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Technical Memorandum: Potential for PCB Contamination from Sampling Equipment Tubing Materials

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1.0 Introduction

Recently Leidos was made aware of issues encountered by the King County Department of Natural Resources and Parks (hereafter 'King County') with contamination of surface water samples by PCBs leaching from the tubing in their ISCO samplers. Leidos is exploring what materials may need to be specifically excluded from use in the groundwater sampling equipment in the upcoming Lower Duwamish Waterway (LDW) sample collection effort targeting PCB congeners. For low-flow groundwater sampling with a shallow water table, a peristaltic pump is typically used, which requires silicone tubing. Down-well tubing material may include polyethylene, Teflon, nylon, or vinyl/PVC. The following synthetic materials are being considered for use in the groundwater sampling process (in addition to copper tubing, which is not evaluated here):

- Standard silicone tubing
- Platinum-cured silicone tubing
- Polyethylene tubing
- Teflon tubing
- Nylon tubing ("Nylaflow")
- Vinyl or PVC flexible tubing

The following sections discuss literature findings regarding the potential presence of PCBs in tubing materials by material.

1.1 Standard Silicone Tubing

As noted above, recent King County surface water sampling in the Green River watershed was impacted by contamination introduced to the samples by the standard silicone rubber tubing in their ISCO samplers (King County 2015, Appendix D). Evaluation of the congener profiles indicates that three congeners (with their coelutions) were strongly associated with blank samples collected with the autosamplers. These congener groups were: PCB-44+47+65,

PCB-45+51 and PCB-68. Together, these congeners comprised between 69 and 89 percent of the total PCBs in the equipment blanks collected for the two studies.

As a result of this finding, King County conducted additional tests to evaluate which piece(s) of the sampling equipment may contribute to equipment blank PCB contamination (Williston et al. 2016). Congeners noted to be elevated were primarily PCB-47, -51, and -68, which comprised 94 and 98 percent of the total PCBs in the two blanks collected through silicone tubing (1,260.5 of a total 1,344 pg/L and 954.7 of a total 973 pg/L, respectively). The researchers hypothesized that the peristaltic pump action warmed the Versilic SPX-50 silicone tubing and facilitated release of PCB-47, -51 and -68 from the silicone tubing. The specific silicone tubing used in the test had previously been used to collect Green River surface water samples.

Perdih and Jan (1994) discuss the formation of PCBs in silicone rubber. These researchers discovered a total of 29 congeners in the silicone rubber tubing they tested. Lower-chlorinated congeners dominated, with PCB-4+10 and PCB-8 both contributing more than 1 mg/kg.

PCB Congener Concentrations in Standard Silicone Rubber

PCB Congener	Silicone Rubber (mg/kg)	PCB Congener	Silicone Rubber (mg/kg)
4/10	1.495	42/37	0.057
6	0.162	44	0.142
7/9	0.052	45	0.043
8	1.735	46	0.121
16/32	0.63	47/48/49	0.482
17	0.487	51/22	0.169
18	0.66	52	0.197
19	0.231	56/60	0.05
24	0.07	66	0.159
25	0.077	68	0.427
26	0.099	70	0.151
28	0.341	74	0.283
33	0.82	99	0.13
40	0.152	101	0.066
		Total PCBs	**9.76 mg/kg**

Source: Perdih and Jan 1994

Dave Hope, CEO of Pacific Rim Laboratories, stated that his lab started noticing PCB-68 in environmental samples; internal work at Pacific Rim has shown PCB-68, along with others, to be present in a variety of plastics, including polyethylene and polypropylene in addition to silicone (Hope 2015, personal communication).

1.2 Platinum-Cured Silicone Tubing

As part of their equipment blank study, King County measured PCB congeners in laboratory reverse osmosis water exposed to platinum-cured silicone tubing (Williston et al. 2016). Results were mixed, with two samples showing no contribution of the tubing to blank contamination and

one showing the tubing contributed 53 percent of the total PCBs (8.2 of a total 15.3 pg/L) when PCB-47, -51,and -68 were subtracted. The tubing used in this test was previously unused.

1.3 Polyethylene

As noted above, Pacific Rim has conducted some internal testing and found PCBs in polyethylene (Hope 2015, personal communication). Congeners detected in plastic housings included PCB-5, -28, -47, -51, and -68 (Hope 2016, personal communication).

After discovering high PCB concentrations in water samples from a relatively pristine area of Norway, Andersson et al. (2012) examined four types of polyethylene plastic (low density polyethylene [LDPE] re-sealable bags, LDPE plastic bags used in a precipitation sampler, high density polyethylene [HDPE] containers, and HDPE container lids) used to store soil and water samples, and found them to be contaminated with PCBs to varying degrees. It is unclear whether this type of contamination would be a problem for tubing, as the authors of this paper noted that "The continued presence of PCBs in plastic materials, 30 years after production and use of PCBs in most countries was prohibited, might be a side effect of the recycling process of plastic materials." If the tubing consists purely of 'virgin' material, could it contain PCBs? Or, might it incorporate recycled plastics that could contain PCBs?

