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Memorandum

From:	Tim Towey, Dave Dilks	**Date:**	January 22, 2018
		Project:	SRRTTF6
To:	Spokane River Regional Toxics Task Force	CC:	

SUBJECT: Comparison of Homolog-Patterns for Groundwater Well Data and Suspected Loads

Summary

LimnoTech compared PCB homolog patterns from relevant Spokane-area groundwater wells, to homolog patterns for suspected groundwater loads identified in the homolog-specific PCB mass balance for the Spokane River (LimnoTech, 2017). This task was identified in Section 5.14.1.a of the Comprehensive Plan (LimnoTech, 2016), with the intent to assess the potential significance of groundwater sites for contributing PCBs to the Spokane River.

Data from multiple data sources were assessed. Key finding of this analysis are:

- Total PCB concentrations in many wells were lower than river concentrations, ruling these wells out as a cause of observed increases in river PCB concentrations.
- Wells from three areas had large enough concentrations to merit further consideration. These areas are: 1) Up-gradient of the Kaiser Trentwood site, 2) the Kaiser Trentwood site, and 3) the General Electric (GE) National Priority List site.
- A cosine similarity (also referred to as cosine theta) analysis was used to assess the degree of correlation between homolog patterns at a given well and homolog patterns imputed from the mass balance assessment. The following correlations were observed:
    - A strong correlation between the homolog patterns on the Kaiser site and the homolog patterns estimated by the mass balance assessment for the Barker/Mirabeau – Trent reach.
    - A strong correlation between the homolog patterns at the GE site and the homolog patterns estimated by the mass balance assessment for the Trent – Greene reach.
    - A partial correlation between the homolog patterns in wells upstream of Kaiser and the homolog patterns estimated by the mass balance assessment for the Barker – Mirabeau reach.
- These results should not be considered proof that groundwater from these well areas is responsible for observed increases in river PCB concentrations, due to the variability in homolog patterns among samples at a given well area and the uncertainty inherent to the mass balance assessment. These results still provide value when used as part of a weight of evidence approach.

This memorandum summarizes that review. It is divided into sections of:

- Available Data
- Pattern Comparison Approach
- Pattern Comparison Findings
- Conclusions

Available Data

LimnoTech gathered all available groundwater PCB data measured using Method 1668, as this is the analytical method capable of generating homolog distributions. This section describes the sources of the data and initial screening of those data to determine which wells had concentrations high enough to cause an increase in Spokane River PCB concentrations.

Data Sources

The data sources can be divided into categories of:

- Historical data available in Ecology's EIM
- Recent data collected jointly by Ecology and Spokane County.
- Data collected as part of the upriver dam remedial activities
- Data collected by Ecology from the GE site
- Data collected by Kaiser on their facility and up-gradient from it.

EIM

EIM had data both for groundwater wells and groundwater seeps. The EPA 1668 data for groundwater wells included in the EIM are limited to data from the Kaiser Trentwood facility. More recent data from this facility were available directly from Kaiser, and are discussed below. EIM also includes 1668 analysis results from a few groundwater seeps from the Urban Waters dataset.

Ecology and Spokane County

Washington State Department of Ecology, Urban Waters, in collaboration with Spokane County collected groundwater data from a select set of Spokane Valley-Rathdrum Prairie aquifer monitoring wells and springs located adjacent to the Spokane River in 2015-2016. Samples were collected at the following locations: Idaho Road, Sullivan Park, Knipwrath, Spokane Community College, Three Springs, Waikiki Springs, and Griffiths Springs. Sample locations are shown in Figure 1.

Upriver Dam Site

A Focused Remedial Investigation was conducted at the Upriver Dam and Power Site (Anchor, 2005). Samples were collected from three wells, the locations of which were selected to reflect the potential maximum impact of PCB mass transfer from the sediments at the Upriver Dam Site to regional groundwater, in 2003.

Ecology – GE Site

Ecology collected groundwater PCB data in October 2016 from the National Priority List site known as the General Electric Spokane site. The site is located at 4323 East Mission Avenue in Spokane, approximately 1200 foot south of the Spokane River (Figure 2). Groundwater samples were taken at eight locations at the site (Figure 3).

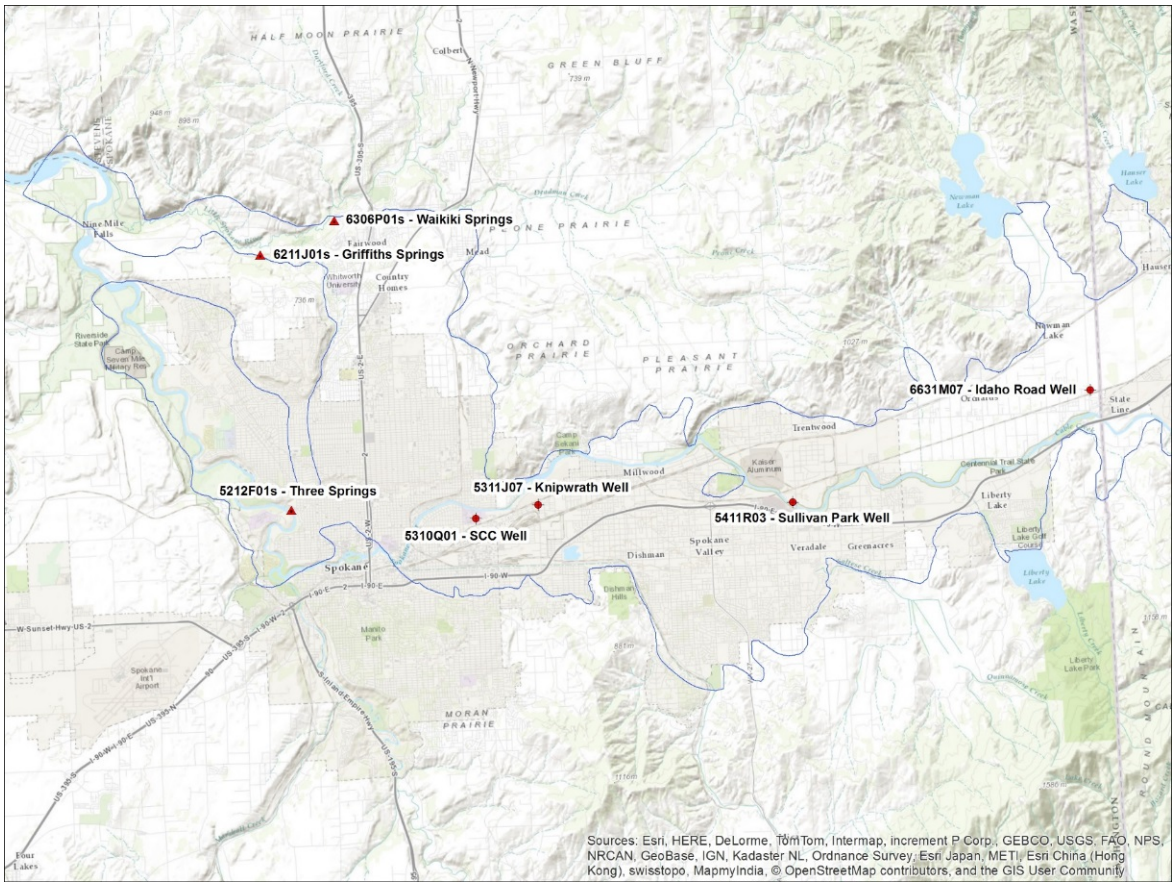


Figure 1. Ecology/Spokane County Monitoring Sites (from Ecology, 2016).

