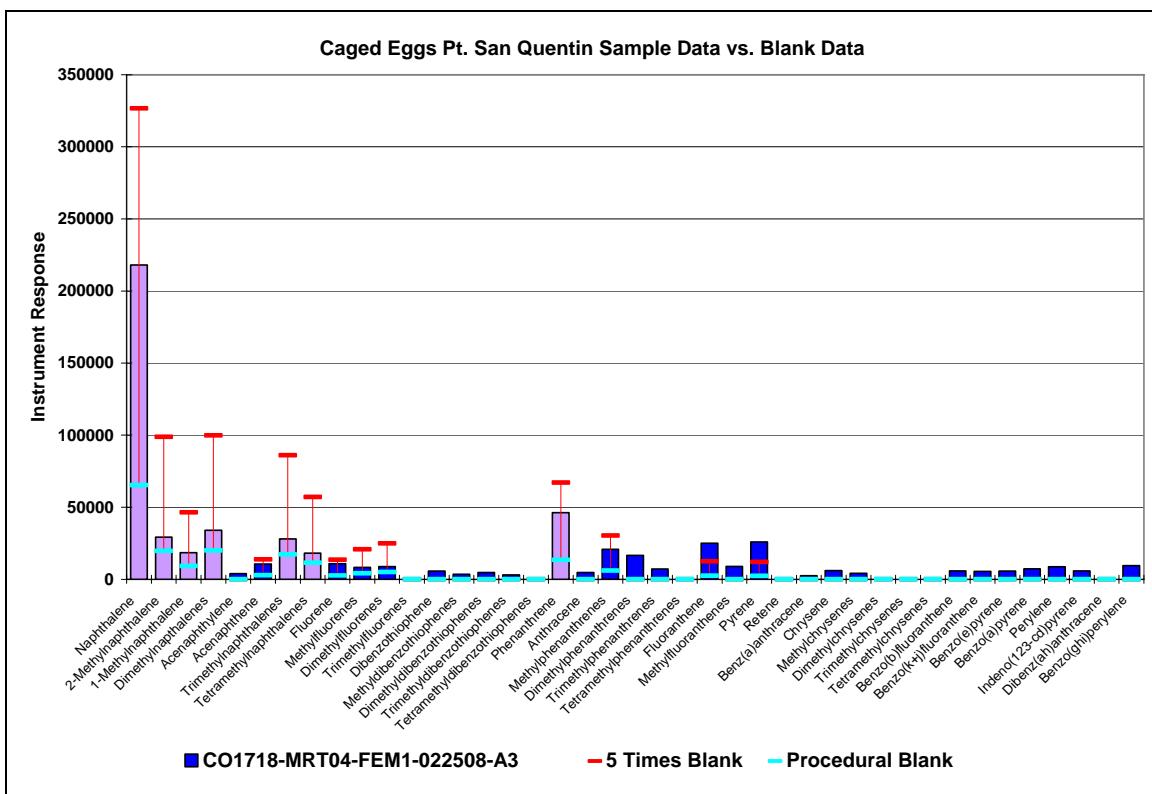
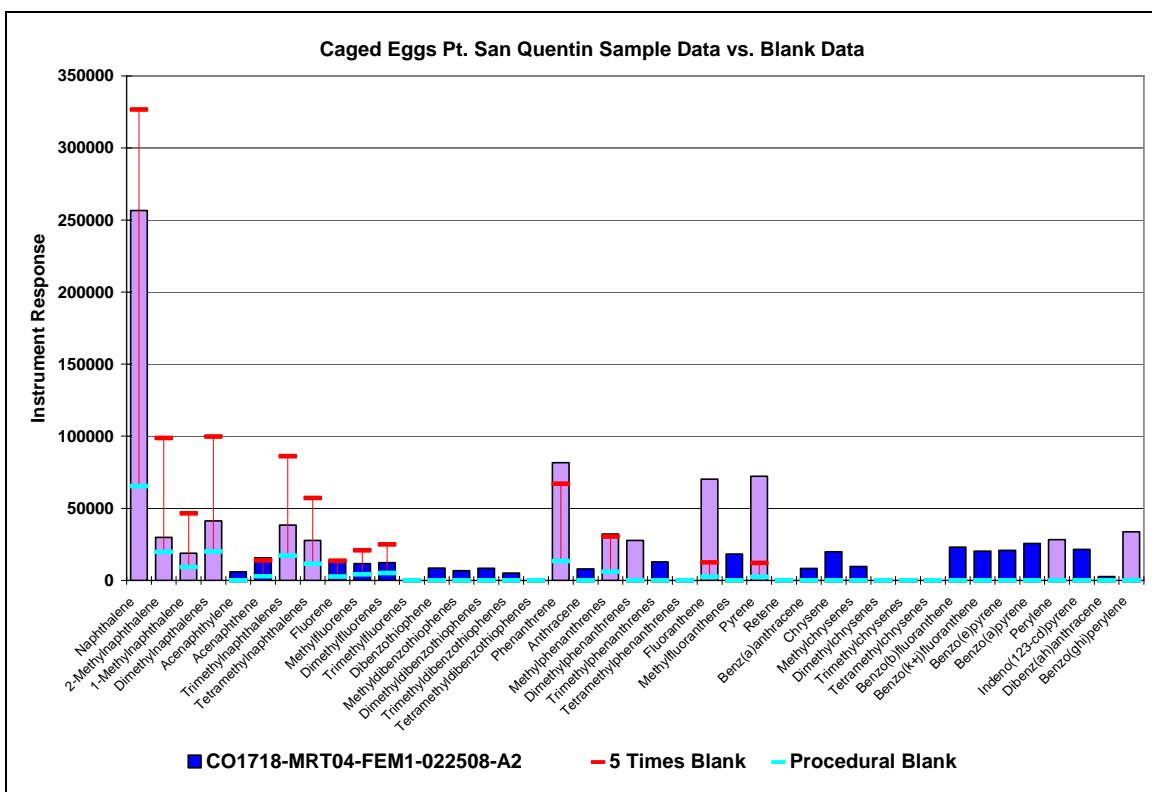


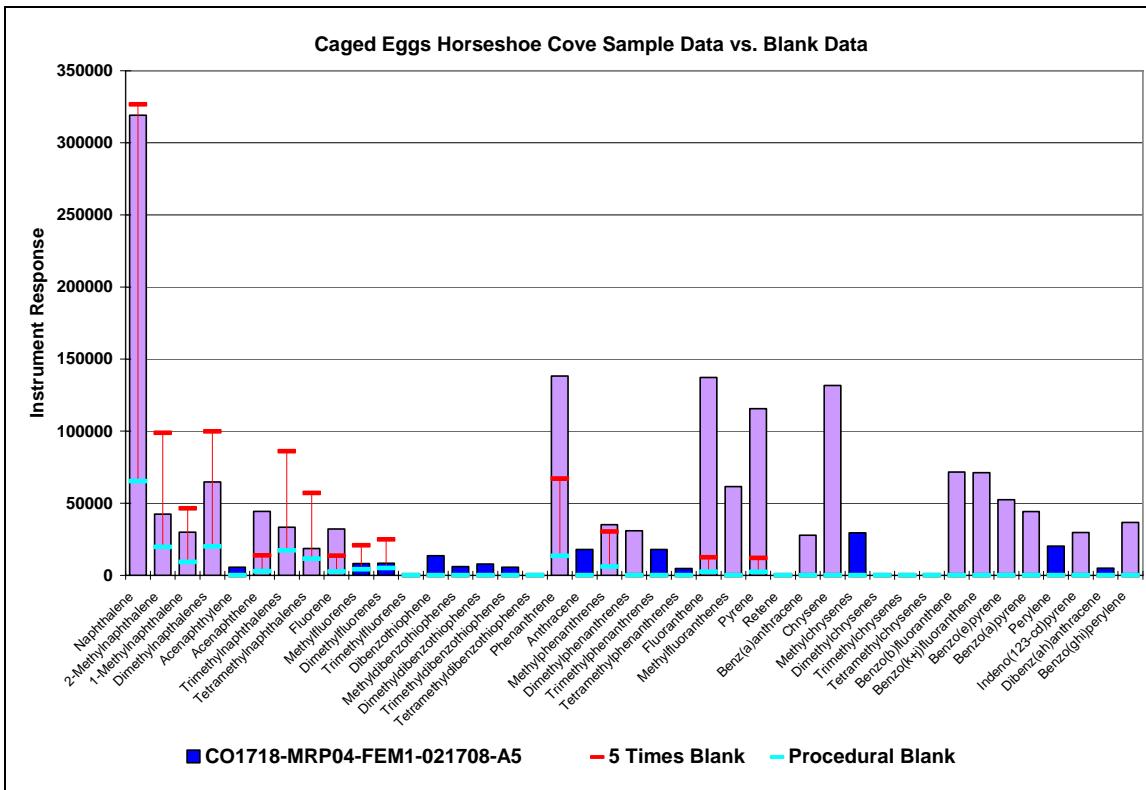
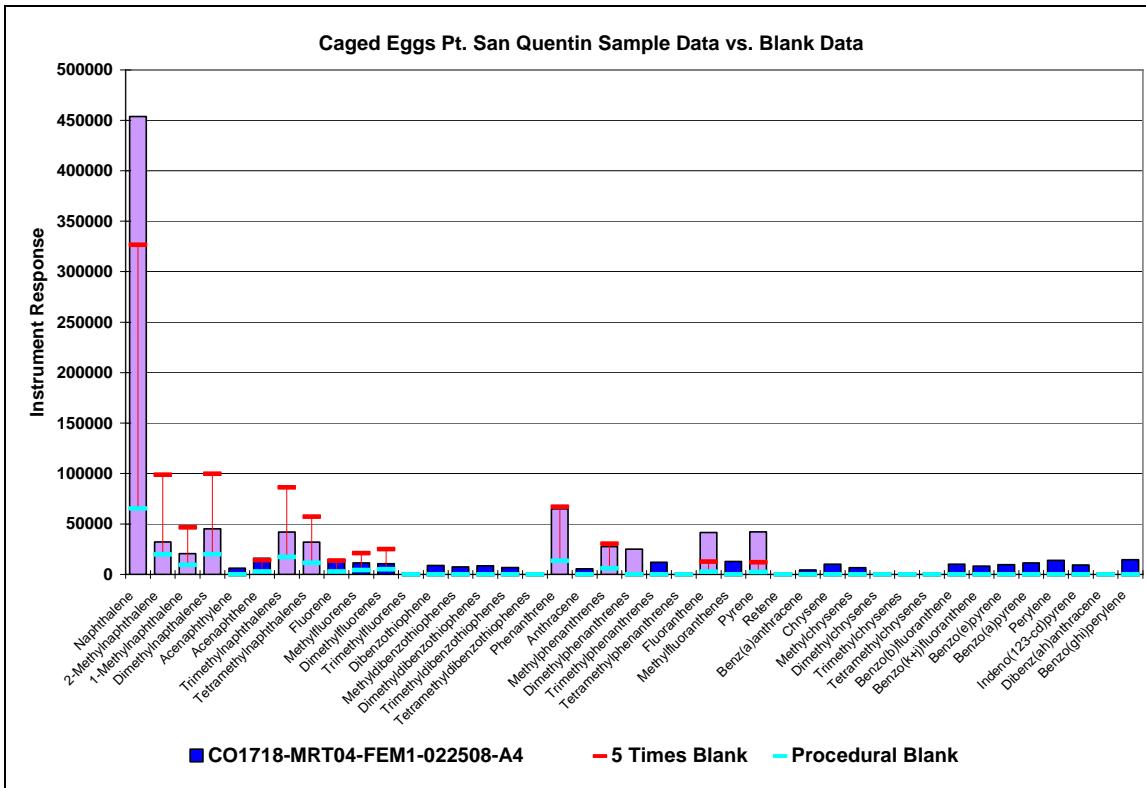


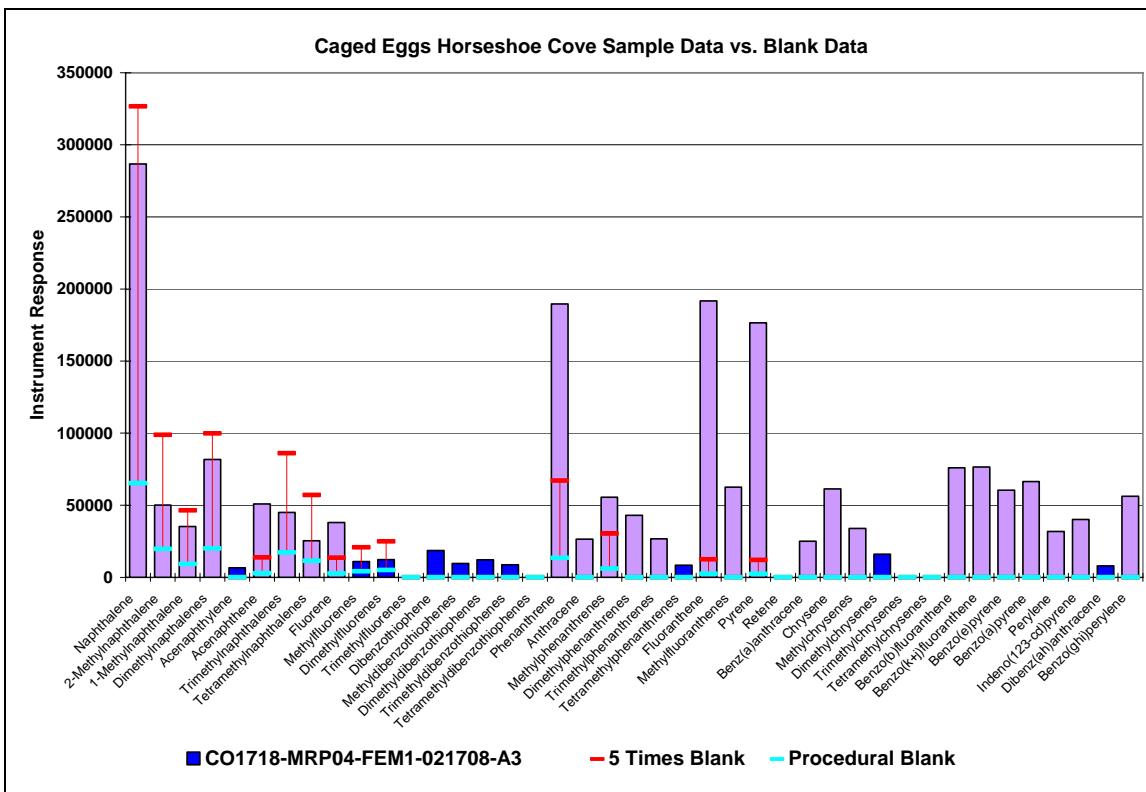
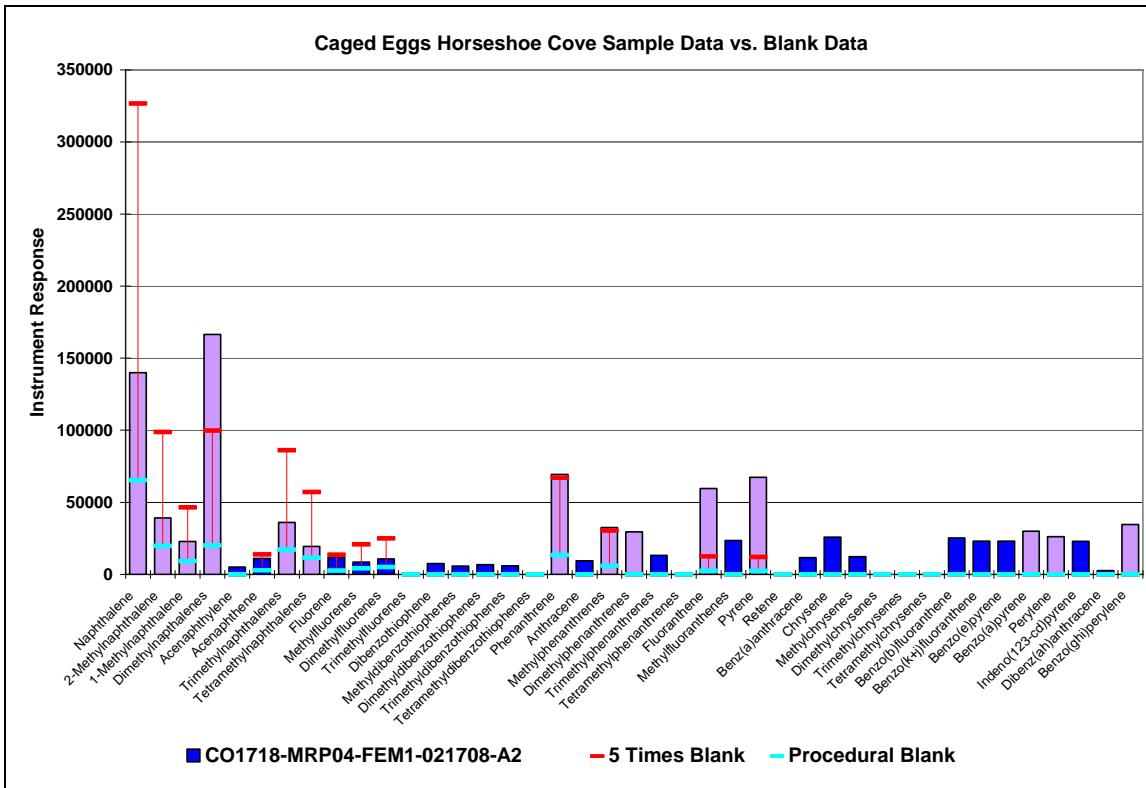


