Proposed approach:

In order to understand the sources of PCBs to the Spokane River, I will conduct factor analysis on PCB data from the Spokane River watershed using PMF2.

Data groups

I proposed to dive the data into four subsets:

1. Surface water data (approximately 159 samples once the 2016 monthly sampling is complete)
2. Groundwater data (approximately 238 samples from on-site monitoring wells, on-site near river monitoring wells, deep supply wells, and site background monitoring wells)
3. Wastewater effluents (about 461 samples including Kaiser, about 122 without Kaiser)
4. Wastewater influents and stormwater (about 151 samples of stormwater plus about 100 wastewater influent samples)

Two criteria are used to group the samples in this way. First, a group of samples should be exposed to roughly the same set of PCB sources. This is why surface water and groundwater are grouped separately. Second, a group of samples should have roughly similar concentrations. This is why wastewater influents are separated from wastewater effluents. This is also why wastewater influents are lumped with stormwater, since these groups of samples usually have similar concentrations. Also, in areas with combined sewers such as the city of Spokane, stormwater and wastewater are hydraulically connected and therefore exposed to similar sources. It may be necessary to remove the 339 samples of Kaiser effluent from the wastewater effluent data set and analyze them separately. This would be necessary if the sources to Kaiser effluent are very different from the sources to the other effluents. In such a case, because almost 75% of all of the wastewater effluent samples are from Kaiser, these samples might dominate the PMF solution, masking the non-Kaiser sources.

This grouping is provisional and may need to be adjusted as the analysis proceeds.

Blank correction

I propose to analyze the wastewater influents and stormwater data without blank correction, since the concentrations in these samples are high enough that blank correction should have little or no effect on concentrations.

For the surface water and wastewater effluent data sets, I will perform PMF analysis both with and without blank correction to determine whether blank correction makes a significant different in the PMF results.

If the PCB concentrations in the groundwater are at least 100 times higher than blank concentrations, then the groundwater data will be analyzed without blank correction. If the concentrations are generally lower than this, then the analyzed with be performed both with and without blank correction.

I will work with the SRRTTF to determine the best method of blank correction. In the PMF analysis of the Spokane County SCRWRF data, blank correction was performed by subtracting the average mass in the blanks collected for each sampling event regardless of the type of blank (i.e. field, lab, travel, etc.).

Deliverables

The following data and reports will be provided:

- Spreadsheets of PMF input and output for all data sets analyzed.
- Heat maps of the absolute (concentration) and relative (percent of total) abundance of the PMF factors by sample location and sampling event.
- A final report investigating all of the questions posed below.

Research Questions

The following research questions have been posed by the SRRTTF. For each question, I have tried to provide an answer based on my previous experience with factor analysis of PCBs.

• **What can be said about the ultimate origin (e.g. legacy sources, inadvertently produced PCBs) of PCBs in the Spokane River?**

Pattern analysis should be able to give a quantitative estimate of the fraction of PCBs coming from legacy sources versus non-Aroclor (inadvertent) PCB sources in the Spokane River. For example, in the Portland Harbor Superfund site, PMF analysis of PCB fingerprints suggested that the factor containing PCB 11 (a known non-Aroclor congener) comprised 6.3% of the mass of PCBs containing in the entire data set (i.e. all samples collected). Dechlorinated PCBs from groundwater comprised 22%, and sources that resemble Aroclors comprised the remainder.

• **Does the nature of the source (or the PCB signature/signal) change as one moves downstream?**

In my previous investigations, the patterns isolated by factor analysis do not appear to change as the river flows downstream. Their *relative abundance* varies in time and space, but the patterns themselves are preserved. The changes in the relative abundance of the factors in time and space is key information used to infer the probable sources of the different PCB factors. This information will be analyzed by generating maps of the concentration and relative abundance (percent of total PCBs) for each factor and each sampling event.

In the pattern analysis that I have performed in the Portland Harbor, San Francisco Bay, and Delaware River, I have not seen a dramatic alteration in congener patterns (i.e. PMF-isolated fingerprints) over the length of the study area. (The largest study area was the Delaware River at over 200 miles of river run).

The one place where I have seen an alteration in congener pattern is the Hudson River. Extensive microbial dechlorination of PCBs occurs in the Upper Hudson River and produces very high levels of PCBs 1 (monochloro) and 4 (dichloro). Because these congeners have few chlorines, they volatilize readily, and there is a slight shift in congener pattern (i.e. these congeners become proportionately less abundant) as the river flows approximately 150 miles into the Lower Hudson River.

- **Can you draw any conclusions regarding relative importance of (1) storm water, (2) groundwater, and (3) wastewater effluent (industrial and municipal) as contributors to observed Spokane River concentrations?**

Probably. In the Delaware River, we noted that the factor that contained a high proportion of PCB 11 was more abundant at high flow, suggesting that it is associated with stormwater and CSO inputs. Similarly, in the Portland Harbor, the factor containing the most PCB 11 was more abundant under stormwater influenced flow. Thus we should be able to use the abundance of PCB 11 as a tracer for stormwater inputs.

In the Portland Harbor, PCBs from groundwater had undergone extensive microbial dechlorination, producing a unique congener pattern that could be traced throughout the estuary. The dechlorination signal was most abundant at low flow, providing strong evidence that it is associated with groundwater inputs.

Industrial wastewater effluents are often characterized by a single Aroclor, so we might be able to identify them as well.

- **Can the handful (three in the Spokane River, two in Latah Creek) of anomalously high river PCB concentrations observed during patchy wet weather during the August 2014 synoptic survey be linked to wet weather sources?**

Given the relatively small amount of data, I'm not as confident that any such link can be established. However, the PMF fingerprinting analysis will reveal which factors are dominant in these anomalous samples, and will tell us if the same fingerprints are elevated during other high flow events, and whether they match fingerprints observed in the stormwater, treated effluent, groundwater, or other samples.

- **Does the contaminated groundwater up-gradient of Kaiser show as a significant contributor to the concentrations observed at Trent Ave. Bridge during the synoptic surveys?**

As noted above, groundwater might have a very distinct congener pattern that can be traced through the river. Even if the groundwater does not display signs of microbial dechlorination, it may be possible to infer groundwater sources from their spatial trends. Groundwater sources should be proportionately more important under low flow conditions, so the monthly sampling, which hopefully covers a variety of flow regimes, might help us tease out the groundwater signal.

Budget

Dr. Rodenburg will bill her time at a rate of $200 per hour. Given the size of the project, the work would be contracted through Rutgers University at an overhead rate of 26%. This cost will be paid by Dr. Rodenburg out of her hourly rate.

PMF analysis: 80 hours per data set x 4 data sets = 320 hours

Mapping of PMF results: 10 hours per data set = 40 hours

Write final report: 40 hours

Total = 400 hours @ $200 per hour = $80,000