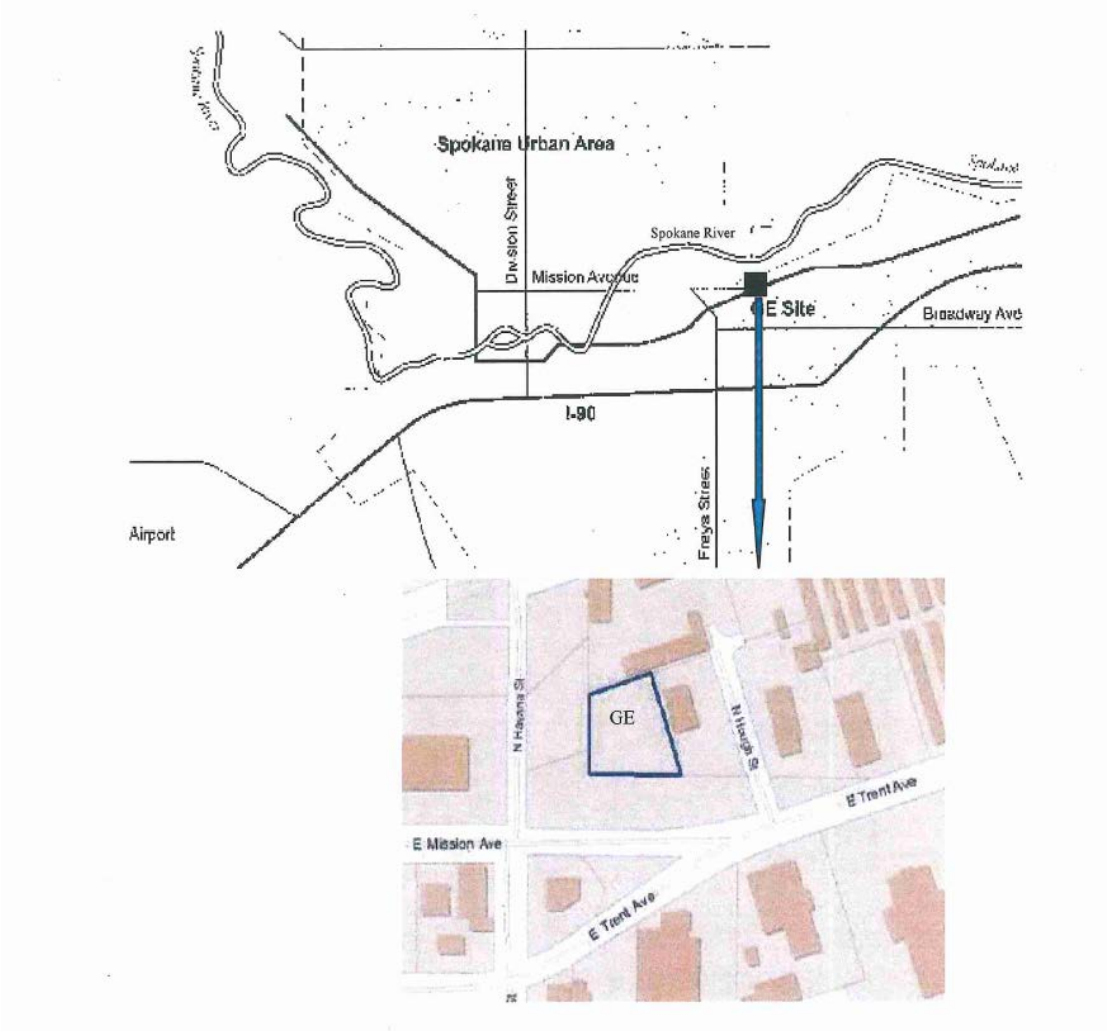
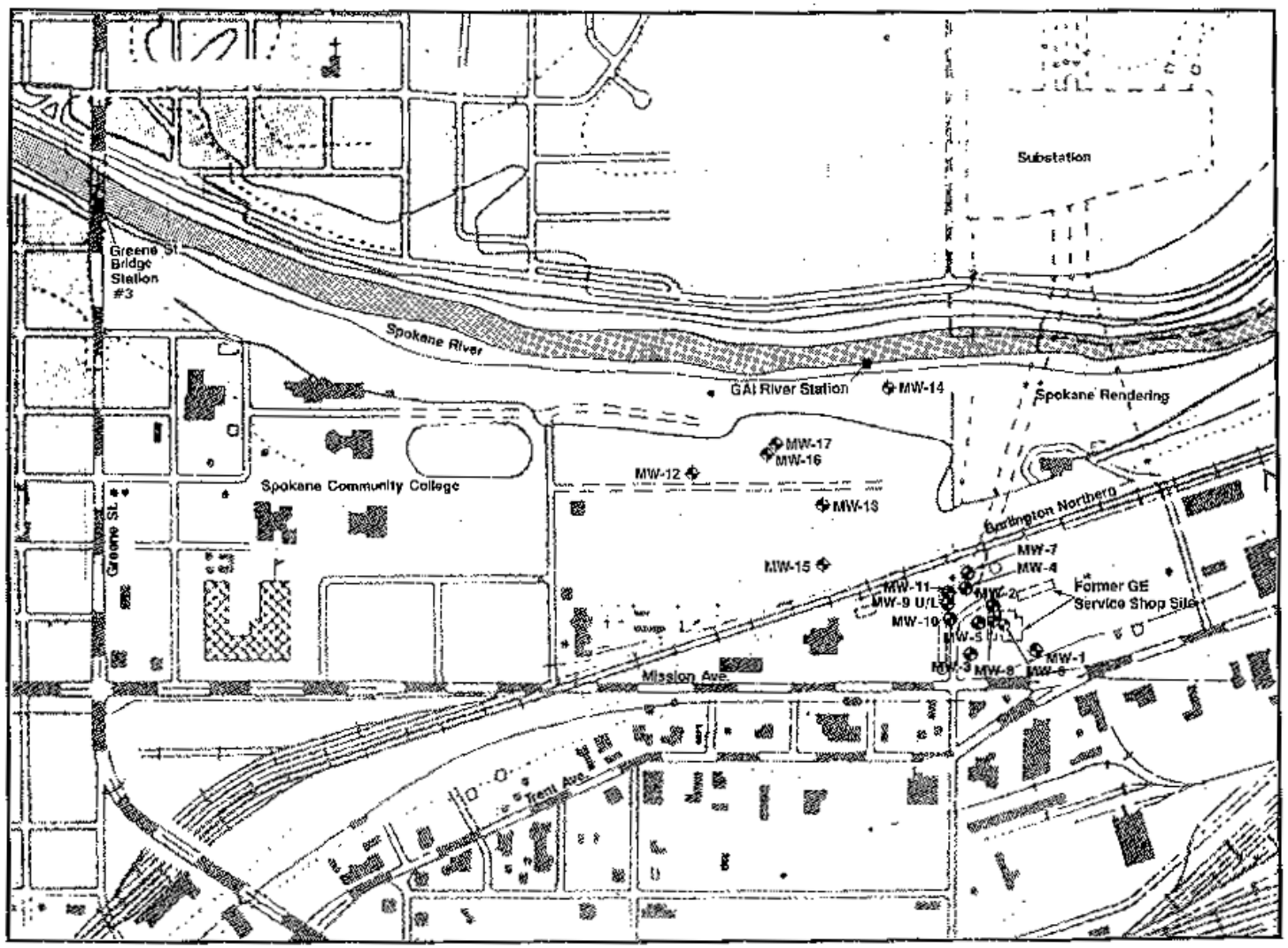


Figure 2. Location of GE Site (from Ecology, 2013)



Not to Scale

Figure 3. Well Locations at GE Site (from Golder Associates, 1993)

Kaiser

Kaiser Trentwood provided data for both the up-gradient groundwater entering their facility and for the groundwater leaving their facility along the Spokane River (Figure 4). Five wells representing up-gradient groundwater (RM-MW-5S, MW-4, MW-11, MW-10, and MW-5) and two wells representing discharge to the river (MW-27 and MW-28) have been sampled consistently in April and October from 2010 through the spring of 2017. The results from these samples were used in the pattern evaluation.

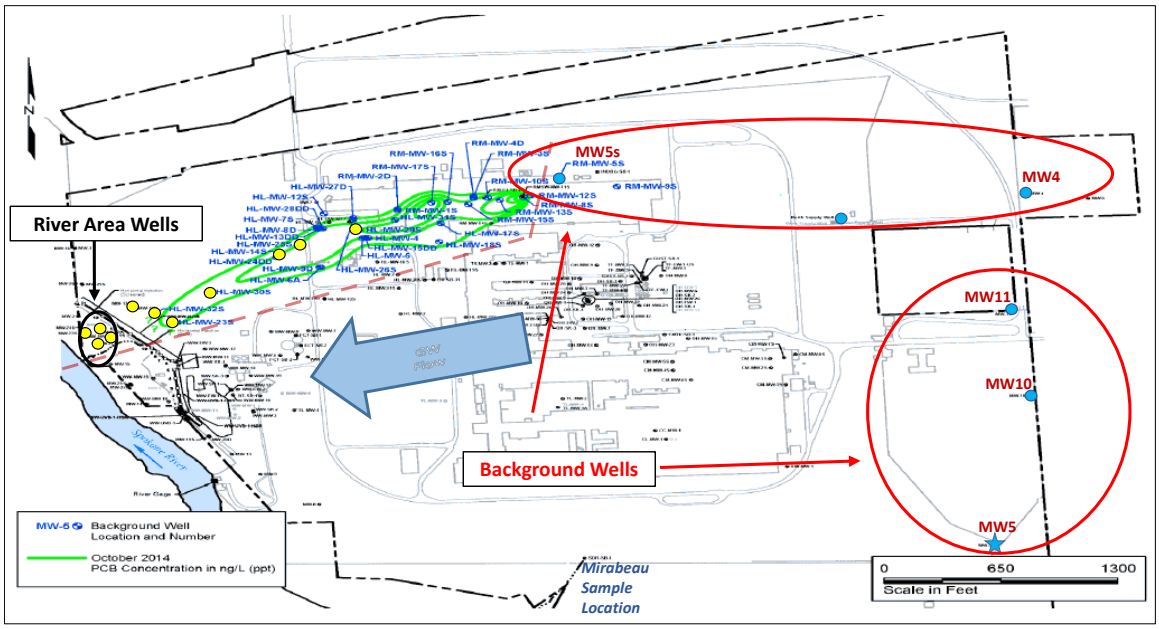


Figure 4. Well Locations Up-Gradient of and at Kaiser

Data are also available from the Kaiser Remedial Investigation collected in 2008 and 2009 (Hart Crowser, 2012) and a few sporadic samples from additional wells or months other than April and October. The homolog patterns from these samples were evaluated visually and compared to the more recent datasets. It was determined that they were very similar to the more recent data. Because the recent data had all been aggregated and processed in a consistent manner, the data for this evaluation was limited to the April and October 2010 to 2016 results. The upgradient Kaiser wells were generally evaluated as a group. However, for the Barker to Mirabeau load estimate, a comparison was also made with the pattern from MW-5. The flow from MW-5 most clearly enters the Spokane River upstream of Mirabeau.

Initial Screening

Well data were initially screened in terms of total PCB concentration to eliminate wells that had observed total PCB concentrations less than observed river concentrations, as these wells should not be responsible for contributing to increases in river PCB concentrations. This screening process eliminated the following sites from further consideration.

- Upriver dam data from the RI Report (maximum total PCB =69.9 pg/L prior to blank correction)
- Urban Waters groundwater seep data available in the EIM (maximum total PCB = 175 pg/L prior to blank correction)

- Ecology and Spokane County sampling at Idaho Road, Sullivan Park, Knipwrath, Spokane Community College, Three Springs, Waikiki Springs, and Griffiths Springs (maximum total PCB =51.5 pg/L)

The well groups that remained after the initial screening were the Kaiser river wells, the Kaiser up-gradient wells, and the wells from the GE site.

Data Handling

The mass balance estimates of loads were based on a blank correction of censoring any detected congener within a factor of 3 of the value detected in the blank. For consistency, the groundwater well data was treated in the same manner. Congeners that were below detection limits were not included in homolog sums.

Sample results were normalized so that each sample summed to 1. The homolog pattern represents the fraction of total PCBs contributed by each homolog.

Some of the comparisons were made to the mean of results from multiple samples from multiple wells. For comparisons using the averages, homolog patterns were calculated using an arithmetic mean of the homolog concentration from each sample prior to normalization, therefore, the higher concentration samples are more influential in the mean homolog patterns. The mean homolog concentrations from each well group are displayed in Table 1.

Table 1. Mean PCB homolog concentrations (pg/L) from each well group used in the evaluation.

	Kaiser MW-5 (n=15)		All Kaiser Upgradient Wells (n=73)		Kaiser River Wells (n=23)		GE Wells (n=8)	
	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
Monochloro Biphenyls	1.75	6.79	0.79	4.01	1.71	2.28	0.00	0.00
Dichloro Biphenyls	16.2	33.8	15.3	46.4	62.1	95.2	20.9	43.2
Trichloro Biphenyls	28.6	57.6	28.5	85.6	2,404	3,385	115	217
Tetrachloro Biphenyls	52.5	120.5	61.4	169.3	3,382	4,303	335	505
Pentachloro Biphenyls	56.7	151.4	96.4	345.5	551	1254	2,822	3,898
Hexachloro Biphenyls	29.8	91.6	40.9	147.8	73.8	187	14,689	20,824
Heptachloro Biphenyls	16.8	46.2	10.5	27.5	33.8	92.4	15,129	20,185
Octachloro Biphenyls	8.12	16.04	5.32	14.90	13.8	31.3	2,943	3,141
Nonachloro Biphenyls	2.46	5.05	1.73	7.47	3.83	7.88	97.1	121.1

Decachloro Biphenyl	0.45	1.08	0.49	0.95	1.20	3.26	0.55	1.56
Total PCBs	**213**	**472**	**261**	**835**	**6,528**	**8,036**	**36,151**	**46,656**

The suspected groundwater loads were calculated based on the increase in each homolog concentrations between sample points along the Spokane River, accounting for measured point sources (LimnoTech, 2017). For the pattern comparisons, all negative changes in the homolog load were set to zero.