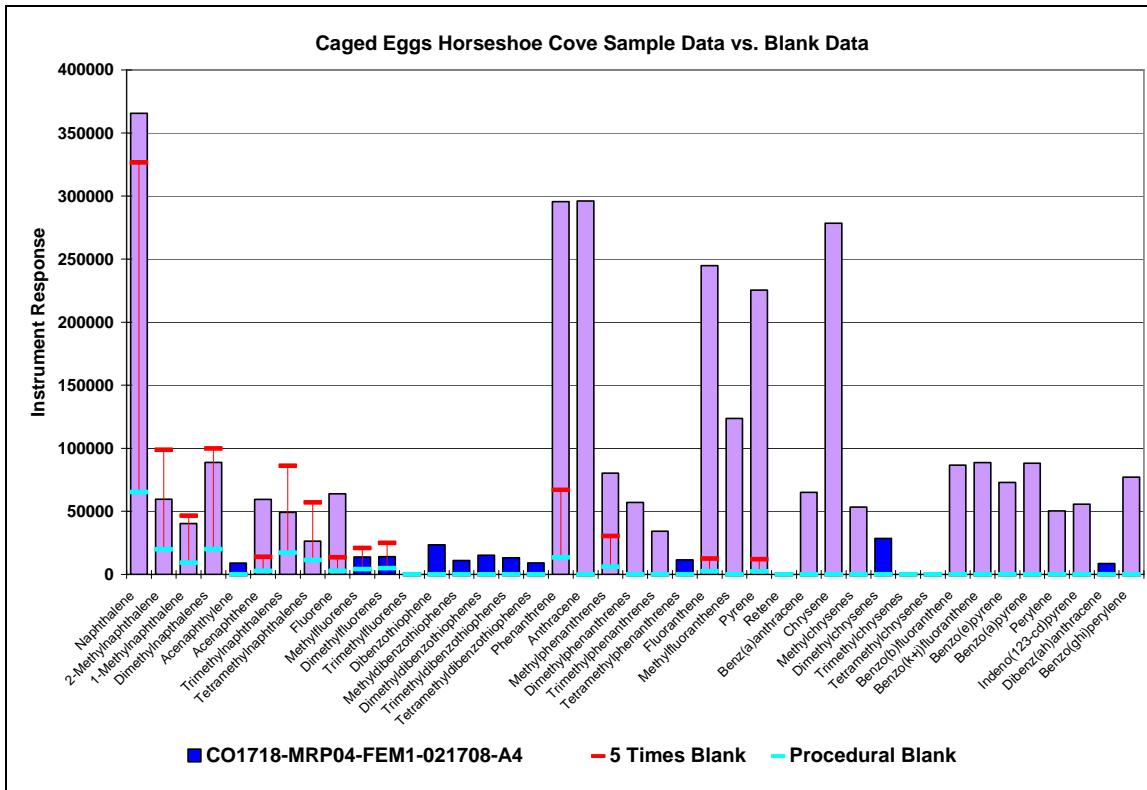


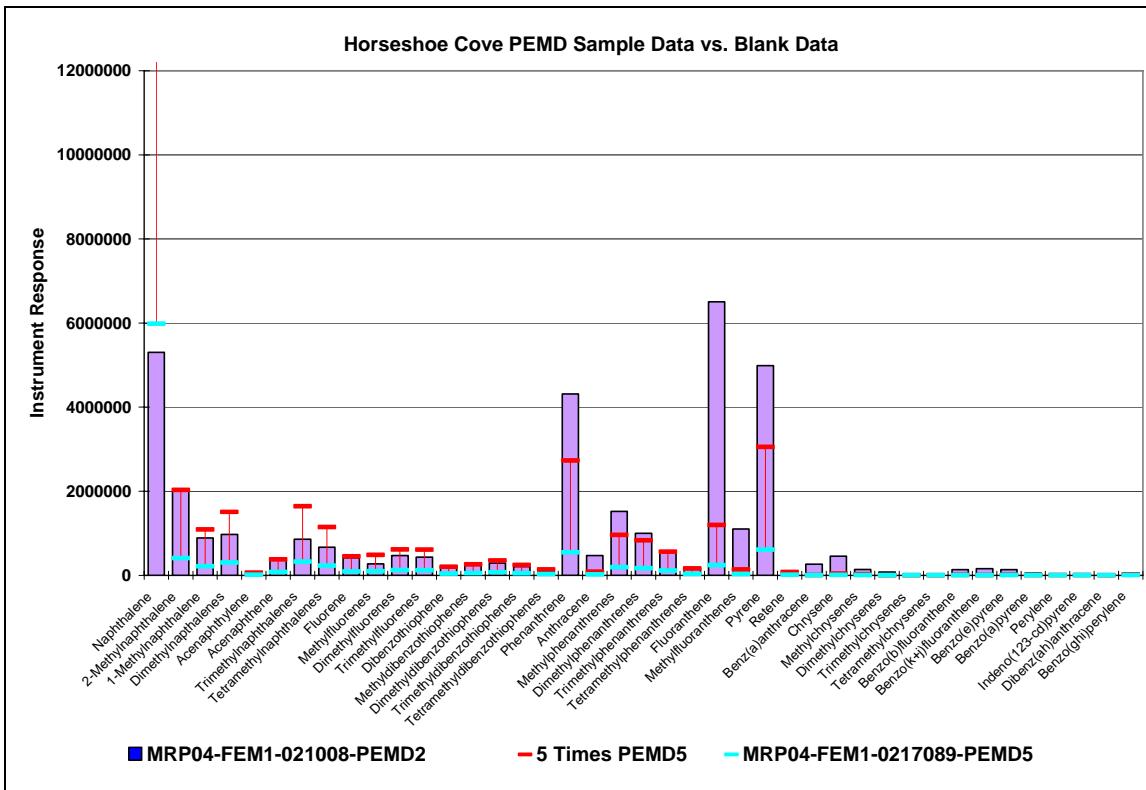
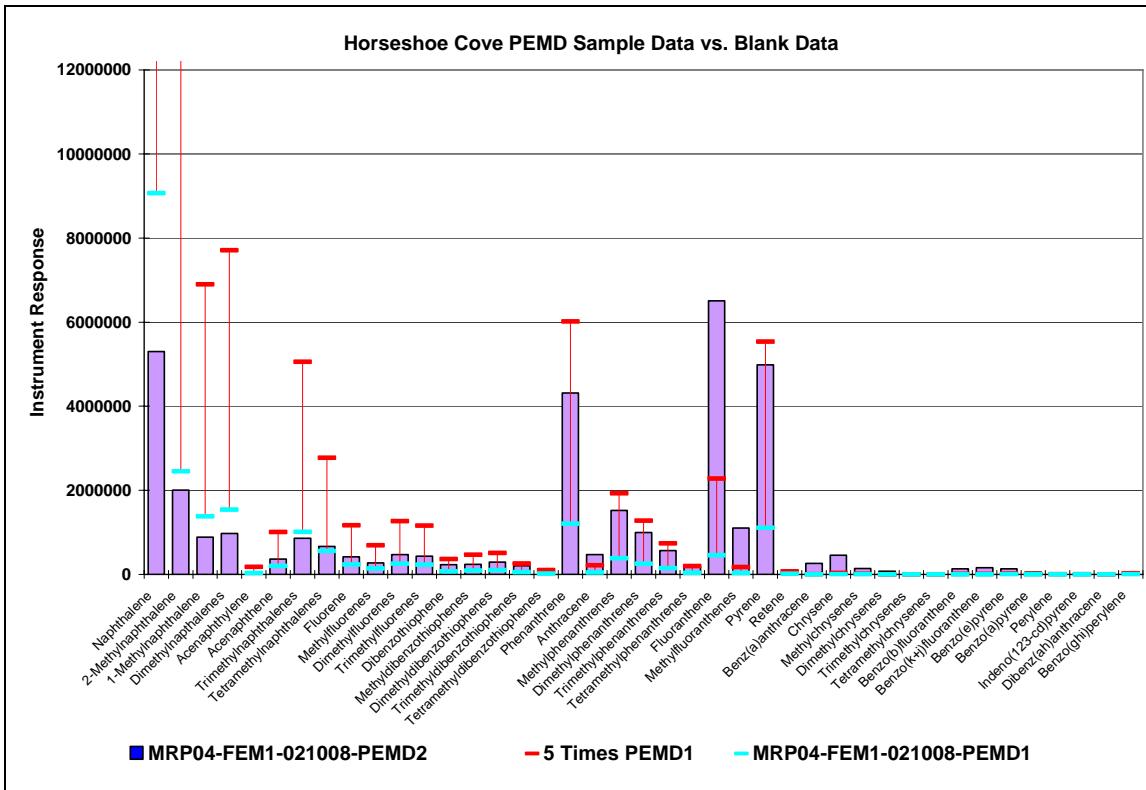


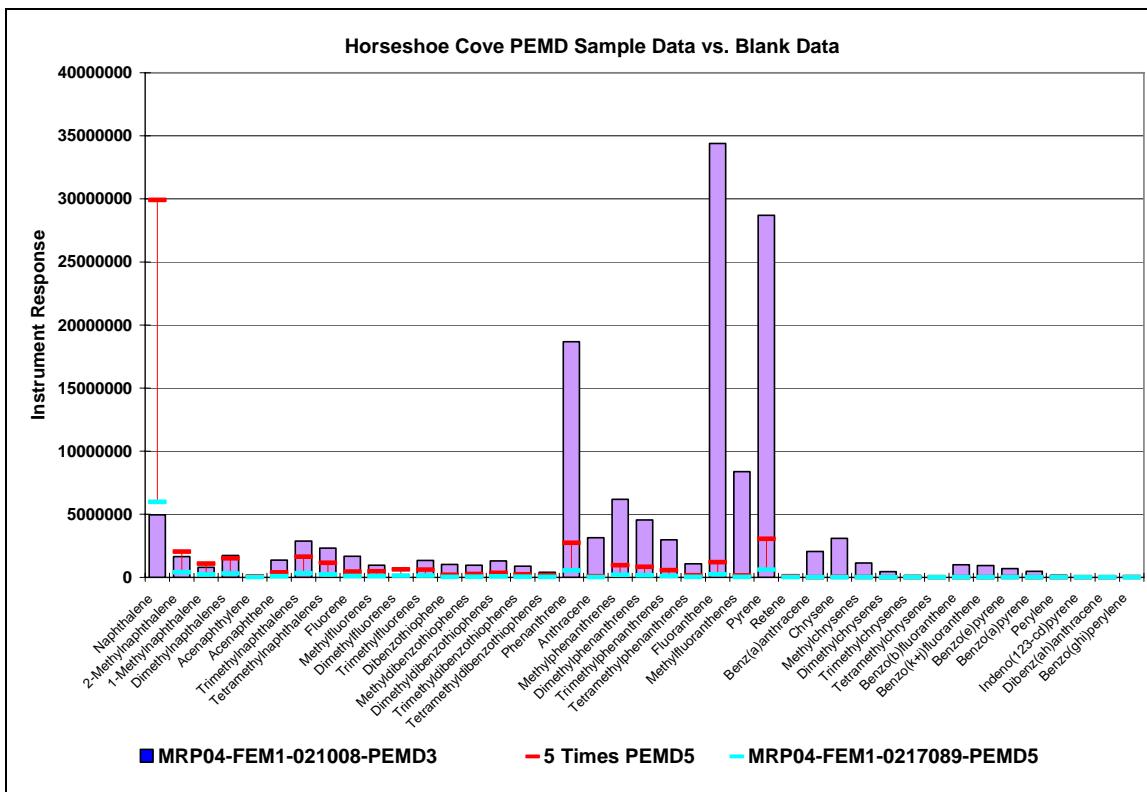
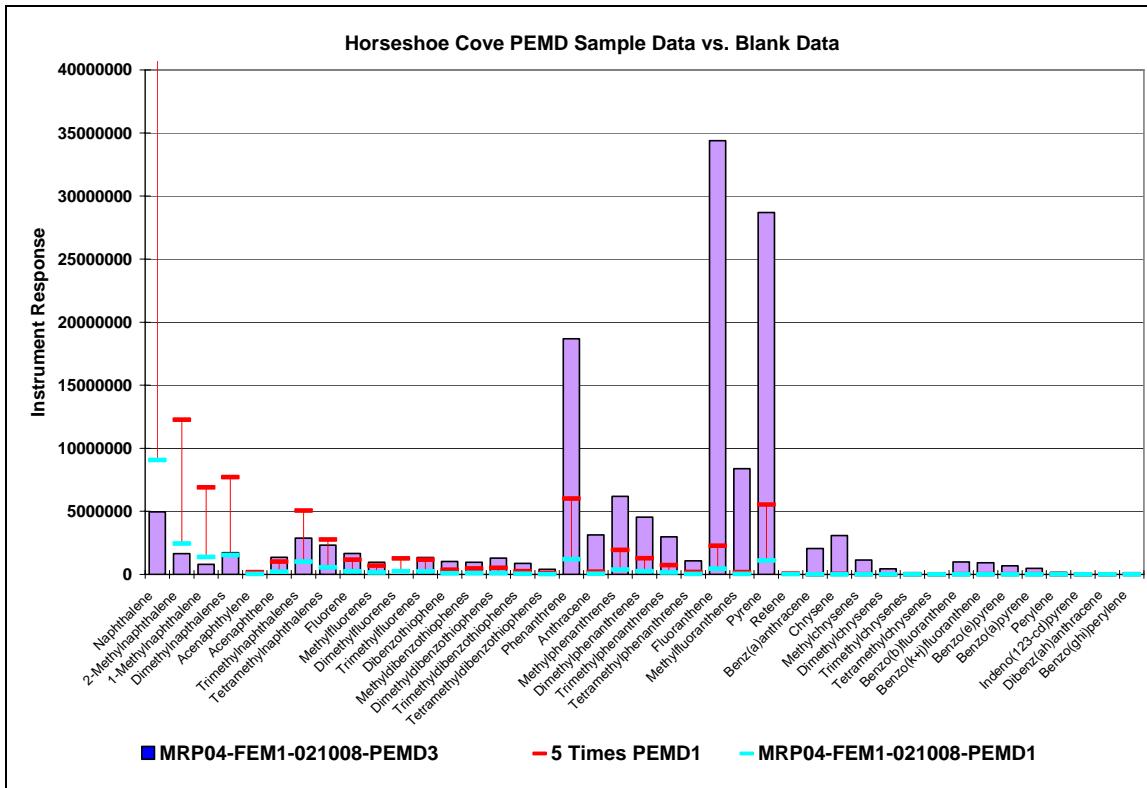


