NOTES ON THE USE OF THE SEDIMENT PCB PARTITIONING STUDY TO PARAMETERIZE COEFFICIENTS IN CPG'S WATER COLUMN PARTITIONING FRAMEWORK, IN SUPPORT OF DISCUSSIONS WITH USEPA ON DRAFT LPR RI COMMENTS

At the September 20, 2016 modeling meeting, USEPA Region 2 suggested that the PCB partitioning study conducted in conjunction with the CPG Low Resolution Coring program could be used to help parameterize the partition coefficient Koc in CPG's proposed water column partitioning framework. That coefficient in the context of the framework characterizes the true equilibrium state of the reversibly sorbed contaminant, i.e., the mass associated with the "fraction equilibrium" (f_E) parameter.

The Koc values reported in the PCB partitioning study (based on the June 17, 2011 technical update[1]) are not reliable choices for parameterizing the framework because of the following concerns:

1. They likely reflect the presence of a resistant phase that did not desorb to equilibrium during the 28-day experiment. Past studies have noted the presence of a resistantly sorbed phase whose desorption time scales for PCBs and other hydrophobic contaminants are much longer than 28 days (e.g., Carroll et al. 1994; Coates and Elzerman 1986; Cornelissen et al. 1997; Hulscher et al. 1999; Pignatello and Xing 1996; Sormunen et al. 2009). Because the concentrations in the dissolved phase and in the polyoxymethylene (POM) sampler can only reflect the contaminant fraction available for desorption within 28 days, the inferred (or apparent) Koc values are likely higher than the true equilibrium values.
2. They may also reflect an incomplete equilibration of the POM sampler with the contaminant fraction that was available for desorption within 28 days, particularly for higher chlorinated congeners. POM kinetic studies (Arp et al. 2015; Smedes et al. 2012) indicate an increase in POM equilibration time with the ratio of sediment mass to POM sampler and non-equilibrium has been observed at 28 days for higher chlorinated congeners using ratios considerably lower than the 500:1 ratio used in the

[1] Transmitted to Region 2 on July 26, 2011 and entitled "Lower Passaic River Restoration Project Technical Update Re: Assessment of PCB Aqueous Partitioning and Availability in Lower Passaic River Sediments (Group C Analytes)."

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LPR study (100 g of sediment and 200 mg of sampler). An incomplete equilibration can reflect limitations associated with both sediment desorption and POM uptake kinetics, and the extent to which these may have impacted the reported Koc values is unknown because the study did not include longer duration experiments to check for equilibration.

3. They rely on POM partition coefficients (Kpom) that may be inaccurate, particularly for higher chlorinated congeners. Past studies have reported that multiple factors can strongly influence Kpom estimates (Arp et al. 2015) and it is uncertain how these factors may have impacted the LPR study. The development of the Kpom values is not well described, e.g., the study-derived Kpom values are only reported for a subset of congeners, and the measured dissolved and POM-sampler congener concentrations are not reported. The comparison of the study-derived Kpom values to literature is limited to a subset of congeners, and shows that the LPR study used consistently higher Kpom values for the higher chlorinated congeners (as noted by the study authors). No evaluation of the potential impact of Kpom uncertainty or bias is provided.

Literature review is ongoing to determine appropriate choices for true equilibrium Koc values for the reversibly sorbed phase within the proposed partitioning framework. It is noted that the desorption experiments of Smedes et al. (2012) found reasonable agreement between Koc values inferred for the "accessible" phase (Kaoc) and the Koc-Kow relationship from Karickhoff et al. (1979), suggesting that this might be a good choice.

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