Pattern Comparison Approach

Similarities in patterns between observed contamination and suspected sources can be used as part of a weight of evidence approach in evaluating the significance of potential sources under consideration.

A range of methods are available for PCB forensics. Many of the methods, such as polytopic vector analysis or positive matrix factorization, are used to "un-mix" environmental samples into the original source contributions by identifying and segregating individual stable patterns that contribute to multiple environmental samples in varying proportions. For purposes of the application described in this memorandum, the intent was to quantify the relative similarity of the PCB homolog patterns, rather than to un-mix source contributions.

A cosine similarity (also referred to as cosine theta or cos-θ) analysis was selected for this pattern comparison. The cos- θ value is the measure of the cosine between two vectors defined by the contribution of each homolog and is calculated as follows:

$$cos\theta = \frac{\sum_{i=1}^{n} AiBi}{\sqrt{\sum_{i=1}^{n} Ai^2}\sqrt{\sum_{i=1}^{n} Bi^2}}$$

where A_i and B_i represent the fraction of each PCB homolog of pattern A and pattern B. In this analysis, the patterns A and B may represent calculated loads to the river, mean PCB levels in a well group, or max PCB levels from a well group.

The cos-θ parameter is similar to a Pearson correlation coefficient. However, cos-θ is always a positive number between zero and one, while other comparable metrics can be negative. In the context of comparing congener patterns, a negative correlation is difficult to interpret. Additionally, the cos-θ calculations are not affected by pairs of zero values making it appropriate for an analysis where only detected values are considered, and zero values for individual homologs are not uncommon. Johnson et al (2006) recommends the cos-θ value as the most appropriate metric for pattern comparison.

Pattern Evaluation Findings

The pattern evaluation consisted of comparing homolog patterns from the available wells to the homolog patterns of suspected groundwater loading generated by the mass balance analysis for the relevant river reach(es) of interest. Cos-θ values were calculated to compare the homolog patterns between the calculated load for each reach to the patterns observed in the groundwater wells that could potentially influence that reach.

The river reaches of interest were defined as the reach closest to the corresponding well locations (Table 2). Multiple river reaches are of interest for the wells up-gradient of and at Kaiser, due to the change in reach definition between the 2014 and 2015 surveys.

Table 2. River reaches of interest and the corresponding wells used in the pattern comparison.

Well Group Location	River Reaches of Interest
Up-gradient of Kaiser	Barker – Trent (2014) Barker – Mirabeau (2015) Mirabeau – Trent (2015)
Kaiser facility along the Spokane River	Barker – Trent (2014) Barker – Mirabeau (2015) Mirabeau – Trent (2015)
GE NPL site	Trent – Greene (2014) Trent – Greene (2015)

To account for multiple samples and multiple wells at each site, the load patterns were compared to both the pattern of the mean homolog concentration and the pattern in the sample with the maximum PCB concentration from a given well group. Table 3 shows the results of the cos-θ evaluation. Values of cos-θ close to 1 indicate a close match in the pattern, while values closer to zero do not match well. The cos-θ metric can vary substantially when comparing PCB homolog patterns. The cos-θ values for the comparisons of homolog patterns of commonly produced Aroclors (based on analytical results from Frame, 1996) varies from 0.06 (for the comparison of Aroclor 1242 to Aroclor 1260) to 0.77 (for the comparison of Aroclor 1242 to Aroclor 1248). Therefore, a cos-θ value greater than 0.77 can be interpreted as a higher degree of similarity than the similarity between any two different Aroclor patterns.

Table 3. Cos-θ similarity comparisons between the patterns of estimated groundwater loads and the patterns observed in relevant groundwater wells.

Well Group Location	River Reach	cos-θ (mean of well samples)	cos-θ (max of well samples)	Sample used for max
Kaiser MW-5	Barker – Mirabeau (2015)	0.65	0.78	MW-5, Apr-2011
Kaiser up-gradient wells	Barker – Trent (2014)	0.66	0.55	RM-MW-5S, Apr-2010
Kaiser up-gradient wells	Barker – Mirabeau (2015)	0.69	0.73	RM-MW-5S, Apr-2010
Kaiser up-gradient wells	Mirabeau – Trent (2015)	0.57	0.46	RM-MW-5S, Apr-2010
Kaiser river wells	Barker – Trent (2014)	0.96	0.94	MW-28S, Apr-2015
Kaiser river wells	Barker – Mirabeau (2015)	0.12	0.07	MW-28S, Apr-2015
Kaiser river wells	Mirabeau – Trent (2015)	0.98	0.97	MW-28S, Apr-2015
GE wells	Trent – Greene (2014)	0.94	0.94	MW-18, Oct-2016
GE wells	Trent – Greene (2015)	0.81	0.78	MW-18, Oct-2016

Figure 5 presents bar charts of the homolog patterns for visual comparison of the estimated loads and the groundwater sources for the Barker to Trent reach. The bar charts show the PCB loads and groundwater concentrations for reference, but the similarity analysis was performed on the normalized values.

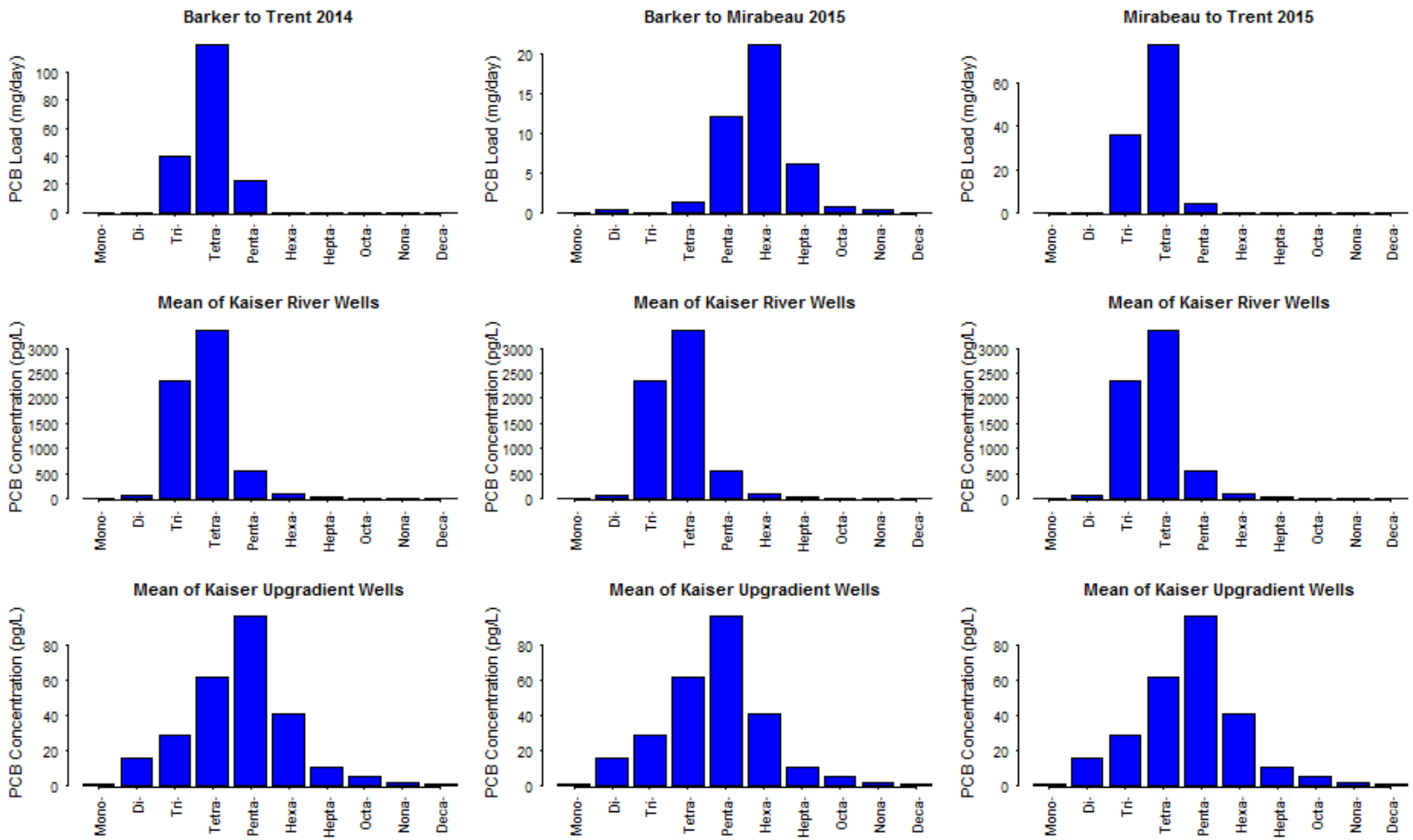


Figure 5. Homolog patterns for the estimated loads and the groundwater wells for the Barker-Trent reach.

The 2015 Barker to Mirabeau load pattern is a partial match with the Kaiser up-gradient well pattern – both have significant contributions from penta-PCB homologs - although there are several issues related to this this comparison that merit further discussion. First, the calculated groundwater load for this reach is driven by a single in-river concentration of 231 pg/l observed during the 2015 synoptic survey. All other in-river concentrations at this station in 2015 were less than 20 pg/l. If the 231 pg/l sample is excluded from the mass balance calculations as anomalous, there would be no calculated PCB load to the river. Conversely, groundwater concentrations in up-gradient wells vary by more than an order of magnitude at the same well, and the cos-θ value is 0.80 for the comparison between peak up-gradient concentration at MW-5 and peak river concentration sample, so the possibility of intermittent groundwater loading in this segment cannot be ruled out. The second complicating factor pertaining to the Barker to Mirabeau comparison is that the largest homolog contribution in the calculated load is from hexa-PCBs, while these homologs are a relatively minor part of the up-gradient well pattern. There may be an unknown source of hexa-PCBs in this reach; however, it may also be an anomaly in the dataset. The hexa-PCB contribution disappears in the Mirabeau to Trent reach in the 2015 data and no increase in hexa-PCBs was observed in the longer Barker to Trent reach in 2014. Whether the hexa-PCB contribution is an unknown source or an artifact of the data, little of it is accounted for by the Kaiser up-gradient wells. If the hexa-PCB contribution in the Mirabeau to Trent load is set to zero, the cos-θ with the up-gradient wells is 0.79, indicating a strong match to the remaining pattern. Kaiser MW-5 is the well that most clearly enters the Spokane River upstream of the Mirabeau sampling point (see Figure 4). Table 2 also includes a comparison of the Barker to Trent load just to the pattern in samples from this well. Limiting the comparison to MW-5 improves the comparison when using the sample with the maximum PCB concentration (cos-θ=0.78).

The pattern in the Kaiser river wells closely matches the load patterns calculated for the 2014 Barker-Trent reach and the 2015 Mirabeau to Trent reach – these patterns are dominated by tri- and tetra- substituted PCB homologs, with a slightly higher contribution from the tetra-PCBs.