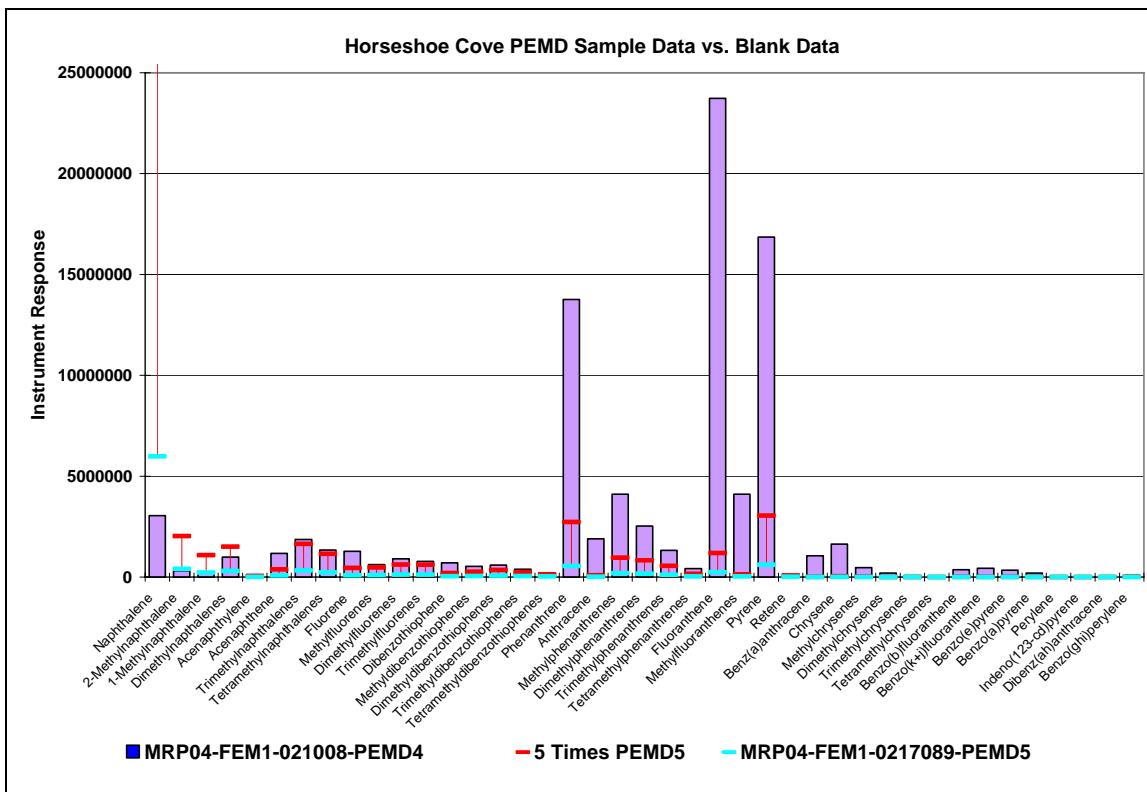
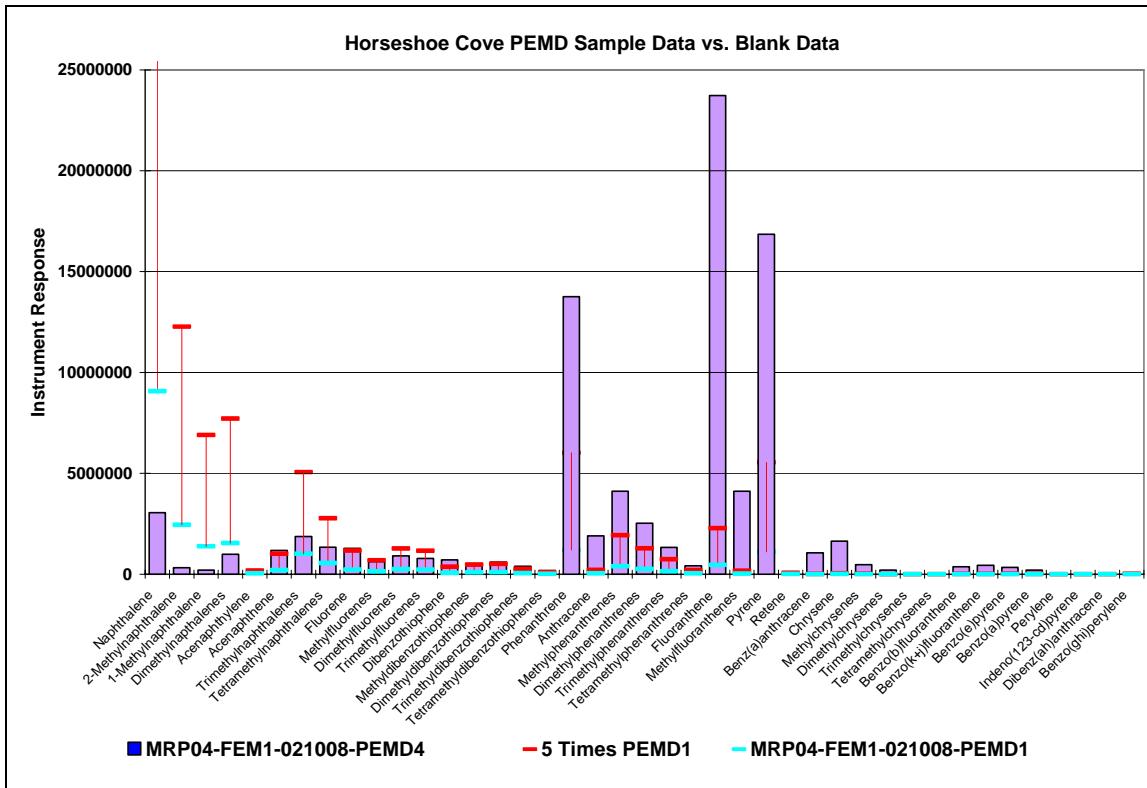


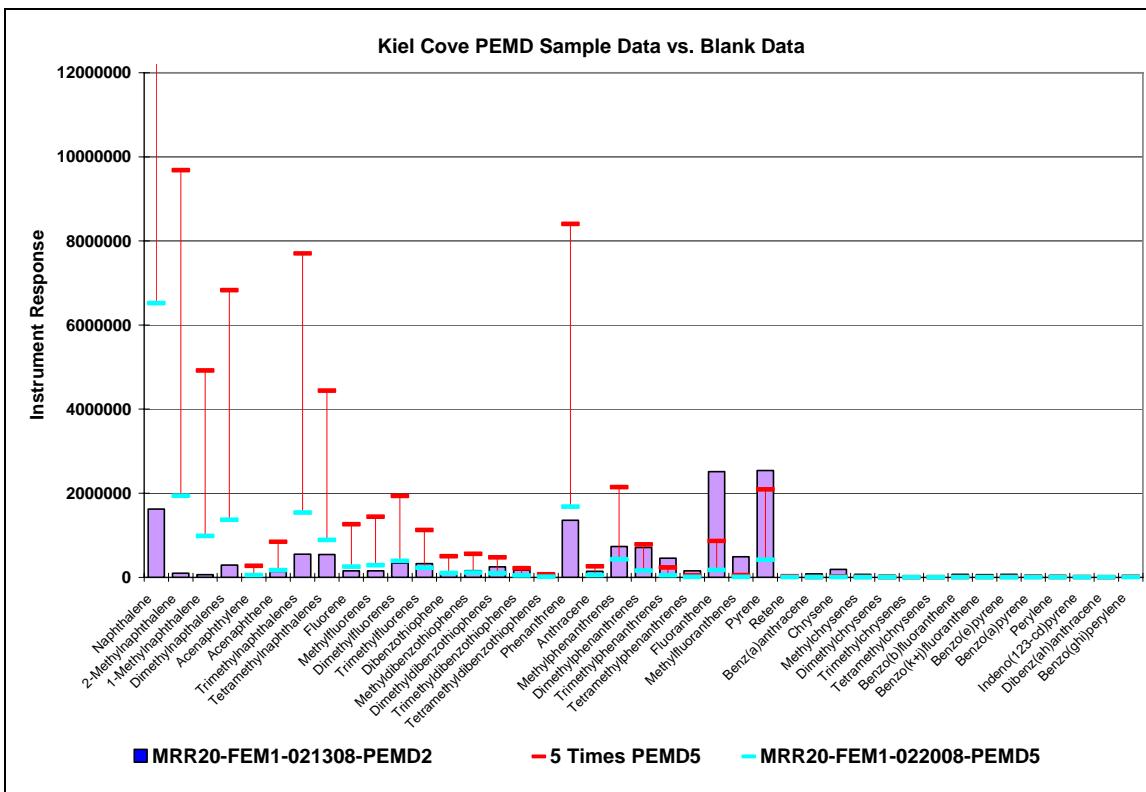
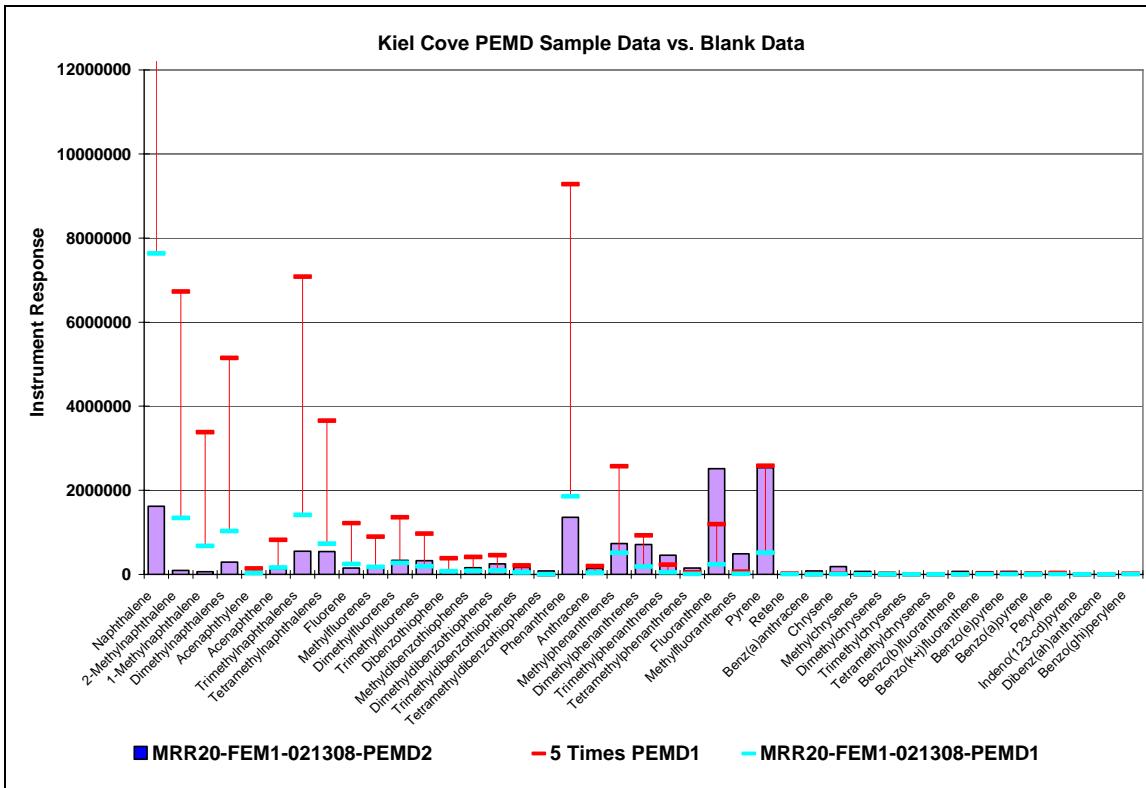


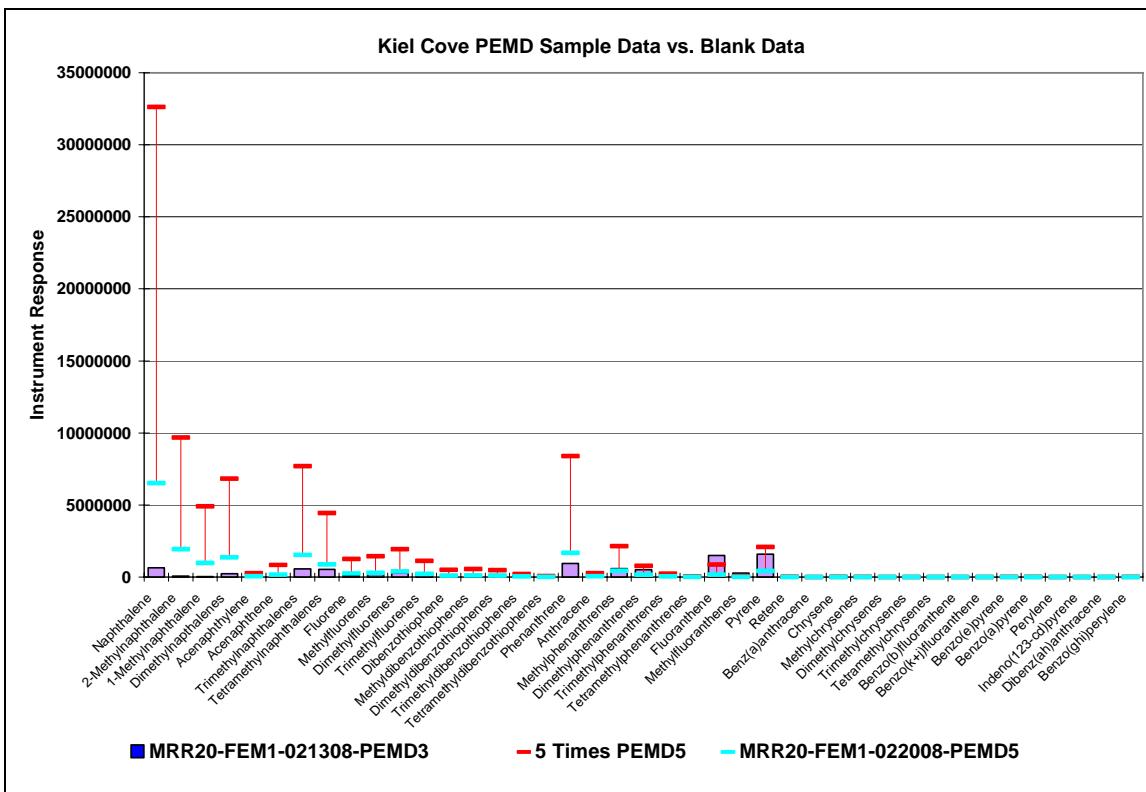
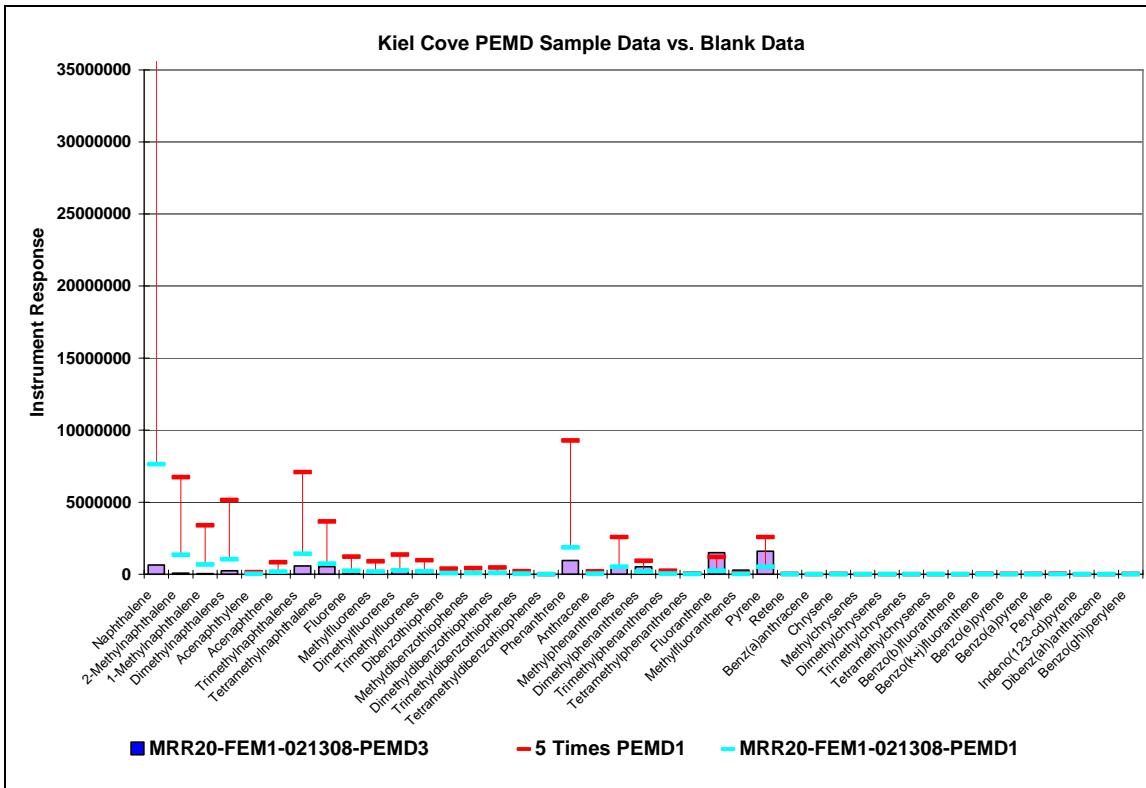