PCBs Leached from LDPE Plastic to Double-Distilled Water

Low Density Polyethylene Bag					
Congener	pg/L	Note	Congener	pg/L	Note
PCB-18	20.7		PCB-128	5.46	
PCB-28	19.5		PCB-138	43.4	
PCB-31	15.5		PCB141	8.27	
PCB-33	11.7		PCB-149	30.8	b
PCB-37	2.07	i	PCB-153	66.9	
PCB-47	9.72	b	PCB-156	2.58	i
PCB-52	18.6	b	PCB-157	2.10	bi
PCB-66	20.6		PCB-167	1.40	
PCB-74	7.52	b	PCB-170	4.83	
PCB-99	27.9		PCB-180	18.7	
PCB-101	42.2	b	PCB-183	4.98	
PCB-105	12.2		PCB-187	12.3	
PCB-114	1.72	i	PCB-189	0.61	<
PCB-118	33.8		PCB-194	2.06	
PCB-122	0.73	<	PCB-206	1.09	<
PCB-123	1.19		PCB-209	0.72	
			Total PCBs	***618***	***pg/L***

<: Lower than detection limit at signal-to-noise 3 to 1

i: Isotope ratio deviates more than 20 % from theoretical value. This may be due to instrumental noise or/and chemical interference.

b: Lower than 10 times method blank.

Notes: Double-distilled water stored with pieces of HDPE plastic container for two weeks. Mono- and di-chlorinated congeners not reported. Data provided by Malin Andersson, Geological Survey of Norway (only a subset of 7 congeners was published in Andersson et al. 2012).

PCBs Leached from HDPE Plastic to Double-Distilled Water

High Density Polyethylene Container & Lid					
Congener	pg/L	Note	Congener	pg/L	Note
PCB-18	87.9		PCB-128	11.7	
PCB-28	70.8		PCB-138	78.9	
PCB-31	73.3		PCB141	19.6	
PCB-33	55.3		PCB-149	75.8	
PCB-37	11.6		PCB-153	143	
PCB-47	41.6		PCB-156	3.68	
PCB-52	75.1		PCB-157	2.08	bi
PCB-66	50.6		PCB-167	2.38	
PCB-74	21.2		PCB-170	5.43	
PCB-99	65.9		PCB-180	19.9	
PCB-101	109		PCB-183	9.21	
PCB-105	30.5		PCB-187	22.6	
PCB-114	4.91		PCB-189	0.79	<
PCB-118	86.3		PCB-194	0.61	<
PCB-122	0.78	<	PCB-206	1.20	<
PCB-123	2.46		PCB-209	0.41	
			Total PCBs	***1,880***	***pg/L***

<: Lower than detection limit at signal-to-noise 3 to 1

i: Isotope ratio deviates more than 20 % from theoretical value. This may be due to instrumental noise or/and chemical interference.

b: Lower than 10 times method blank.

Notes: Double-distilled water stored with pieces of HDPE plastic container for two weeks. Mono- and di-chlorinated congeners not reported. Data provided by Malin Andersson, Geological Survey of Norway (only a subset of 7 congeners was published in Andersson et al. 2012).

PCB concentrations of packaging material (ng/kg)

Material	Σ 7 PCBs	PCB-28	PCB-52	PCB-101	PCB-118	PCB-138	PCB-153	PCB-180
Ziploc Bag	4,300	2,400	900	480	140	140	200	<100
Plastic Bag	2,500	1,300	460	320	110	110	160	<100
HDPE container	870	510	230	130	<100	<100	<100	<100
HDPE container lid	400	290	110	<100	<100	<100	<100	<100

PCB concentrations of 3 replicate analyses of HDPE container plastic (ng/kg)

Replicate	Σ 7 PCBs	PCB-28	PCB-52	PCB-101	PCB-118	PCB-138	PCB-153	PCB-180
1	61,000	11,000	6,000	21,000	4,100	7,200	11,000	690
2	39,000	4,300	3,200	14,000	3,100	6,000	7,900	300
3	51,000	7,500	6,300	23,000	2,800	3,900	7,200	230

1.4 Teflon Tubing

Teflon is a fluorinated polymer compound, and so would not be expected to become contaminated with PCBs during manufacture because there are no chlorinated compounds introduced in the process. However, when testing Teflon tubing, King County obtained inconsistent results from the two blank samples they analyzed (Williston et al. 2016). In one sample, PCB-47, -51, and -68 accounted for 77 percent of the total PCBs in the blank (74.7 pg/L of a total 97 pg/L), but in the second sample these congeners accounted for only 18 percent of the total PCBs in the blank (11.4 pg/L of a total 63.2 pg/L). The Teflon tubing used in the test had previously been used as an intake line during Green River sampling, so it is possible it might have been contaminated in the field.

1.5 Nylon Tubing

There are many different types of nylon, each with their own manufacturing processes. Based on information received from Nylaflow, they do not chemically alter the nylon pellets they receive. Jennifer Wallin of Leidos requested information about the source of the nylon pellets they use, but no reply has been received as of the date of this memo.

1.6 Vinyl and Polyvinyl Chloride Flexible Tubing

Vinyl chloride is listed by the EPA as a product with the potential for PCBs to be created during its manufacture. Polyvinyl chloride (PVC) is created by polymerization of vinyl chloride. A literature search conducted by Leidos did not identify any information regarding PCBs measured in vinyl or PVC, but apparently PCBs were formerly added to PVC before the ban.

2.0 Recommendations

- Given the potential for PCBs to occur in recycled materials, based on the research by Andersson et al. (2012), it is recommended that recycled materials not be used.
- Teflon tubing is a fluorinated, not chlorinated, material and would not be expected to be contaminated with PCBs. However, because the King County results were inconsistent, Teflon tubing should be considered for further blank testing, to explore if the contamination they found may have been from previous field use.
- Platinum-cured silicone tubing could be a potential source of PCBs to samples (one of three blank samples run through this material by King County had silicone-associated PCB contamination), but at low concentrations (8.2 pg/L), and is recommended for use in the upcoming groundwater sampling effort. Standard silicone tubing should not be used.
- PVC and vinyl materials should be avoided.
- Other non-organic material should also be considered, such as flexible copper tubing.

3.0 References

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