An evaluation was performed to determine the impact on the value of cos-θ when the mixture of the patterns observed in the Kaiser river wells and Kaiser up-gradient wells was varied from 100% river wells to 100% up-gradient wells relative to the load estimate for the 2014 Barker to Trent reach. Figure 6 shows how the cos-θ value changes with an increasing fraction of the up-gradient wells pattern. The value of cos-θ ranges from about 0.95 to 0.90 as the percentage of up-gradient wells pattern increases from 0% to approximately 50% with the value of cos-θ declining to 0.80 with the pattern percentage for the up-gradient wells at about 75%. Thus the value of cos-θ appears be relatively insensitive to a wide range of mixtures of river wells pattern and up-gradient wells pattern.

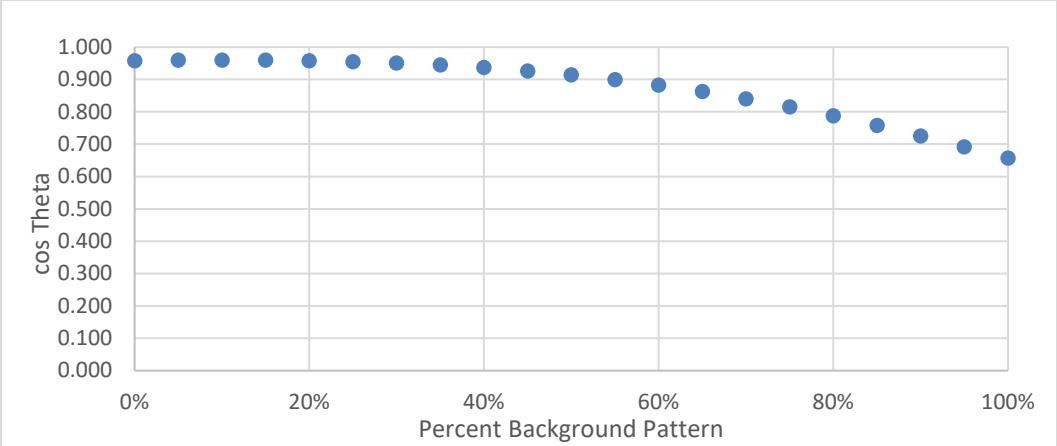


Figure 6. Cos-θ values comparing the 2014 Barker to Trent load to various mixtures of the Kaiser river wells and Kaiser up-gradient wells - 0% on the x-axis represents pure river well and 100% represents pure up-gradient wells.

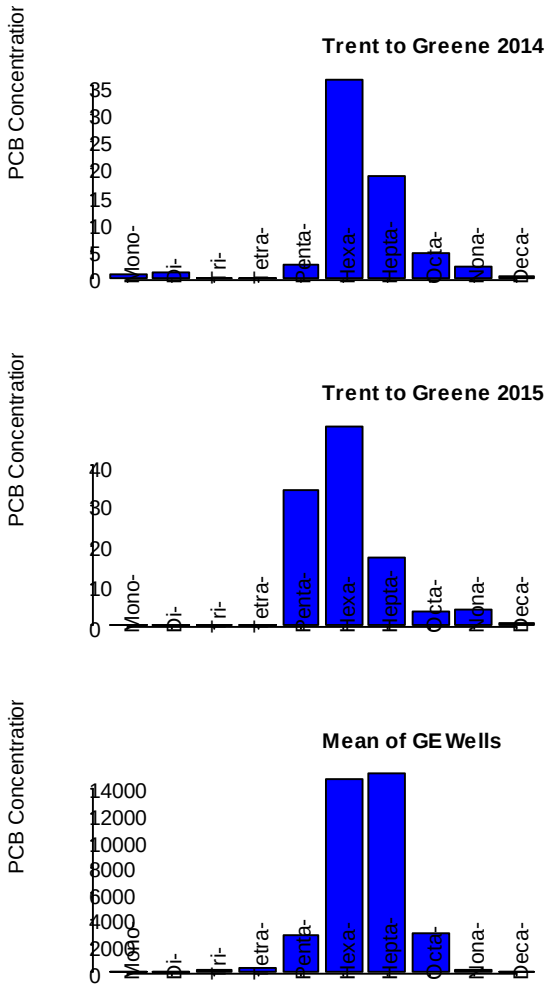


Figure 7. Homolog patterns for the estimated loads and the groundwater wells for the Trent to Greene Reach.

Table 3 shows a fairly strong match between the homolog pattern in the GE wells and the calculated load estimate entering the Trent to Greene reach. Figure 7 shows that the GE wells have a higher contribution of hepta-PCBs in mean pattern than is reflected in the mass balance estimates, but otherwise look the patterns are very similar. Some of the individual GE Well patterns are even closer matches (see MW-21 and MW-22 in Figure A-12 in the appendix).

It should be noted that some variability in patterns was observed within the well groups. Bar charts showing the homolog patterns for each sample from each of the wells included in the pattern evaluation after the screening is included as an appendix to this memo. The figures show that, although the wells in each of the areas are generally consistent in terms of homolog patterns, there are anomalous samples. The Kaiser up-gradient well patterns are particularly variable. However, patterns in the Kaiser river wells and GE wells are also occasionally substantially different from the typical pattern - see 2012 samples from the Kaiser river wells (Figure A-1) or the GE Well MW-20 sample (Figure A-20).

Conclusions

The results of the cosine theta pattern analysis provide evidence that groundwater up-gradient of Kaiser, at Kaiser, and at the General Electric NPL site are each providing observable signals in Spokane River PCB concentrations. Moderately high correlation coefficients (0.62 to 0.73) were calculated between groundwater wells up-gradient of Kaiser and the back-calculated load for the Barker to Mirabeau reach. This correlation coefficient increases to 0.81 if estimated loads are corrected to remove anomalous results for the hexa-PCB homolog. Very high correlation coefficients (0.94 to 0.98) were calculated between the groundwater wells at Kaiser and the back-calculated loads for the Barker to Trent (2014) and Mirabeau to Trent (2015) reaches. Analysis of combined loading from wells up-gradient of Kaiser and the wells at Kaiser suggest that up to 20% of the Barker to Trent (2014) load could be attributed to up-gradient sources. High correlation coefficients (0.78 to 0.94) were calculated between the groundwater wells at the GE site and the back-calculated loads for the Trent to Greene reaches.

Observed groundwater concentrations were not large enough at other well locations to indicate that they could be significant contributors of PCBs to the Spokane River.

These above findings should not be considered proof that groundwater from these well areas are responsible for observed increases in river PCB concentrations, due to the observed variability in homolog patterns among samples from a given well group and the uncertainty inherent to the mass balance assessment. In particular, additional investigation may be merited verifying the potential loading originating from wells up-gradient of Kaiser prior to initiating new groundwater monitoring. Nonetheless, these results should be considered as part of a weight of evidence approach when assessing potential sources of groundwater contamination to the Spokane River.

References

Anchor Environmental, LLC. 2005. Focused Remedial Investigation Report Upriver Dam PCB Sediments Site. Prepared for Avista Development, Inc. and Kaiser Aluminum & Chemical Corporation for Submittal to Washington Department of Ecology. February 2005.

Frame, G.M., Cochran, J.W., Boewaldt, S.S. 1996. Complete PCB congener distributions for 17 Aroclor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener-specific analysis. *J. High Res Chromatogr*. 19: 657-668.

Golder Associates Inc., 1993. First 1993 Semi-annual groundwater sampling event at the former General Electric facility East 4323 Mission Avenue Spokane Washington. March 12, 1993.

Hart Crowser. 2012. Final Site-Wide Groundwater Remedial Investigation Kaiser Trentwood Facility Spokane Valley, Washington. Prepared for Kaiser Aluminum Washington. May 2012.

Johnson, G.W., Quensen, J.F., Chiarenzelli, J.R., Hamilton, M.C. 2006. In Environmental Forensics: Contaminant Specific Guide. Murphy, B. Morrison, R. Eds. Academic Press, New York. pp 189-292.

LimnoTech, 2017. Homolog-Specific PCB Mass Balance for the Spokane River. Prepared for Spokane River Regional Toxics Task Force. August 16, 2017.

Washington Department of Ecology, 2013. Addendum 3 to Quality Assurance Project Plan Spokane River Toxics Reduction Strategy Study. Draft 5 – September 6, 2016.

Washington Department of Ecology, 2013. Third Periodic Review (Draft Final), General Electric Spokane Site. Eastern Regional Office. Toxics Cleanup Program. March, 2013.