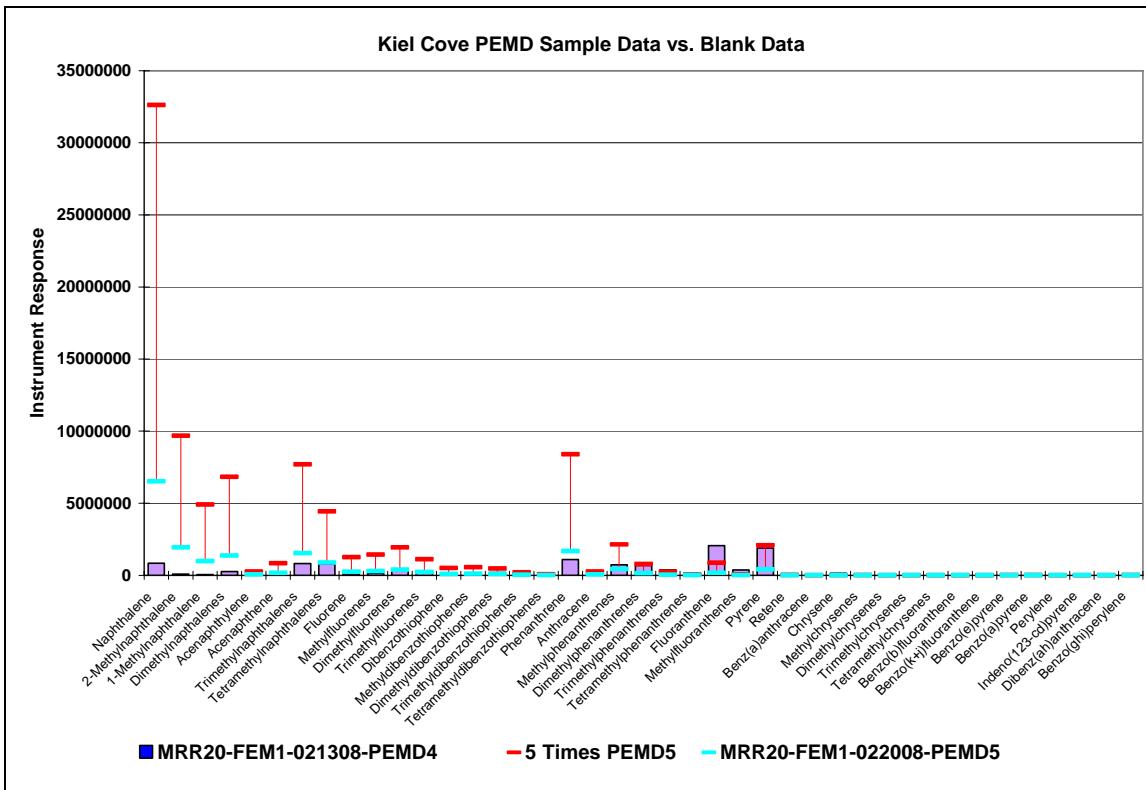
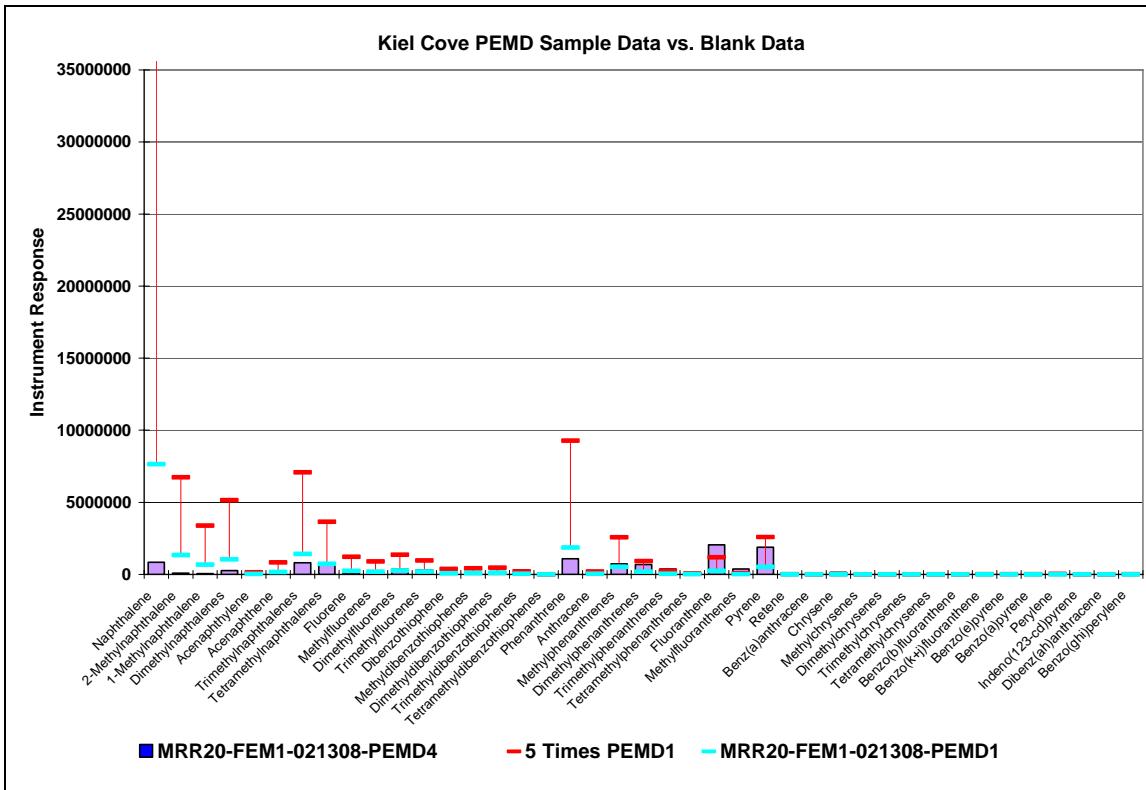


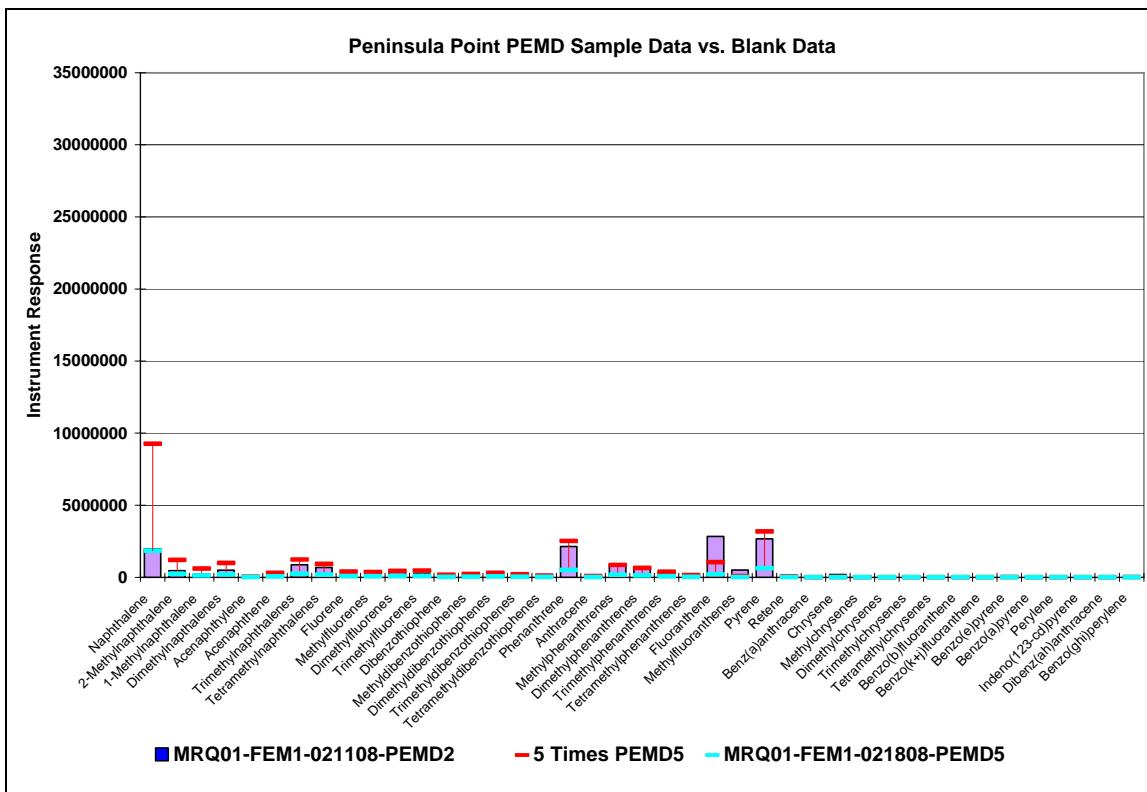
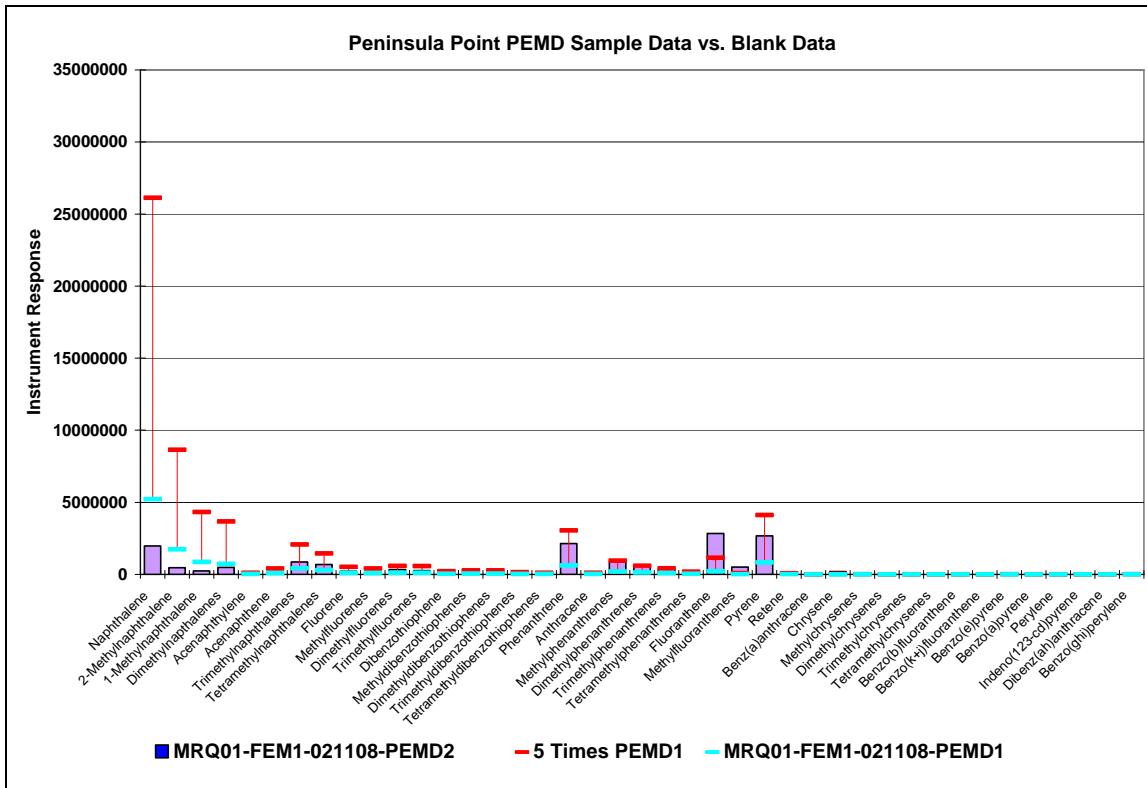