Appendix: Homolog Patterns for Each Groundwater Well

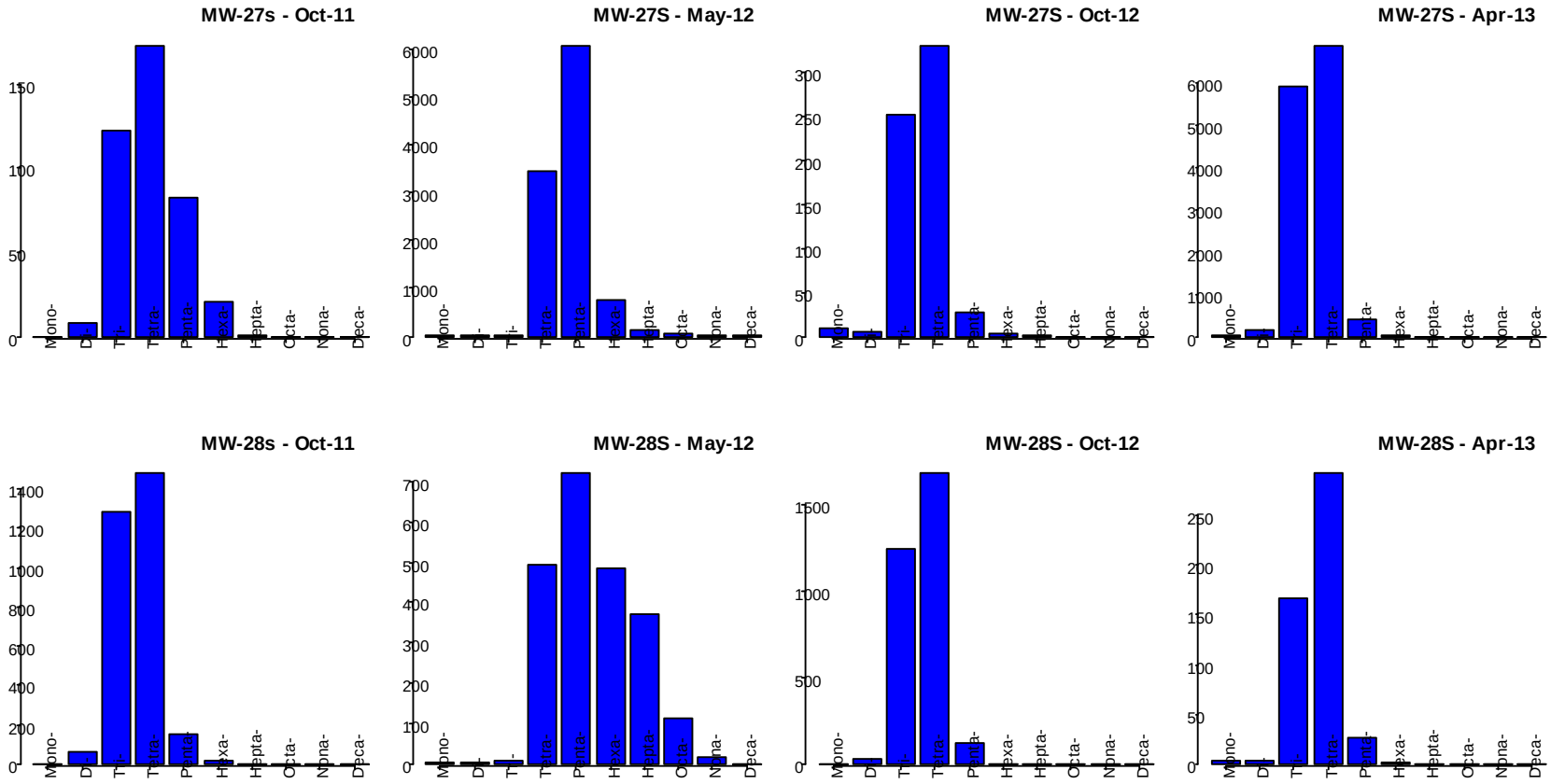


Figure A-4. Homolog patterns for samples from Kaiser river wells (October 2011 – April 2013). PCB homolog concentrations in pg/L.

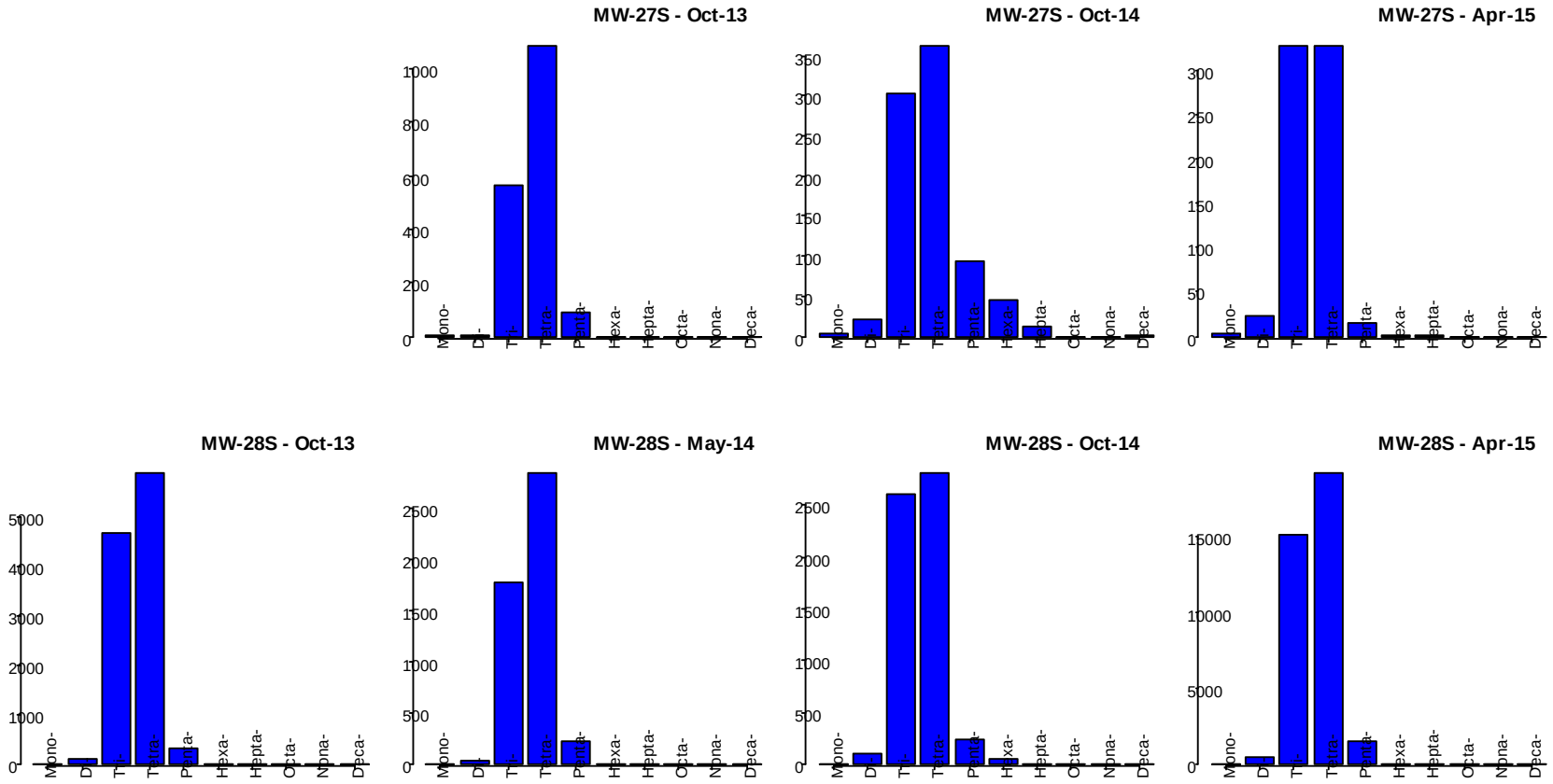


Figure A-5. Homolog patterns for samples from Kaiser river wells (October 2013 – April 2015). PCB homolog concentrations in pg/L.

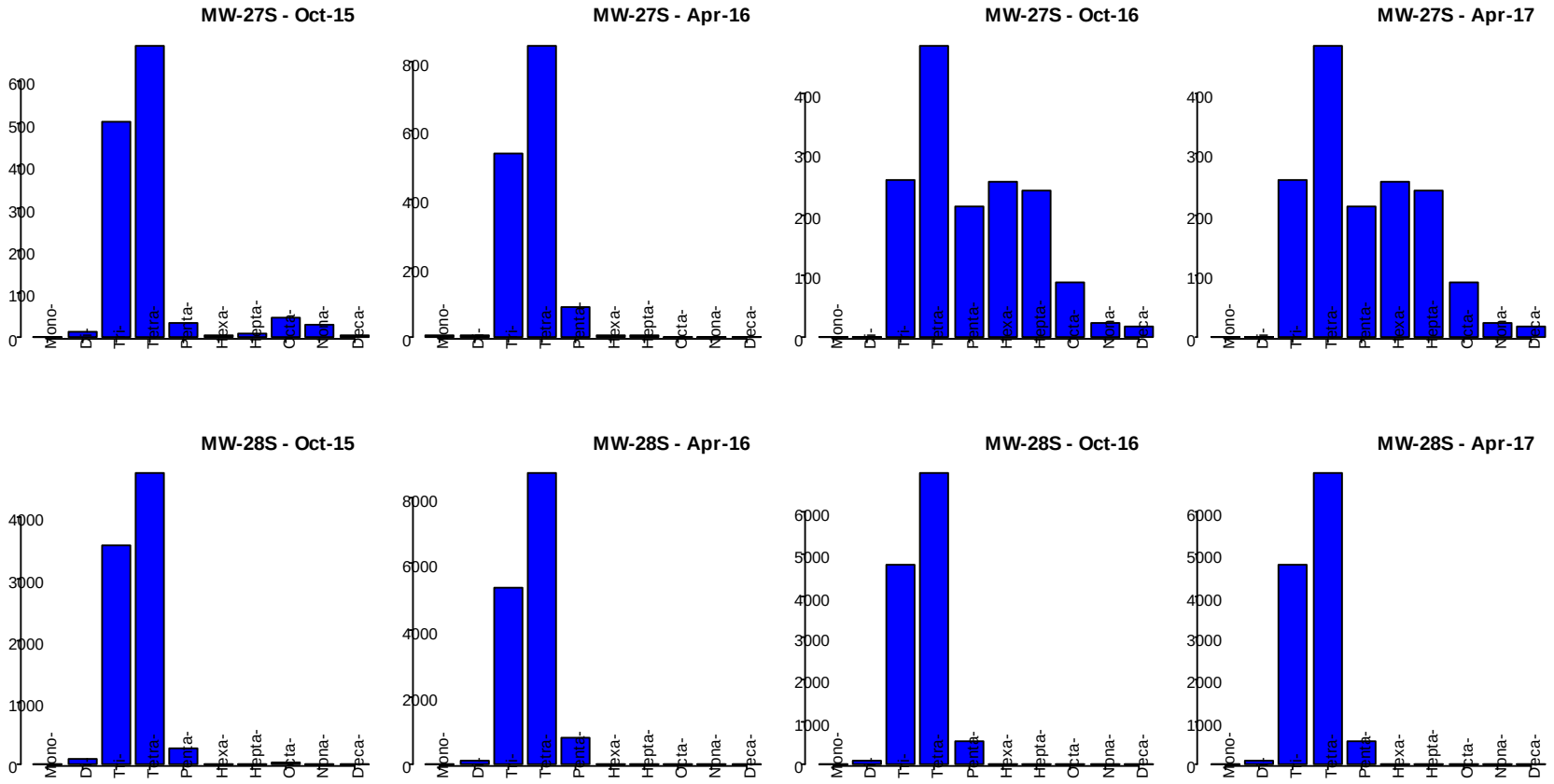


Figure A-6. Homolog patterns for samples from Kaiser river wells (October 2015 – April 2017). PCB homolog concentrations in pg/L.

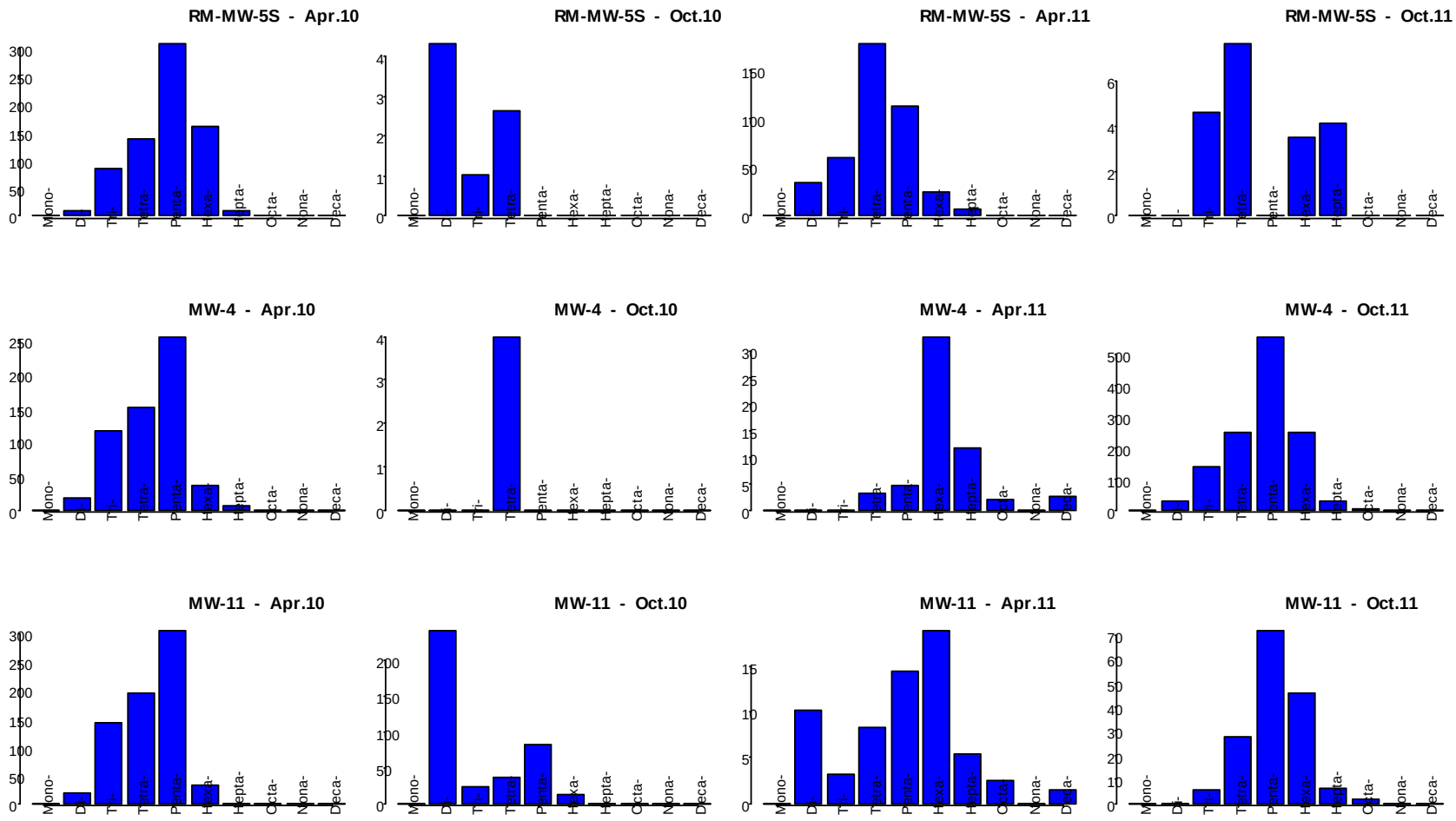


Figure A-7. Homolog patterns for samples from Kaiser up-gradient wells (April 2010 – October 2011). PCB homolog concentrations in pg/L.

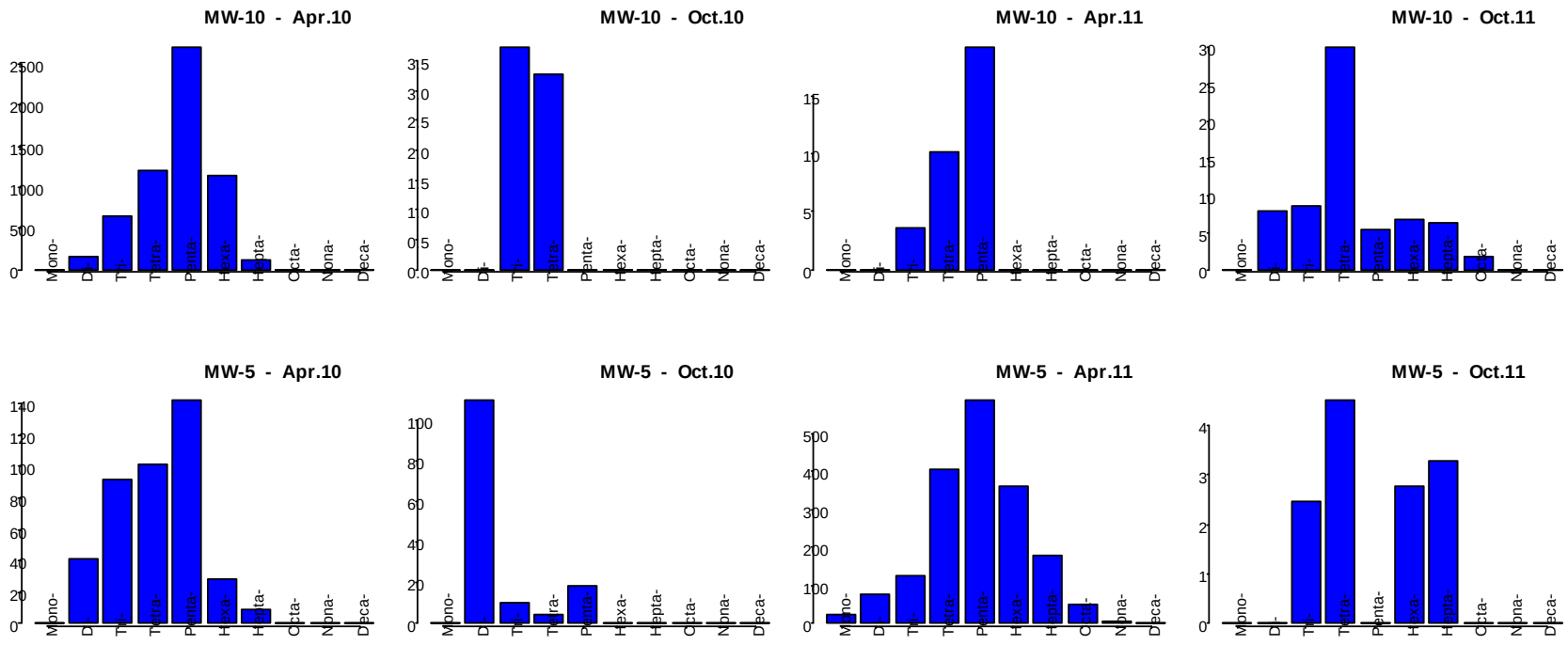


Figure A-8. Homolog patterns for samples from Kaiser up-gradient wells (April 2010 – October 2011). PCB homolog concentrations in pg/L.

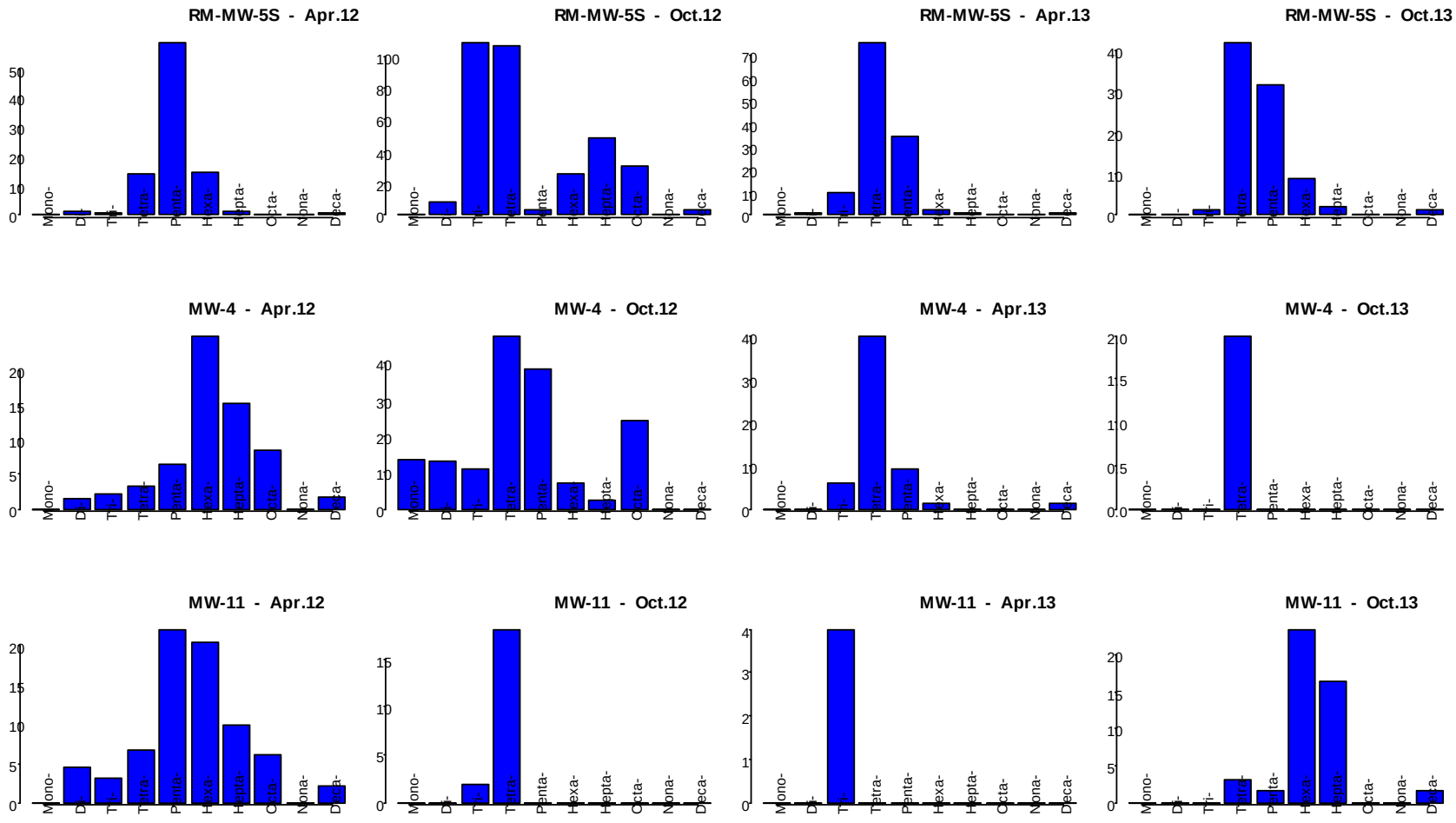


Figure A-9. Homolog patterns for samples from Kaiser up-gradient wells (April 2012 – October 2013). PCB homolog concentrations in pg/L.