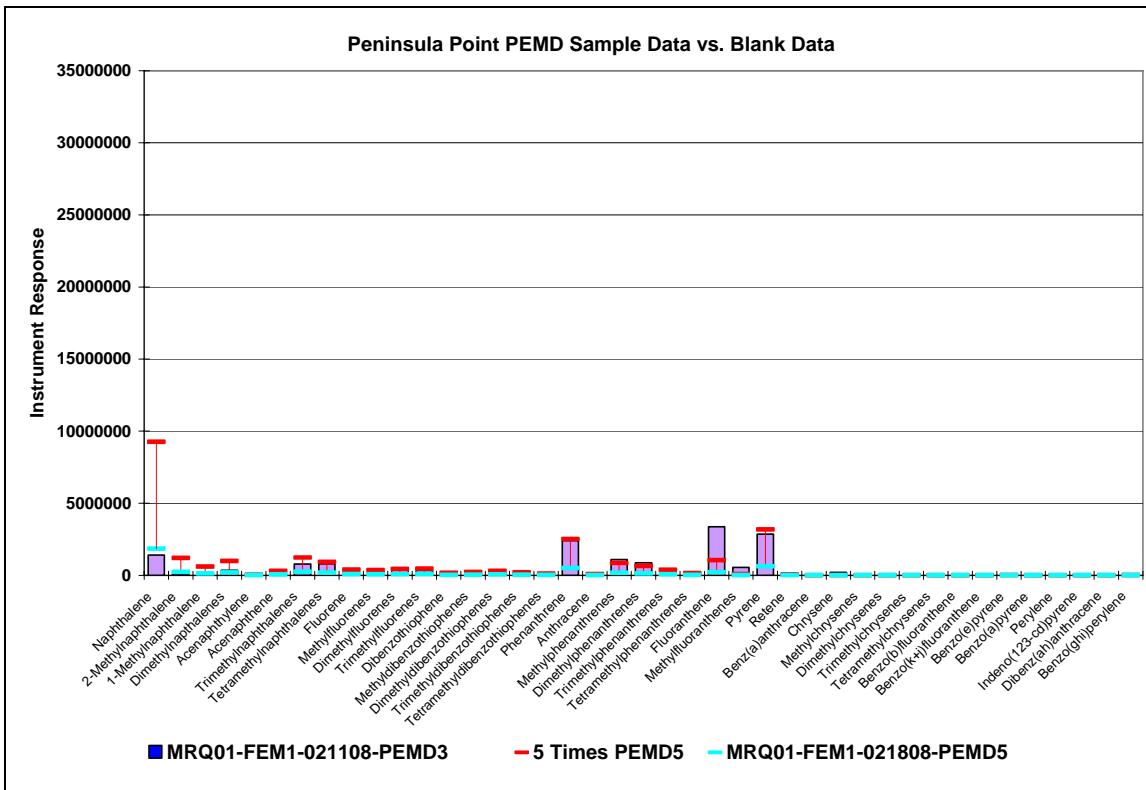
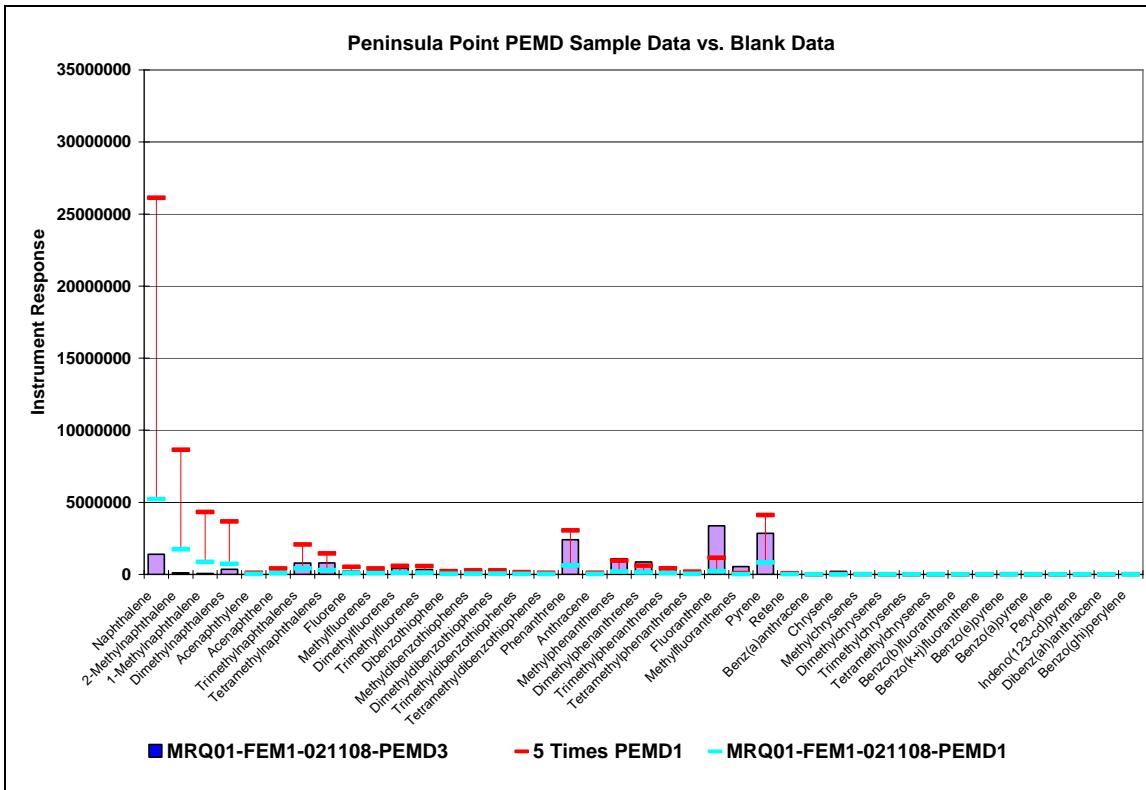


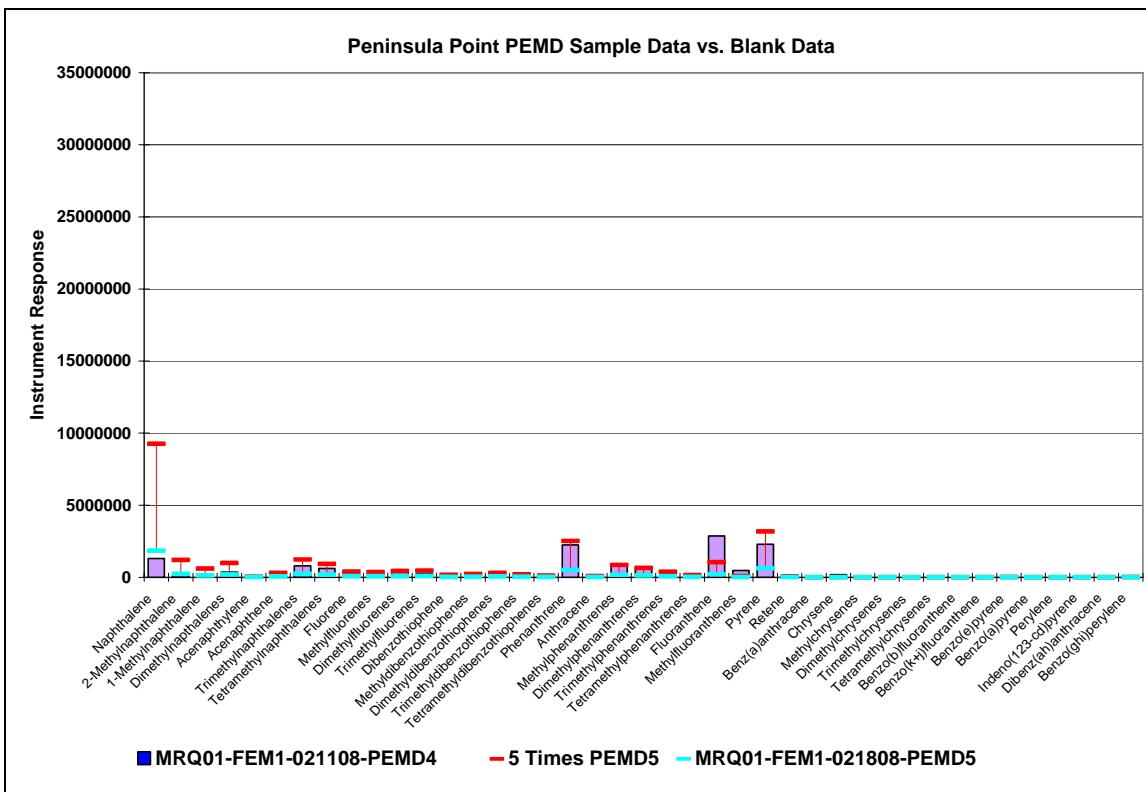
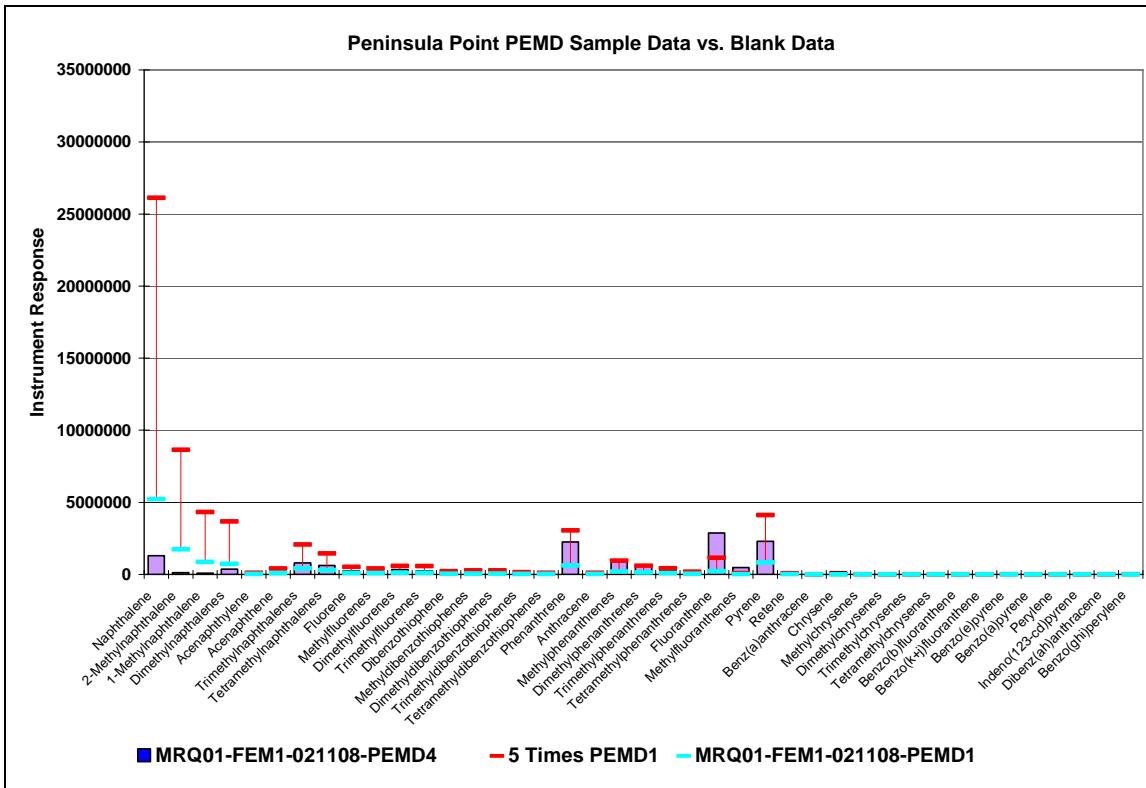


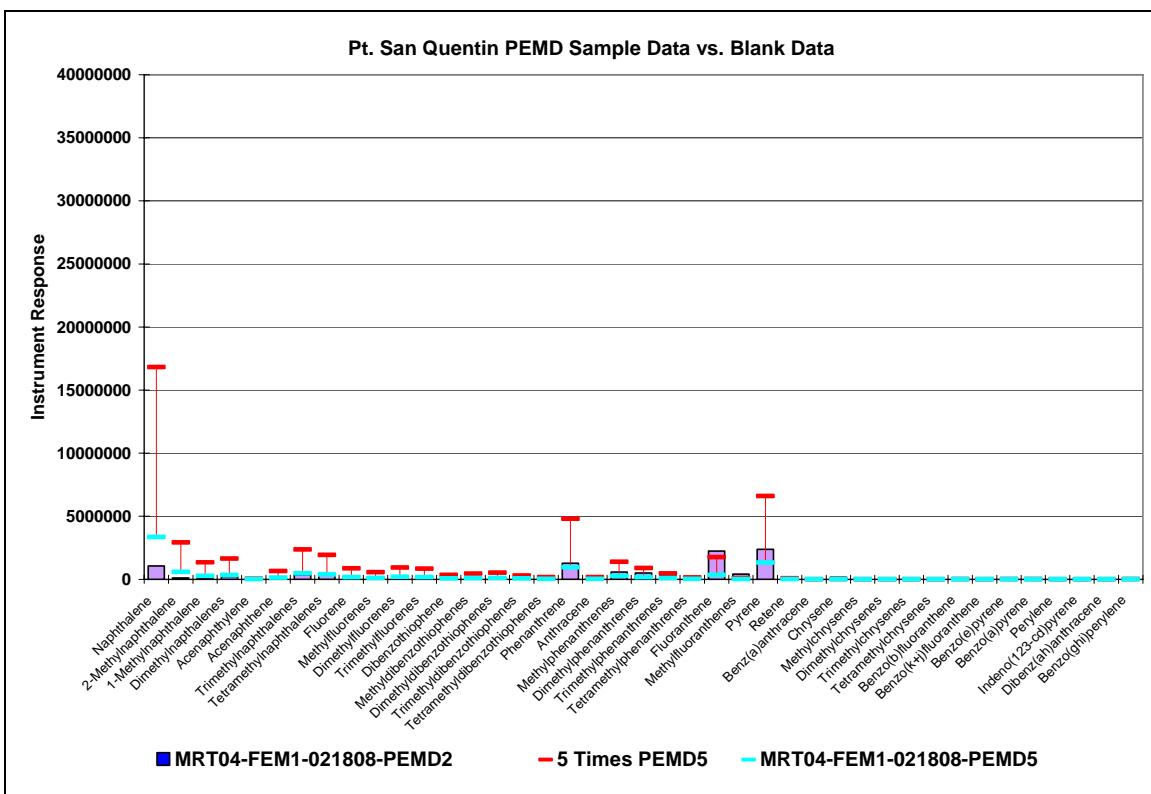
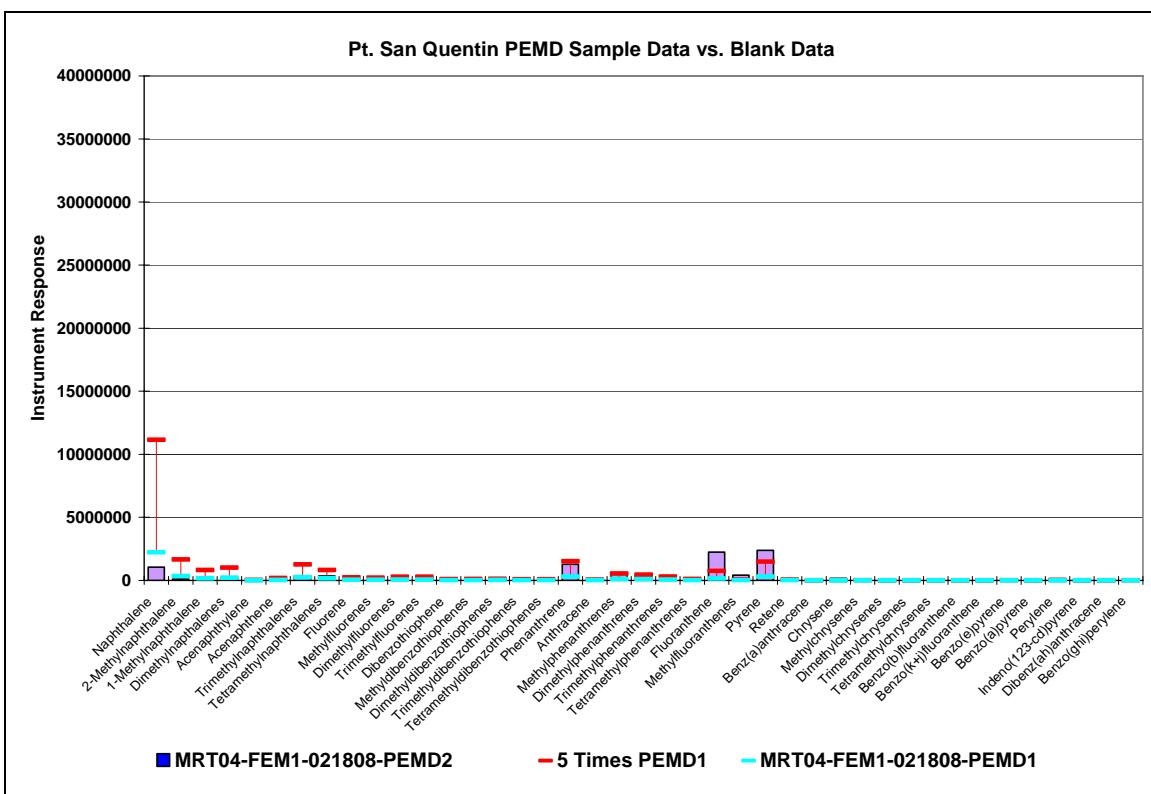