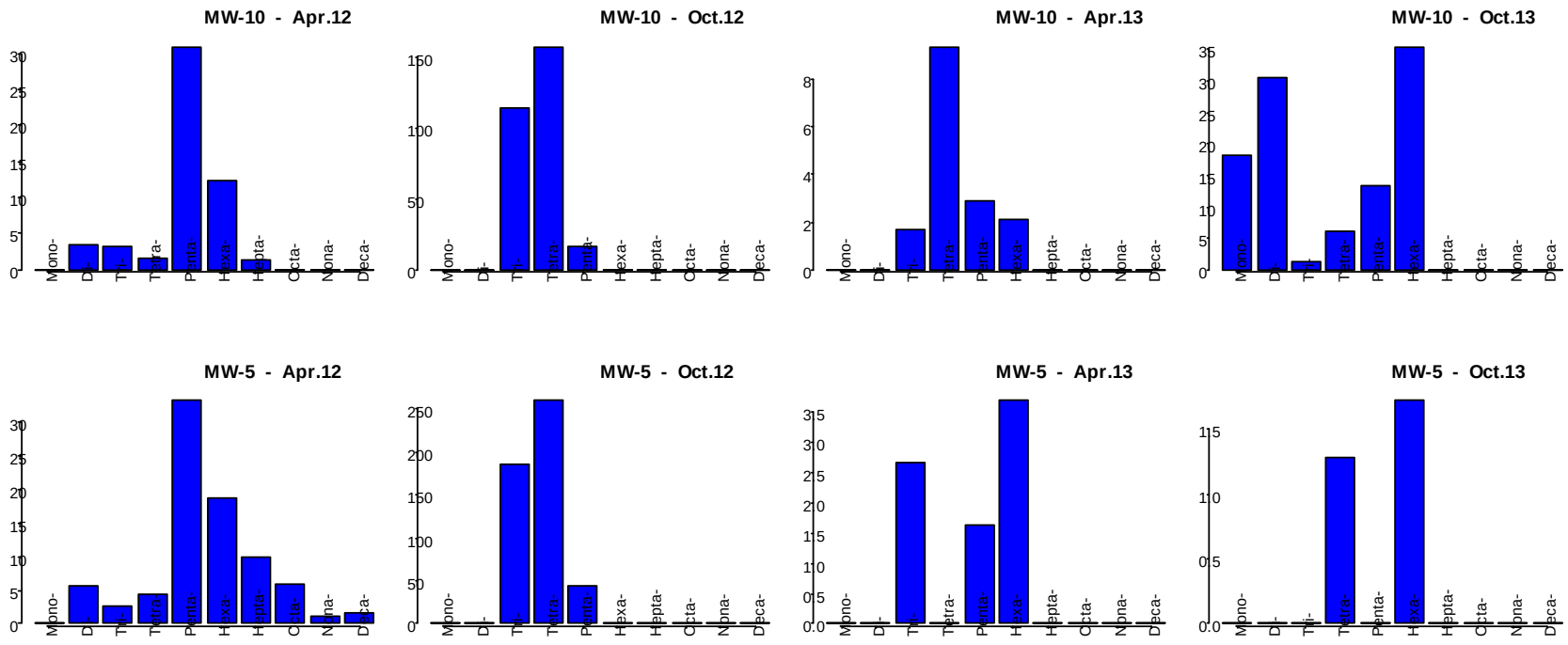


Figure A-10. Homolog patterns for samples from Kaiser up-gradient wells (April 2012 – October 2013). PCB homolog concentrations in pg/L.

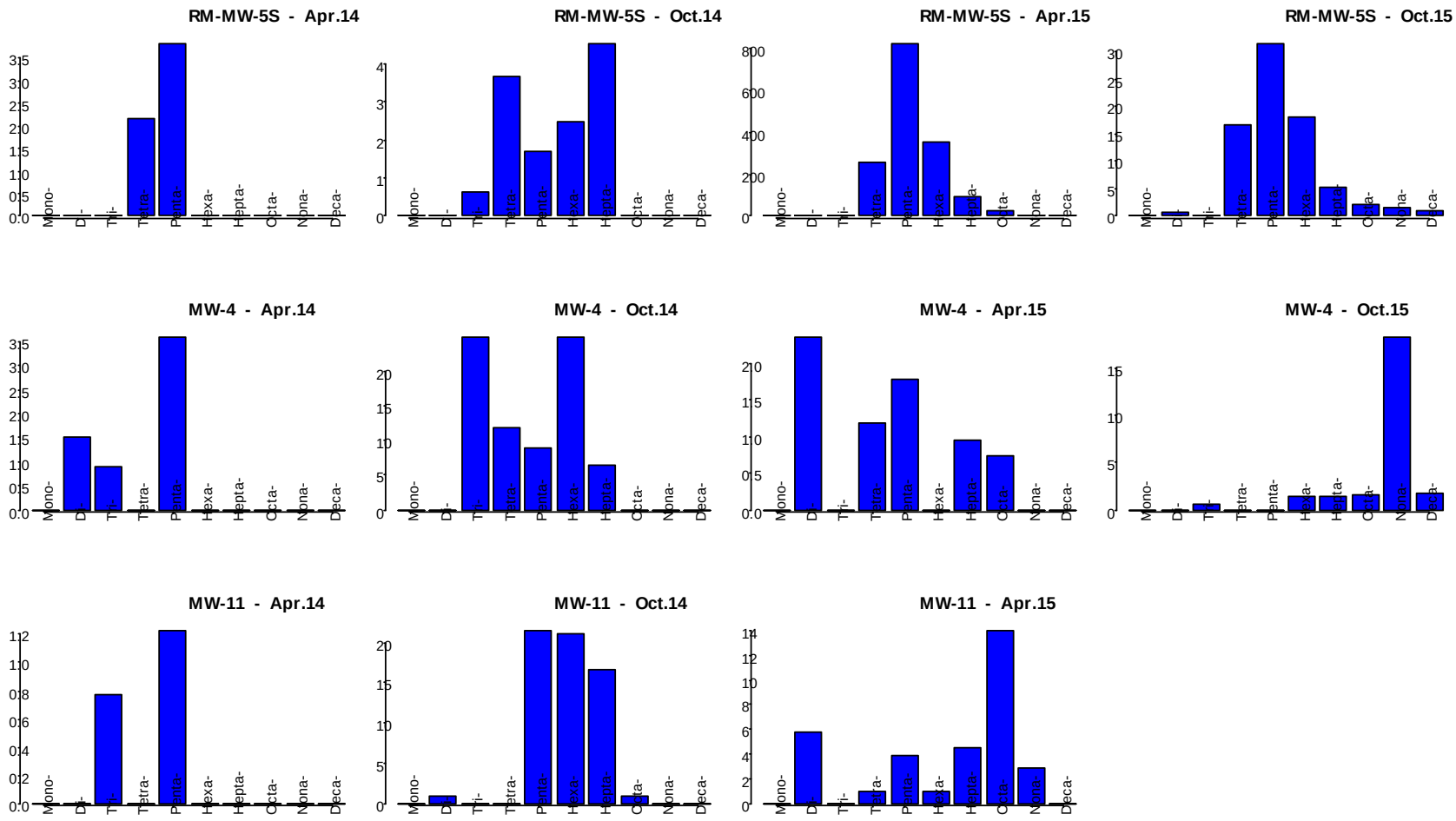


Figure A-11. Homolog patterns for samples from Kaiser up-gradient wells (April 2014– October 2015). PCB homolog concentrations in pg/L.

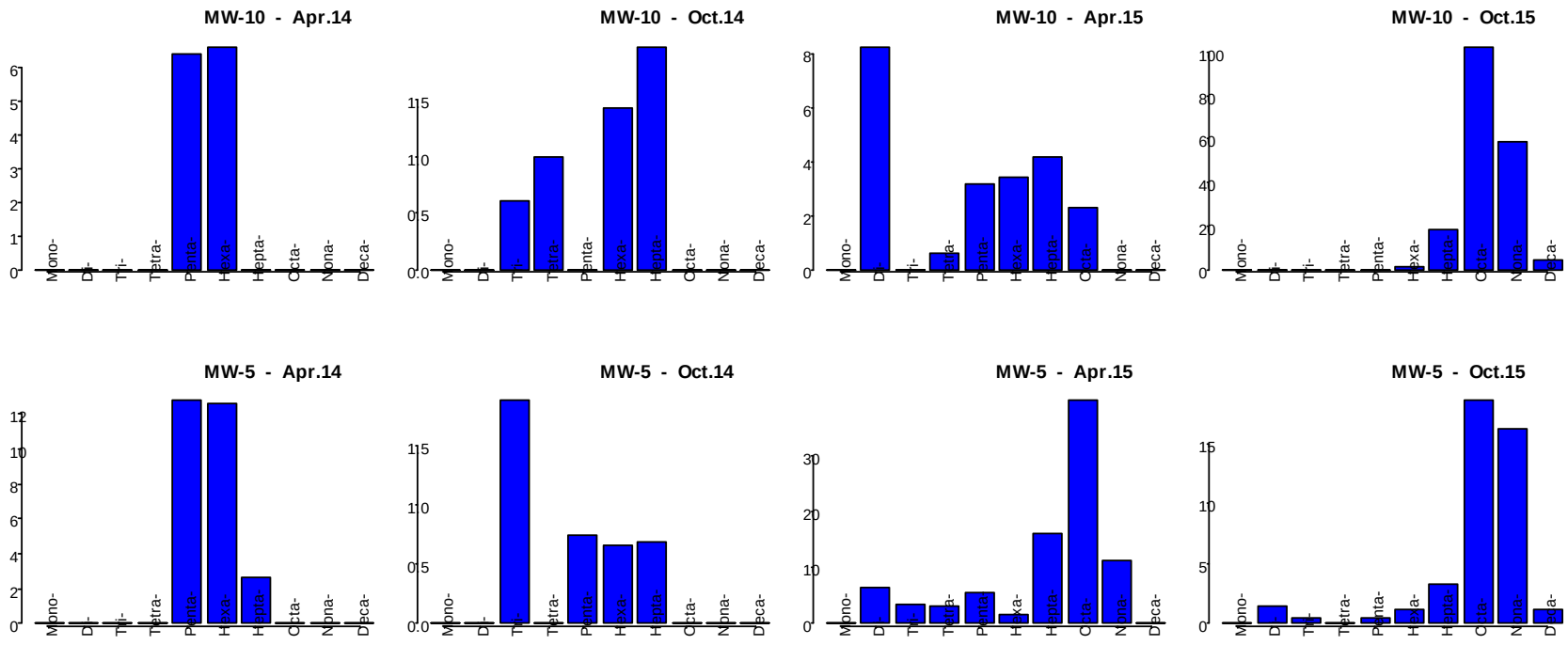


Figure A-12. Homolog patterns for samples from Kaiser up-gradient wells (April 2014– October 2015). PCB homolog concentrations in pg/L.