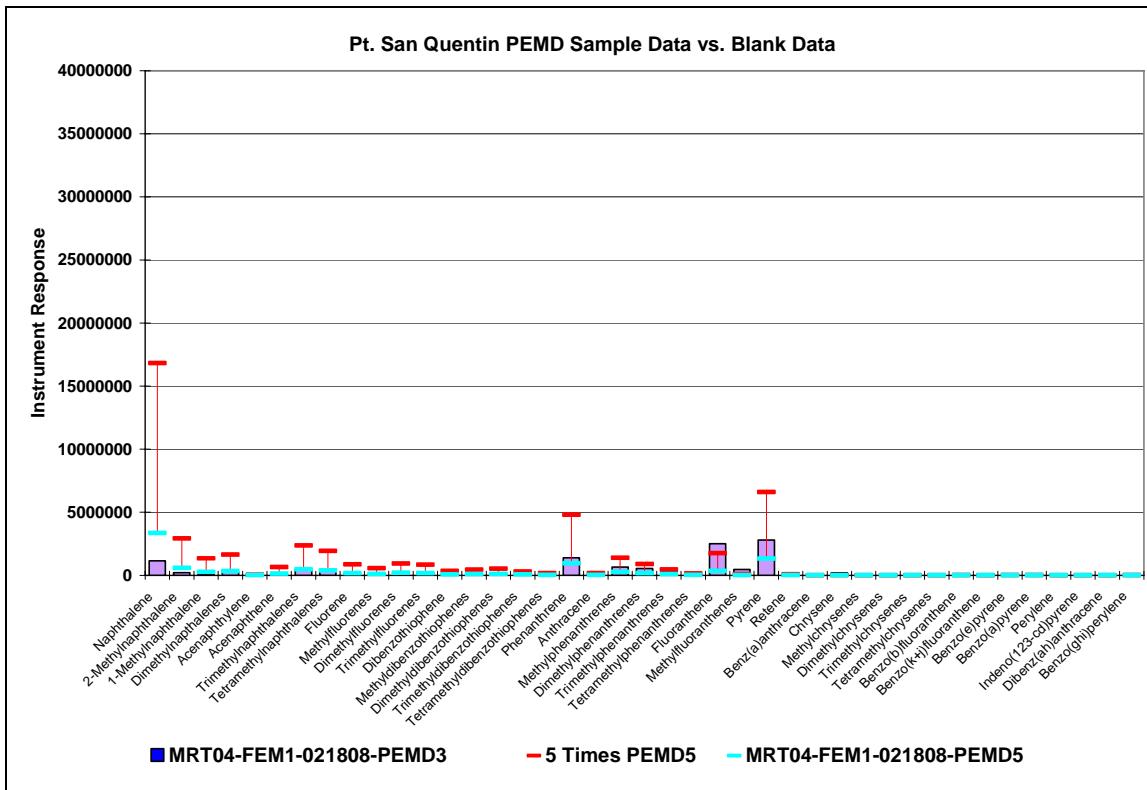
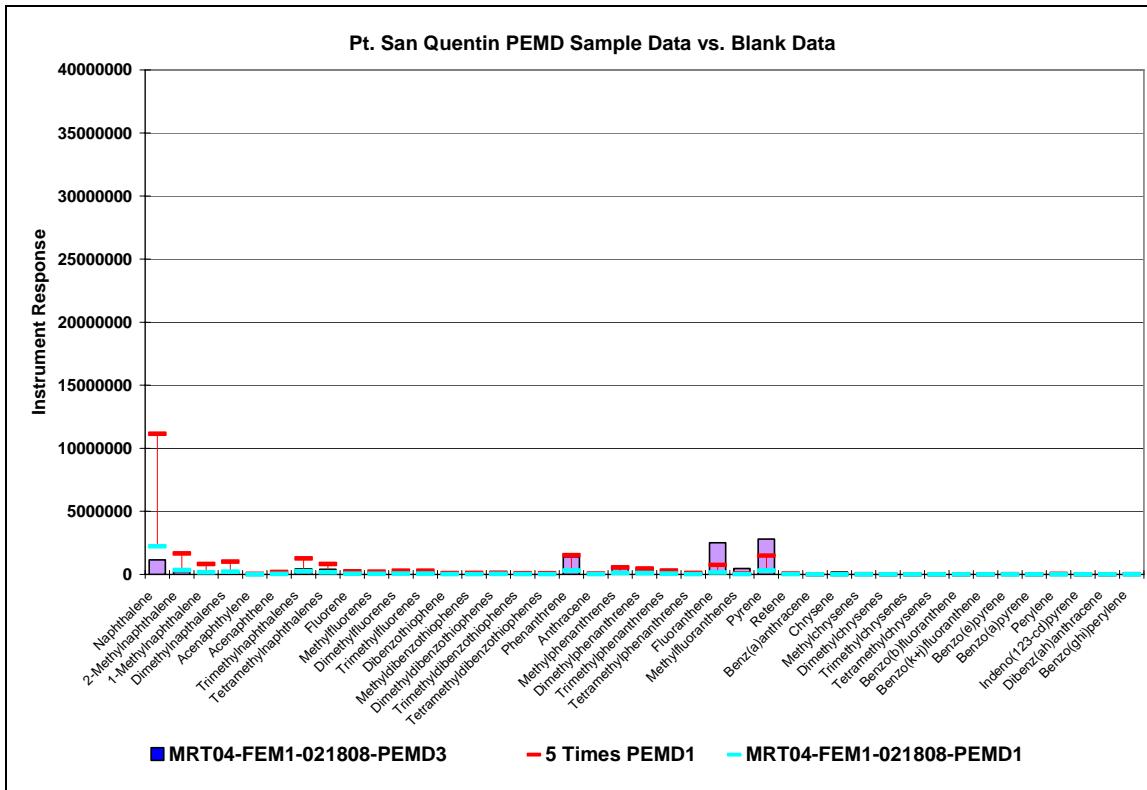


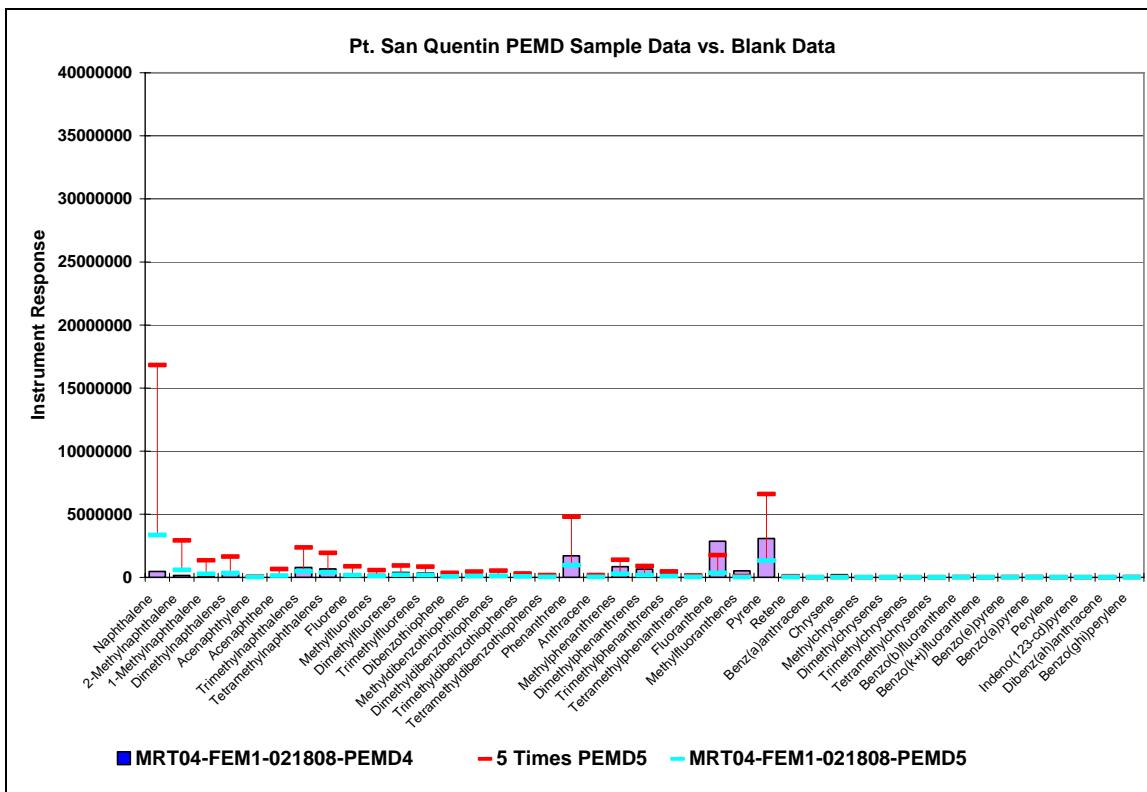
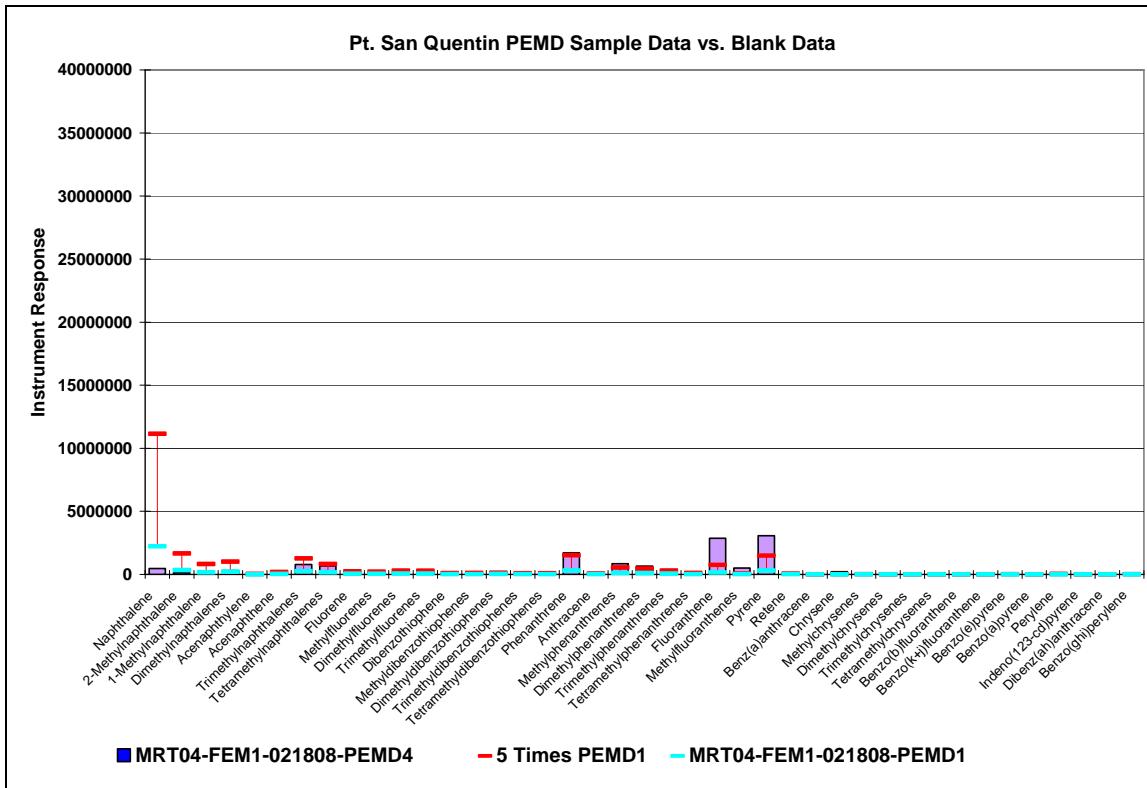


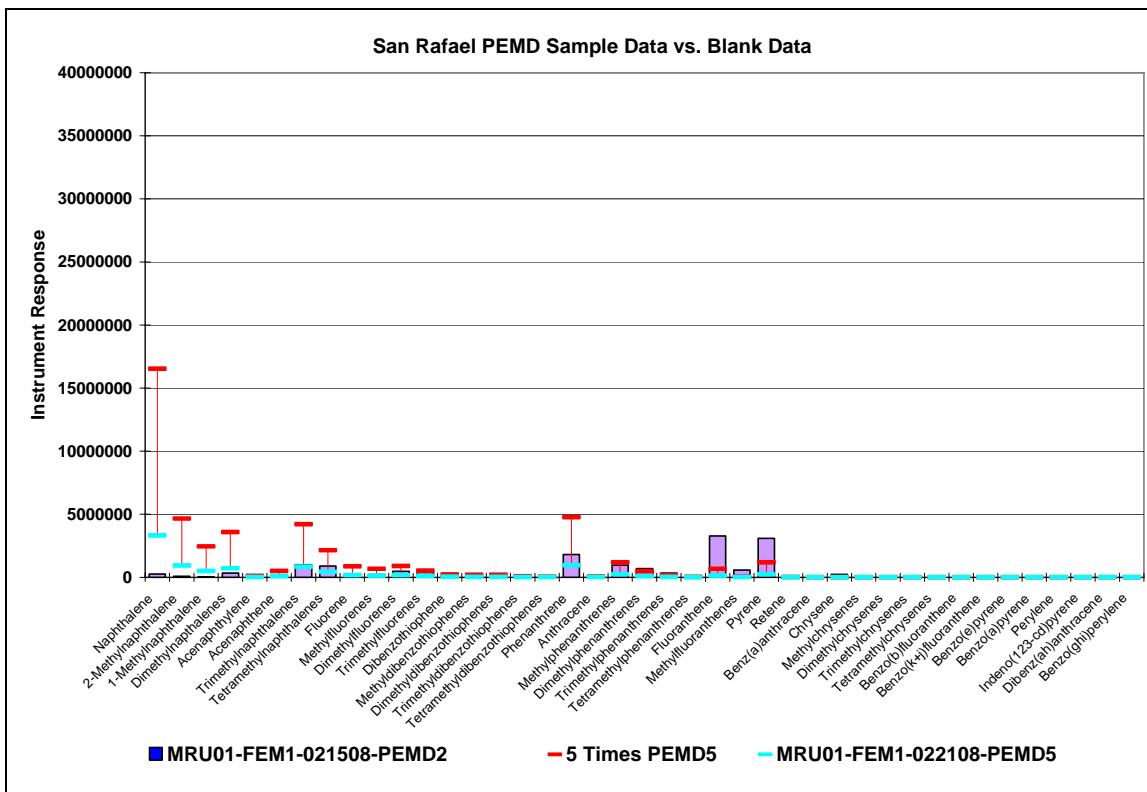
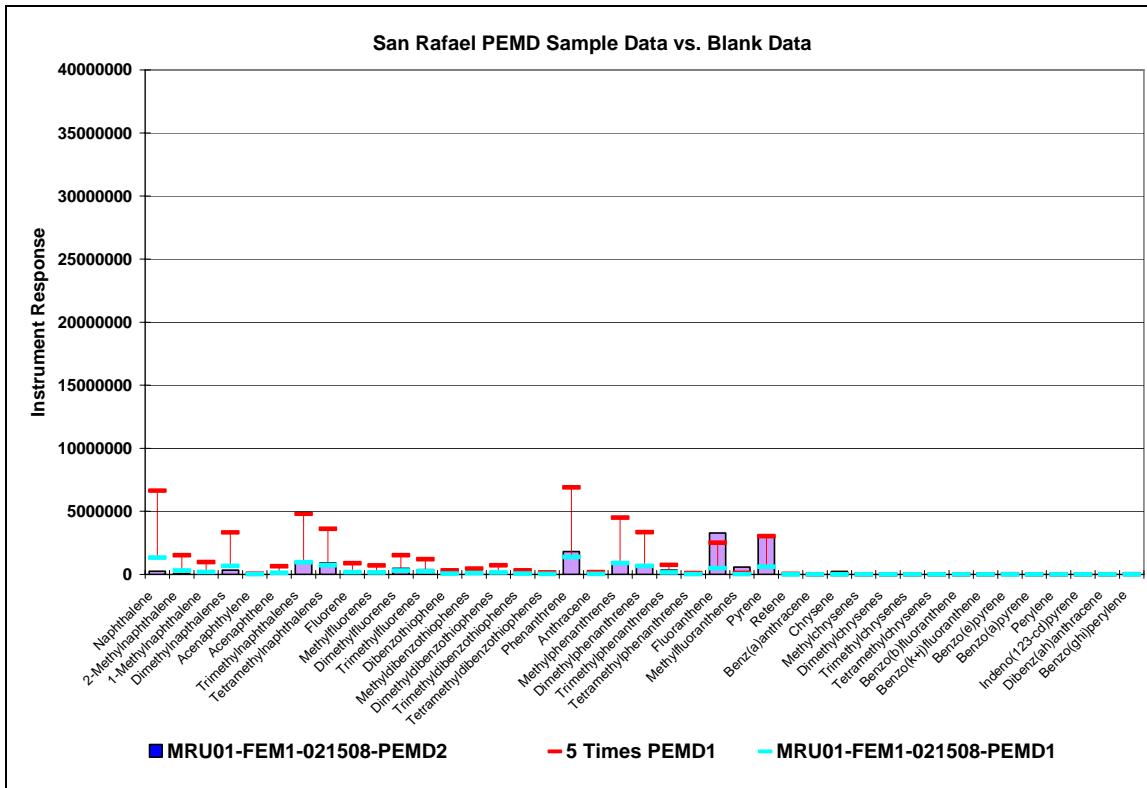


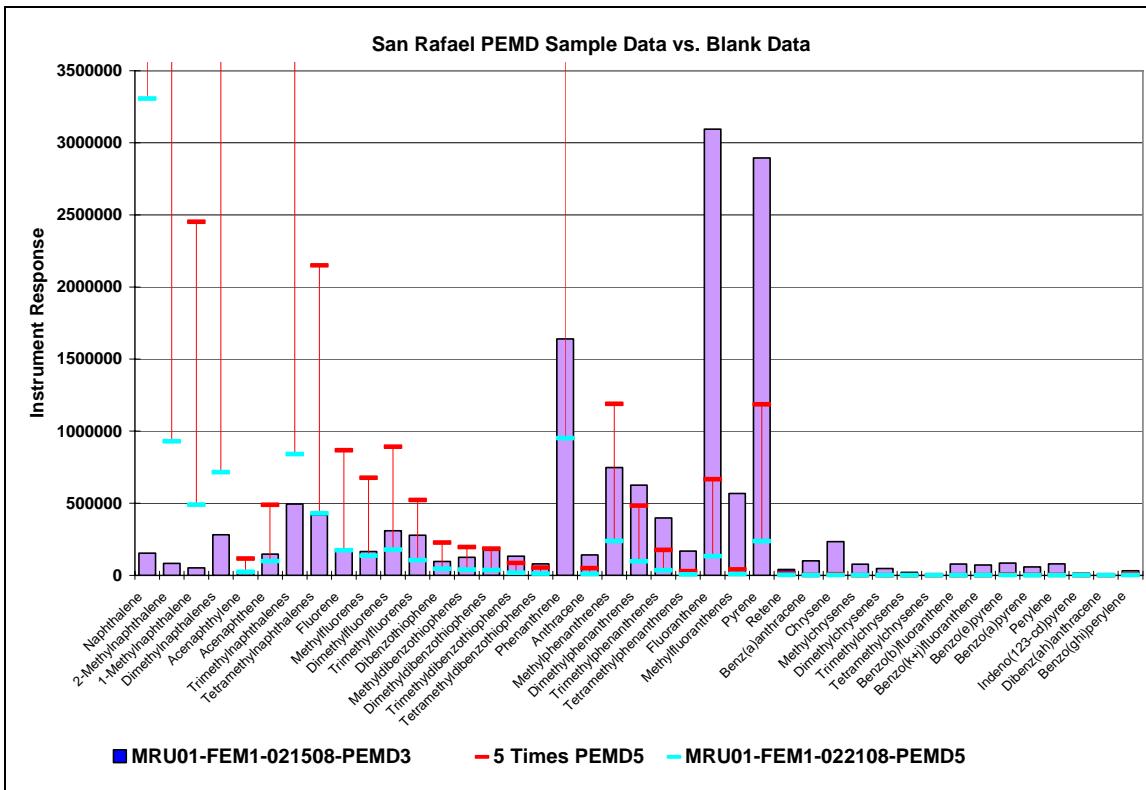
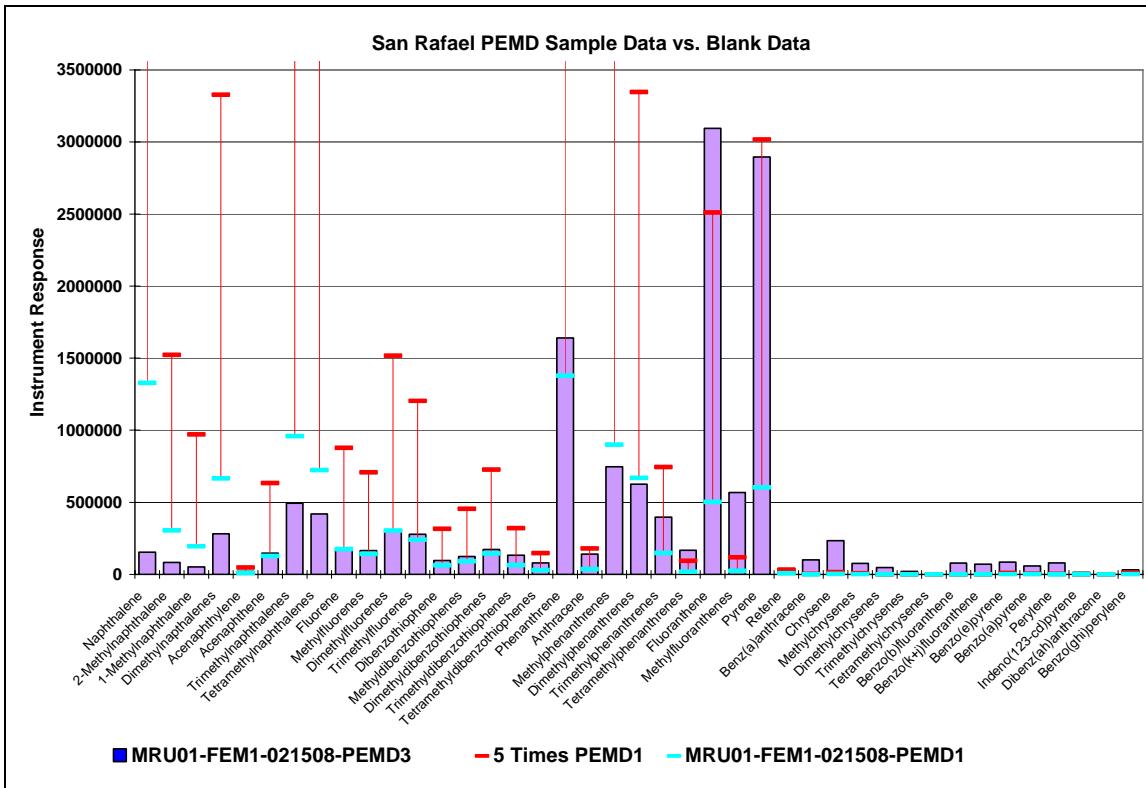


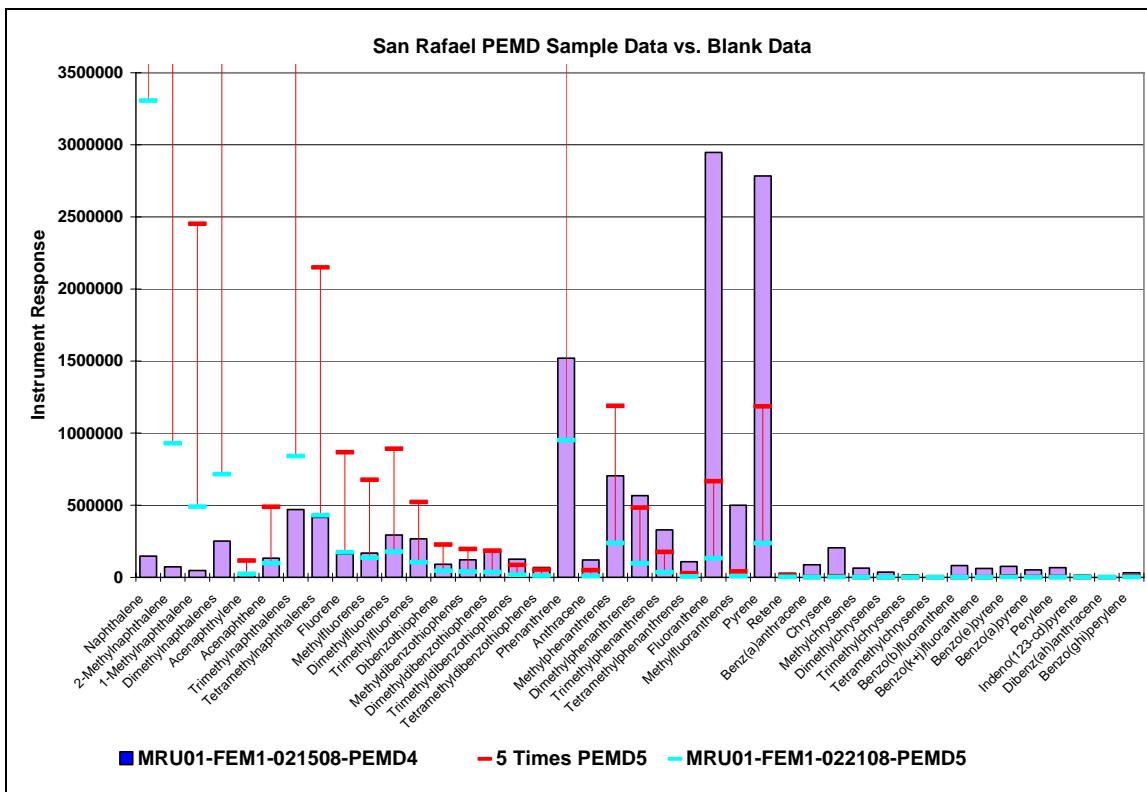
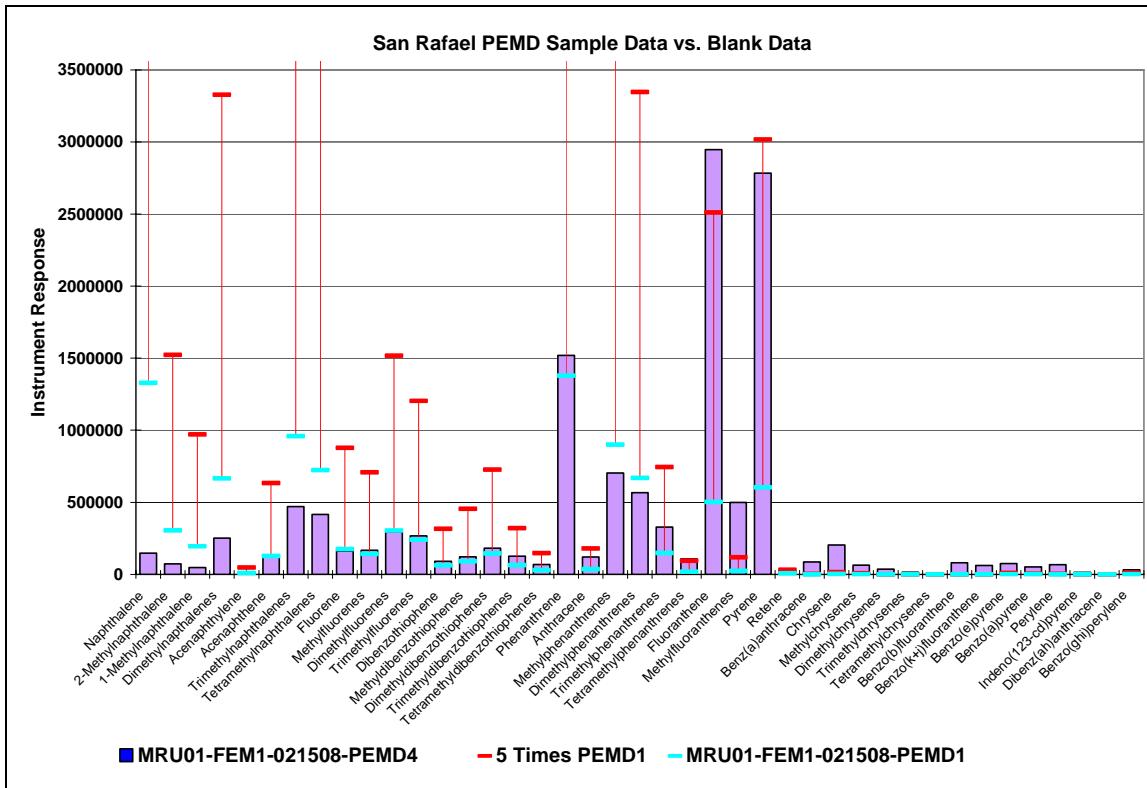