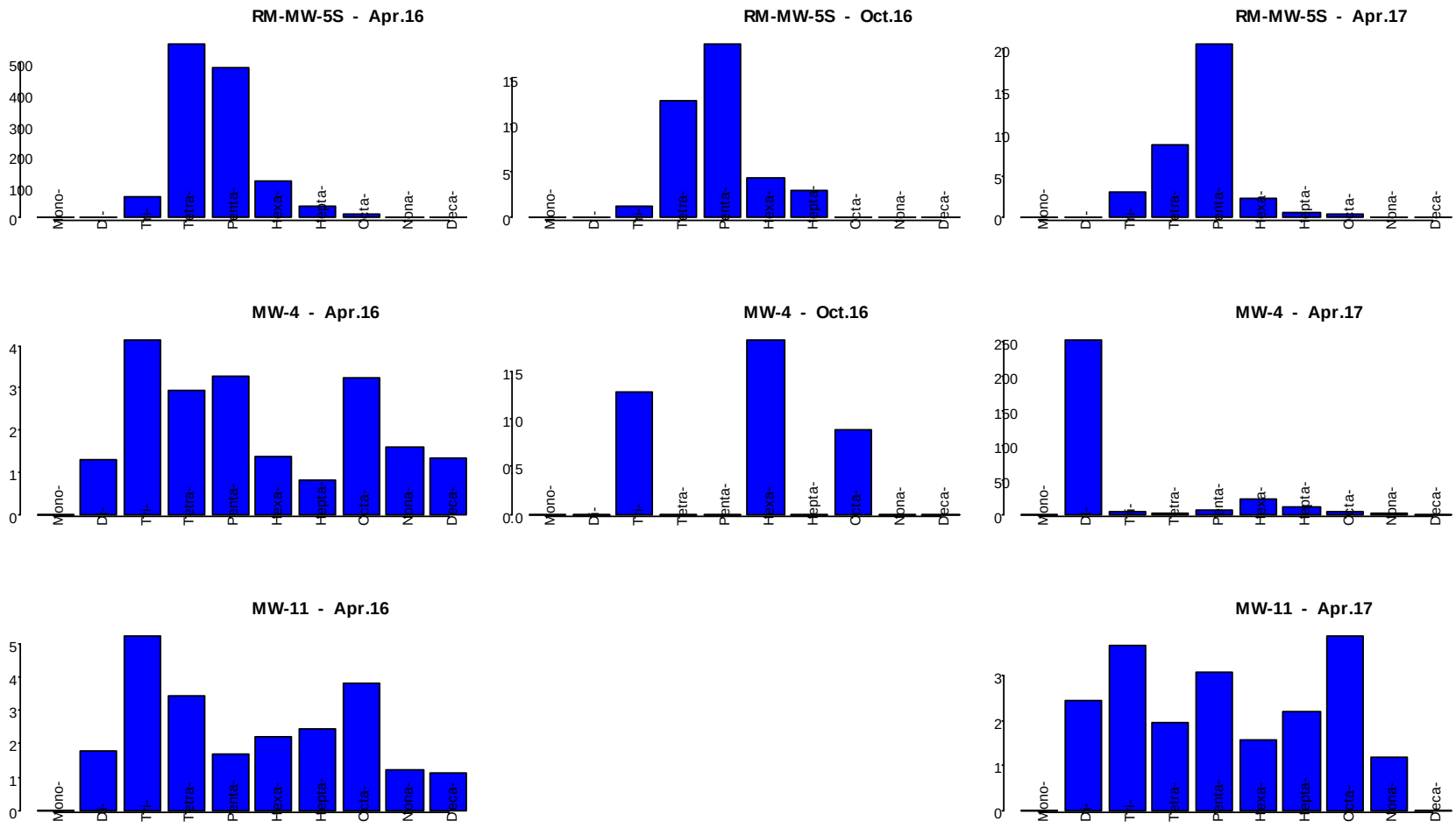


Figure A-13. Homolog patterns for samples from Kaiser up-gradient wells (April 2016– April 2017). PCB homolog concentrations in pg/L.

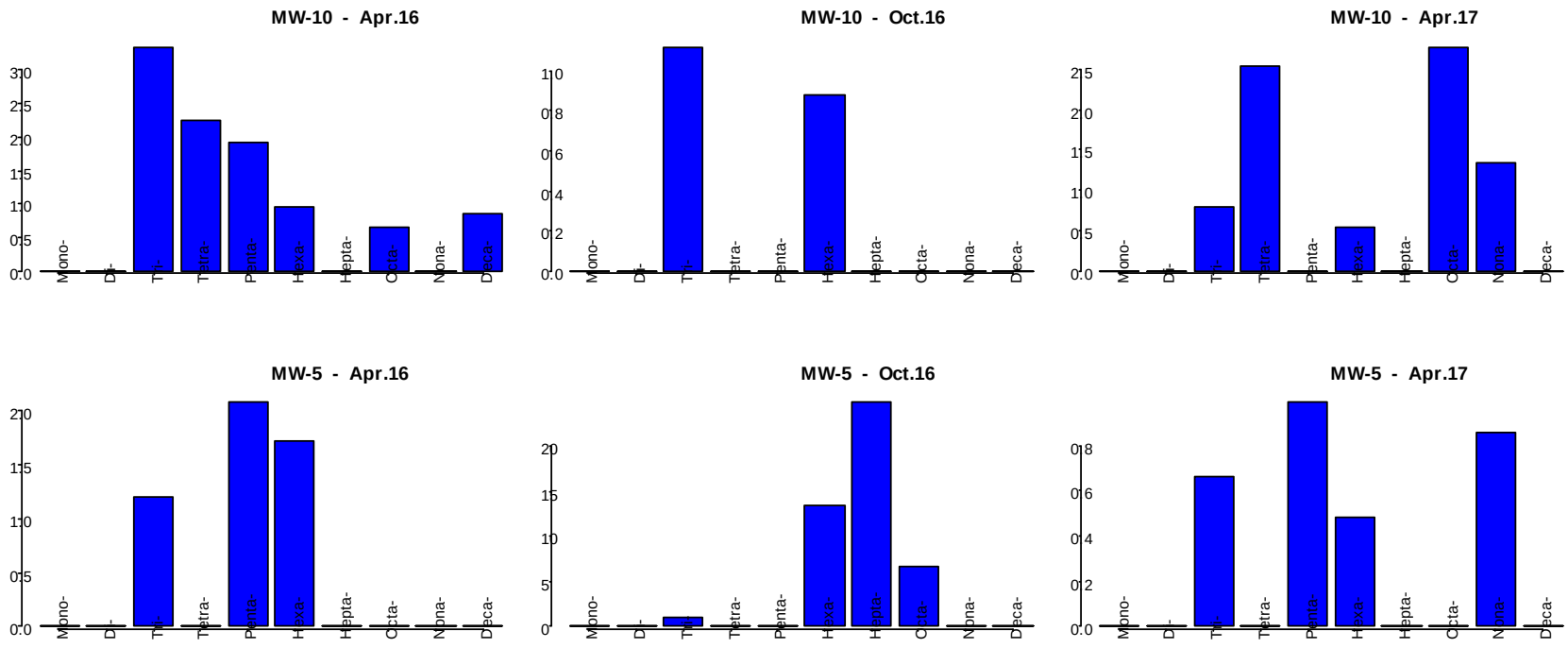


Figure A-14. Homolog patterns for samples from Kaiser up-gradient wells (April 2016– April 2017). PCB homolog concentrations in pg/L.

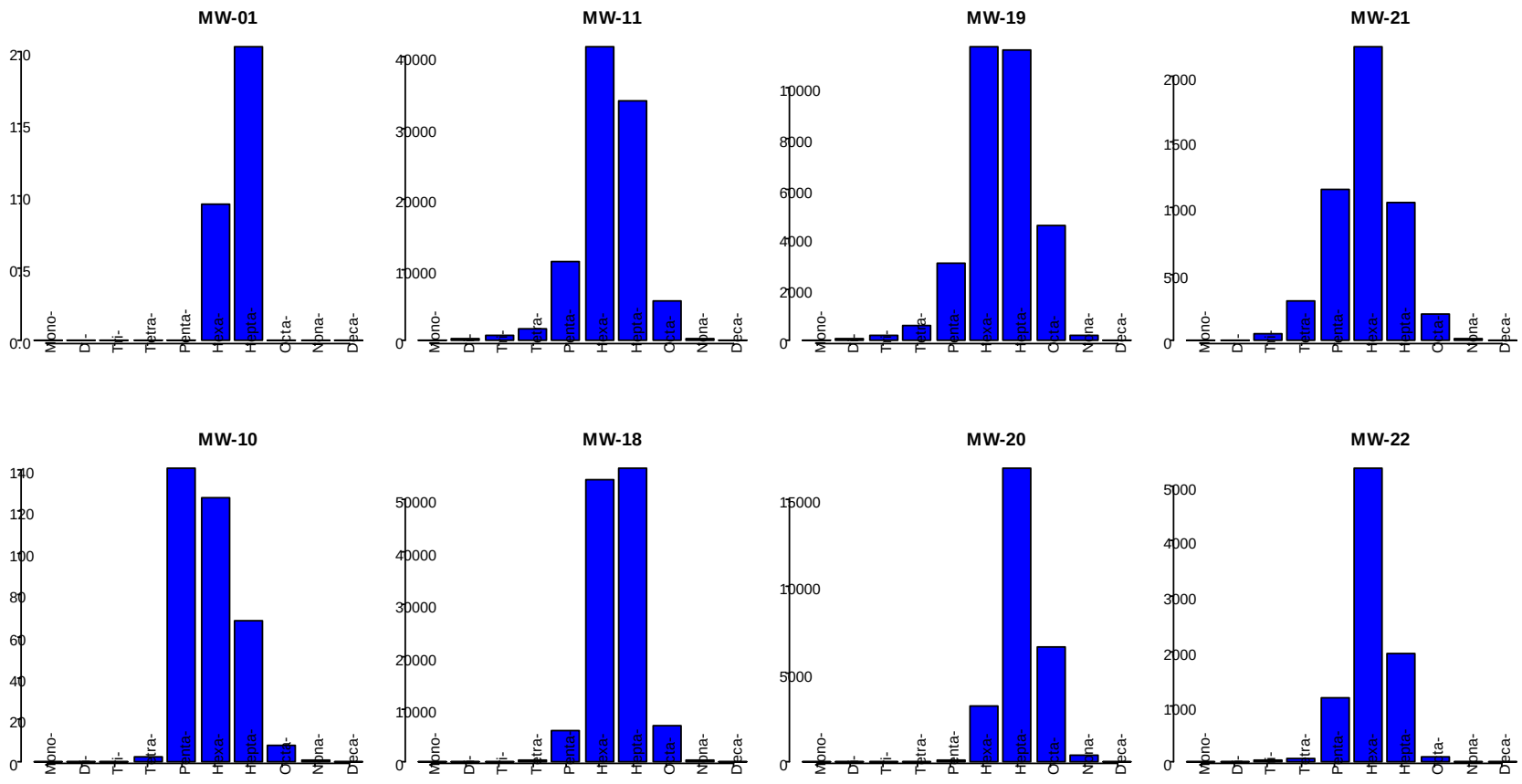


Figure A-15. Homolog patterns for samples from GE wells collected in October 2016.. PCB homolog concentrations in pg/L.