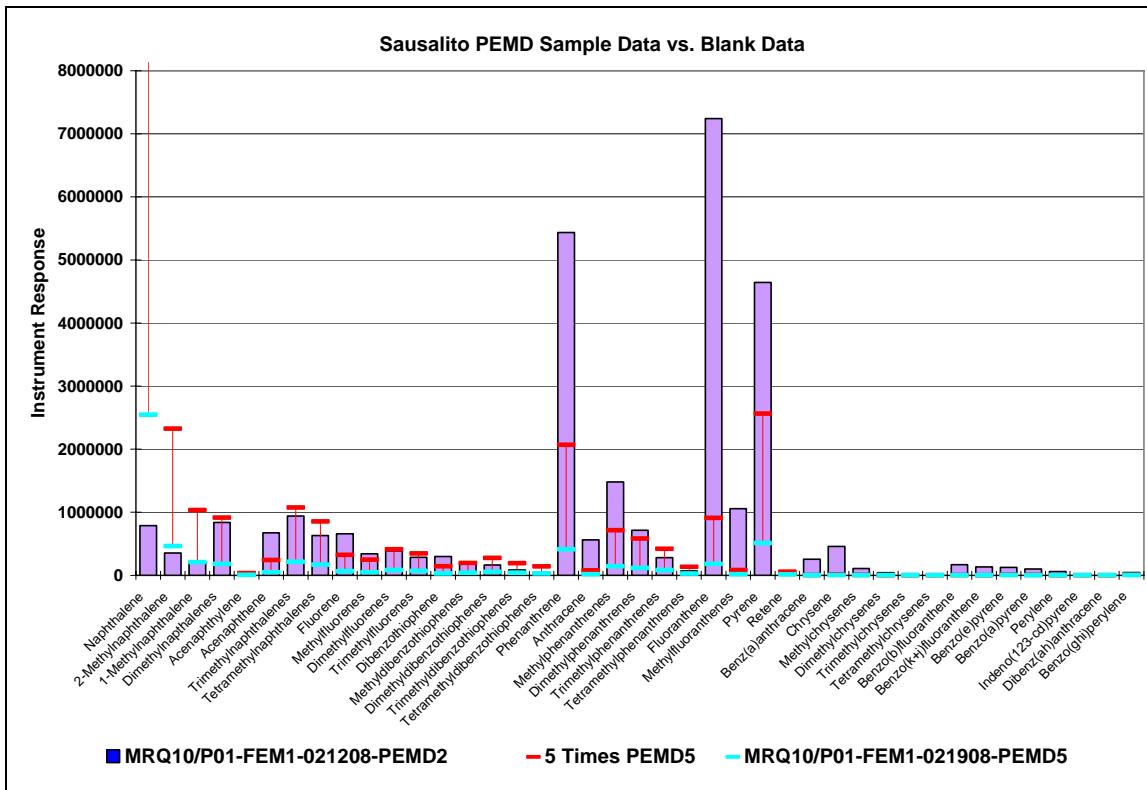
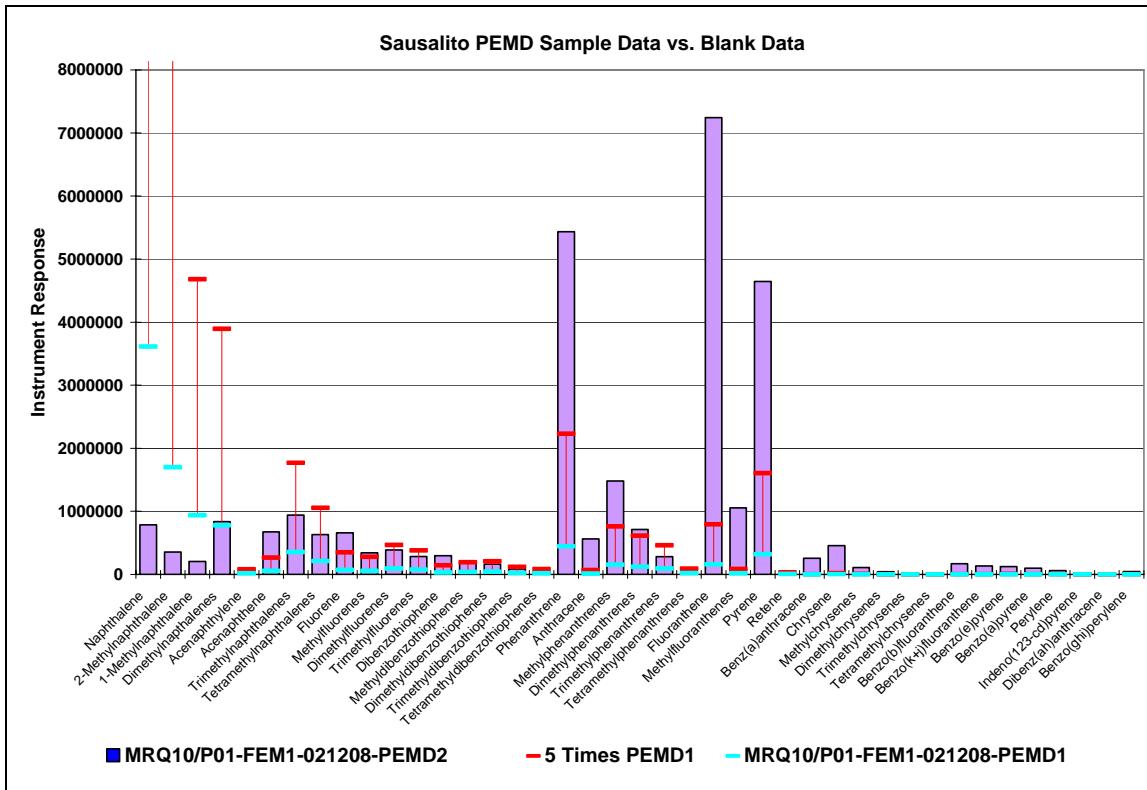


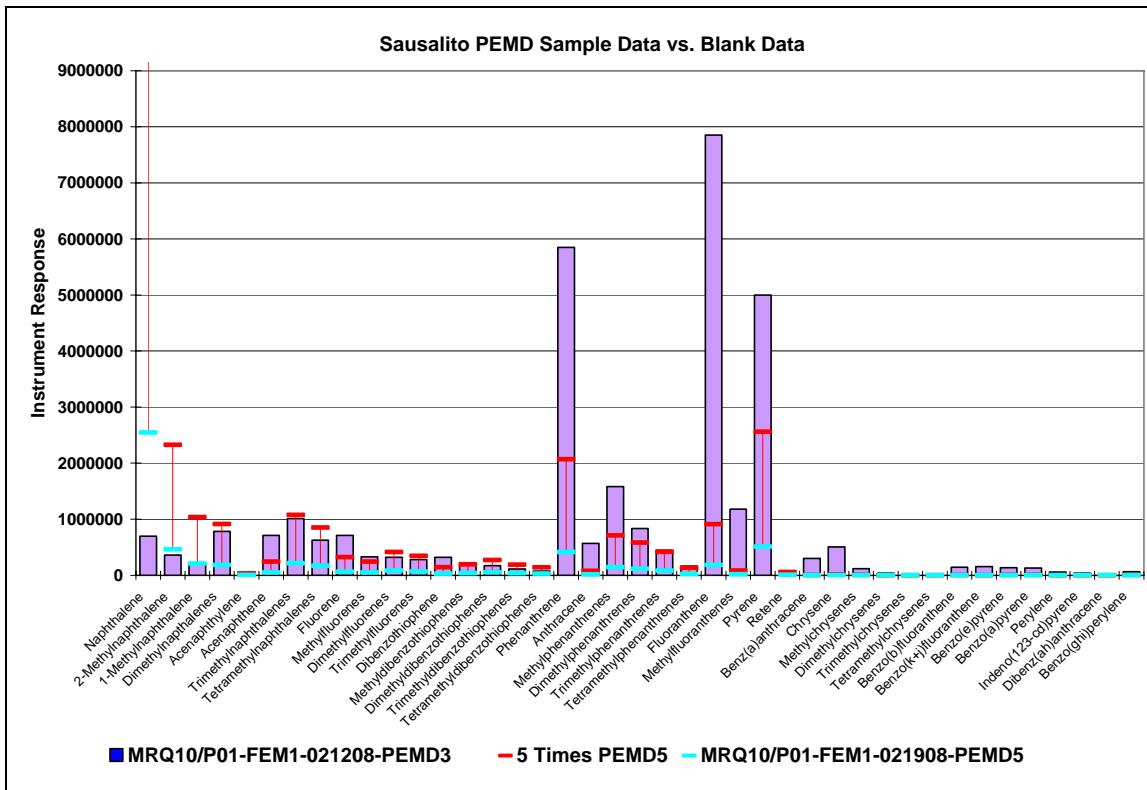
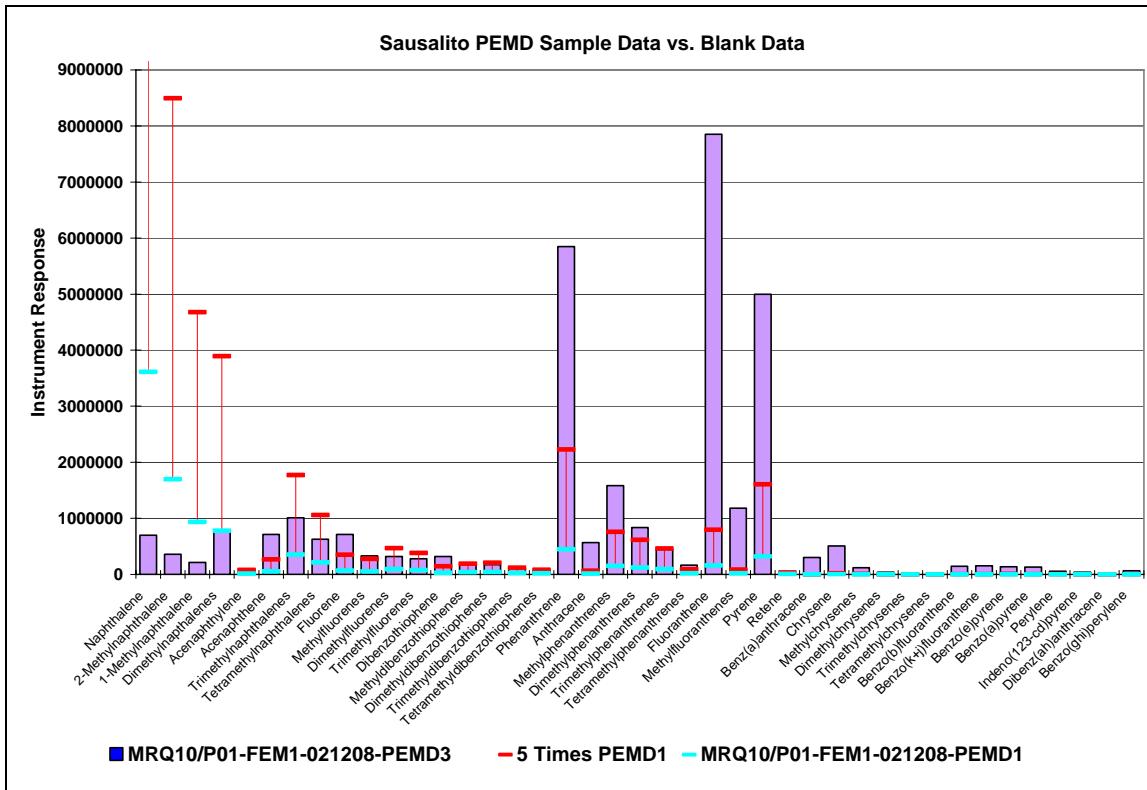


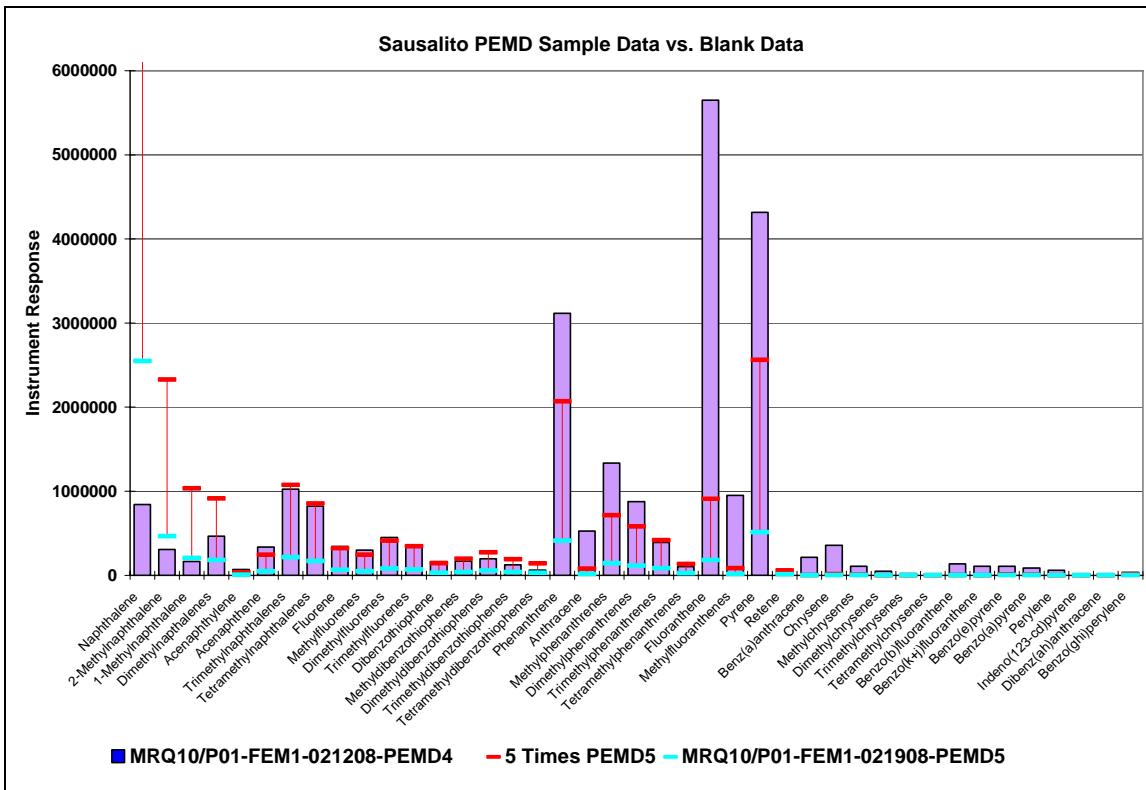
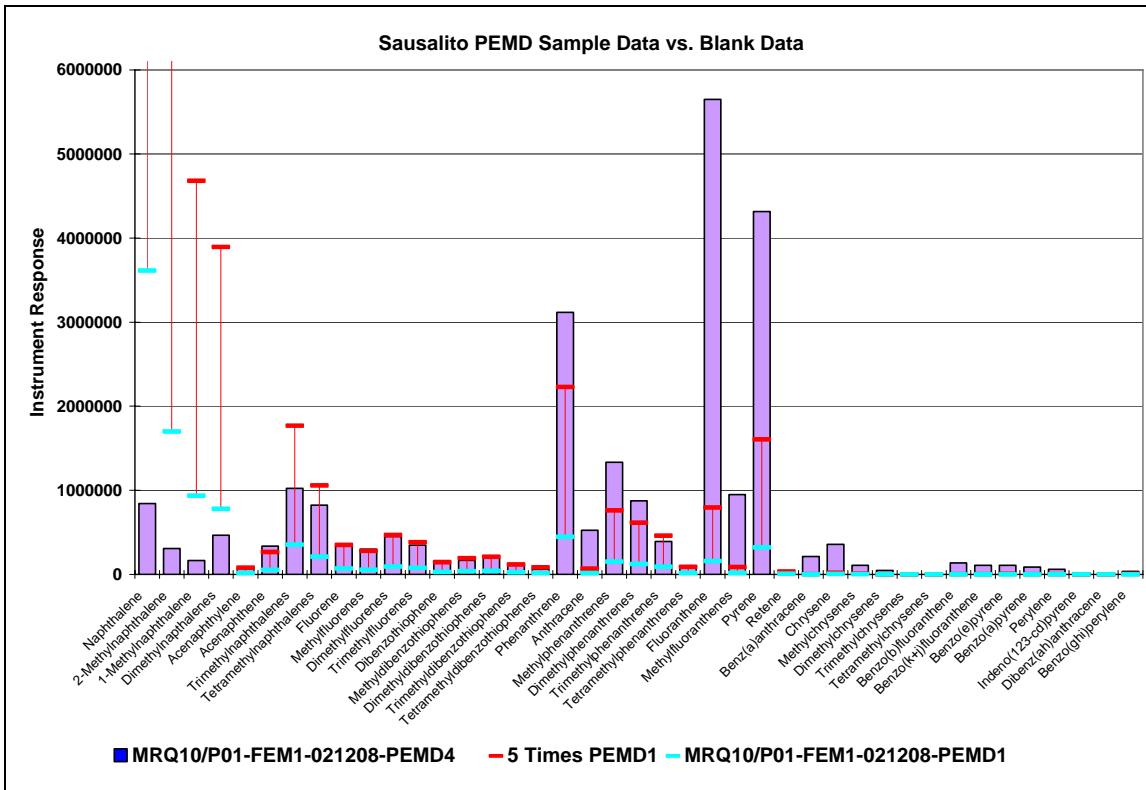












Attachment 2

**PAH Concentration Histograms in Herring Egg, Herring
Tissues and Associated PEMDs**

