PFAS levels in Michigan Deer from the Huron River Area

Michigan Department of Health and Human Services

Division of Environmental Health

Michigan Fish Consumption Advisory Program

October 1, 2019

Summary

In April 2019, samples were taken from 20 white-tailed deer within five miles of Norton Creek in the Proud Lake Recreation Area to test for PFAS. Samples of muscle, liver, kidney, and heart were tested for multiple PFAS. No PFAS were found in any muscle or heart samples. In liver and kidney samples, PFOS was the only PFAS found.

Muscle and liver samples were also tested for polychlorinated biphenyls (PCBs) and other chemicals. No PCBs or other chemicals were found in muscle samples. Some liver samples had very low detectable levels of PCBs.

Based on this data, MDHHS concluded consumption guidelines are not needed for deer from the Norton Creek area. Organs (liver and kidneys) may contain higher levels of chemicals than muscle, so MDHHS recommends that people not eat the organs.

This additional deer testing was a follow-up to Michigan's previous deer testing, from areas known to have PFAS contamination in lakes or rivers. In August 2018, elevated PFOS levels were identified in fish collected from Kent Lake, an impoundment of the Huron River. Surface water samples collected in July, August, and October 2018 from Norton Creek - which flows into the Huron River – and from the Huron River (downstream of Norton Creek) had elevated levels of PFOS.

In 2018, the State of Michigan collected tissue samples from 128 white-tailed deer across Michigan to test for per- and polyfluoroalkyl substances (PFAS). In October of 2018, the Michigan Department of Health and Human Services (MDHHS) and Michigan Department of Natural Resources (MDNR) issued a 'Do Not Eat' advisory for deer taken within five miles of Clark's Marsh in Oscoda Township. The advisory was due to high levels of PFAS, specifically perfluorooctane sulfonate (PFOS), found in a single deer taken within five miles of the Marsh, which has elevated levels of PFAS in the surface water. The advisory encircles the five-mile radius around the former Wurtsmith Air Force Base property and covers what the MDNR has estimated to be the expected travel range of deer living in or near Clark's Marsh.

Given the high PFOS levels in a single deer previously collected in an area with high levels of PFOS in surface water, and the August 2018 results showing high PFOS levels in surface water and fish tissue samples from Huron River watershed, the decision was made to harvest white-tailed deer from the Huron River/Norton Creek area for tissue testing.

Based on this data, MDHHS concluded consumption advisories are not needed for deer from the Norton Creek area. MDHHS recommends that people not consume organs (liver and kidneys) due to the potential for higher levels of chemicals to be in the organs compared to muscle tissue.

Norton Creek and Huron River area PFAS, including surface water levels

In August 2018, MDHHS received Kent Lake fish filet PFOS data. Based on the elevated levels of PFOS in the fish filets, MDHHS issued a "Do Not Eat" fish advisory for the Huron River at Milford to the Livingston/Washtenaw County line. The Michigan Department of Environment, Great Lakes, and Energy (EGLE) had collected surface water samples in July 2018 from multiple locations in Norton Creek and the Huron River. Later in August, the surface water results were available. Levels of PFOS were 5,500 nanograms per liter (ng/L or parts per trillion) in Norton Creek water samples near the confluence with

the Huron River and 1,400 ng/L in a Huron River water sample collected at Burns Road downstream of Norton Creek. An upstream water sample, collected from the Huron River at N. Wixom Road had a PFOS level of 2.4 ng/L.

Based on elevated levels of PFOS in surface water from Norton Creek and the Huron River near Norton Creek, the "Do Not Eat" fish advisory was expanded upstream of Milford to N. Wixom Road. Several days later, MDHHS received fish filet data from locations downstream of the Livingston/Washtenaw County line. This additional fish filet PFOS data prompted the final expansion of the "Do Not Eat" fish advisory to Lake Erie.

EGLE continued to monitor surface water PFOS levels in Norton Creek and the Huron River after the initial samples were collected. Initial samples were collected in July 2018, with more intensive follow-up sampling in August and October 2018, and April 2019. To date, no other surface water location in the Huron River watershed has been found to have PFOS levels similar to those measured in Norton Creek in July 2018. Additional information on the on-going work in the Huron River watershed can be found at Michigan.gov/pfasresponse under Investigations and Sites, Sampling in Lakes and Streams, Huron River Watershed (https://www.michigan.gov/pfasresponse/investigations/lakes-and-streams/huron-river).

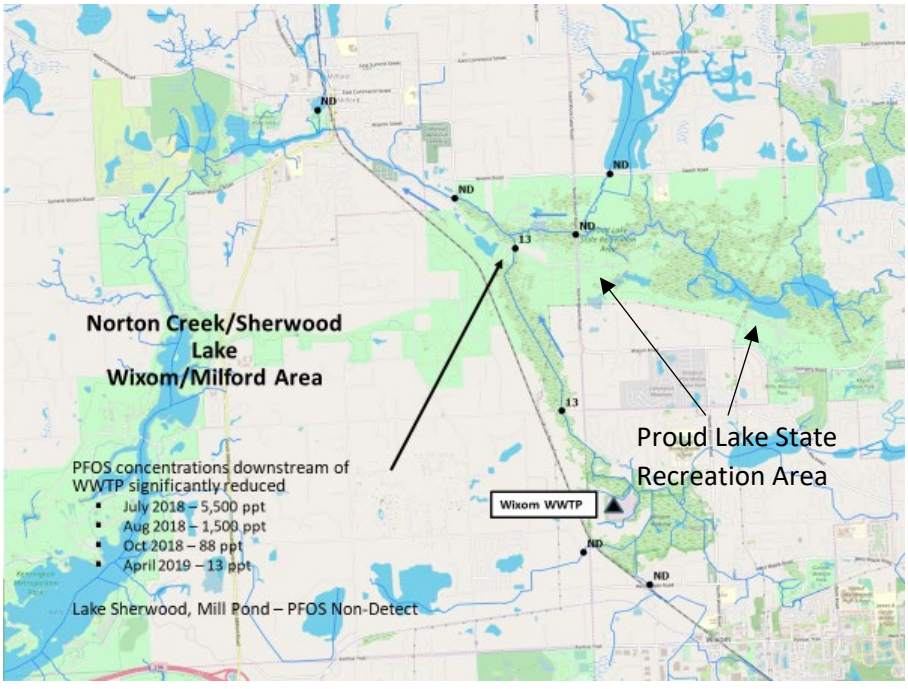

Figure 1: Surface water sampling results from the Norton Creek and Huron River area. The Wixom Wastewater Treatment Plant (WWTP) is the triangle. The Wixom WWTP installed the PFOS removal treatment system in October 2018.

Deer tissue sample collection and testing

In April 2019, the U.S. Department of Agriculture (USDA) Animal and Plant Health Inspection Service (APHIS) sharpshooters harvested the deer and collected all tissue samples through an inter-agency

agreement with MDNR and funding provided to MDNR through MDHHS. Protocols for tissue sampling were standardized and followed those used in the MDNR Wildlife Disease Laboratory.

Twenty deer (age 1 and older; both sexes) were sampled from the Proud Lake Recreation Area (Figure 2). All deer were harvested from within 5 miles of Norton Creek which represents a typical approximate range of travel for deer and a potential for exposure to PFAS by drinking contaminated surface water.

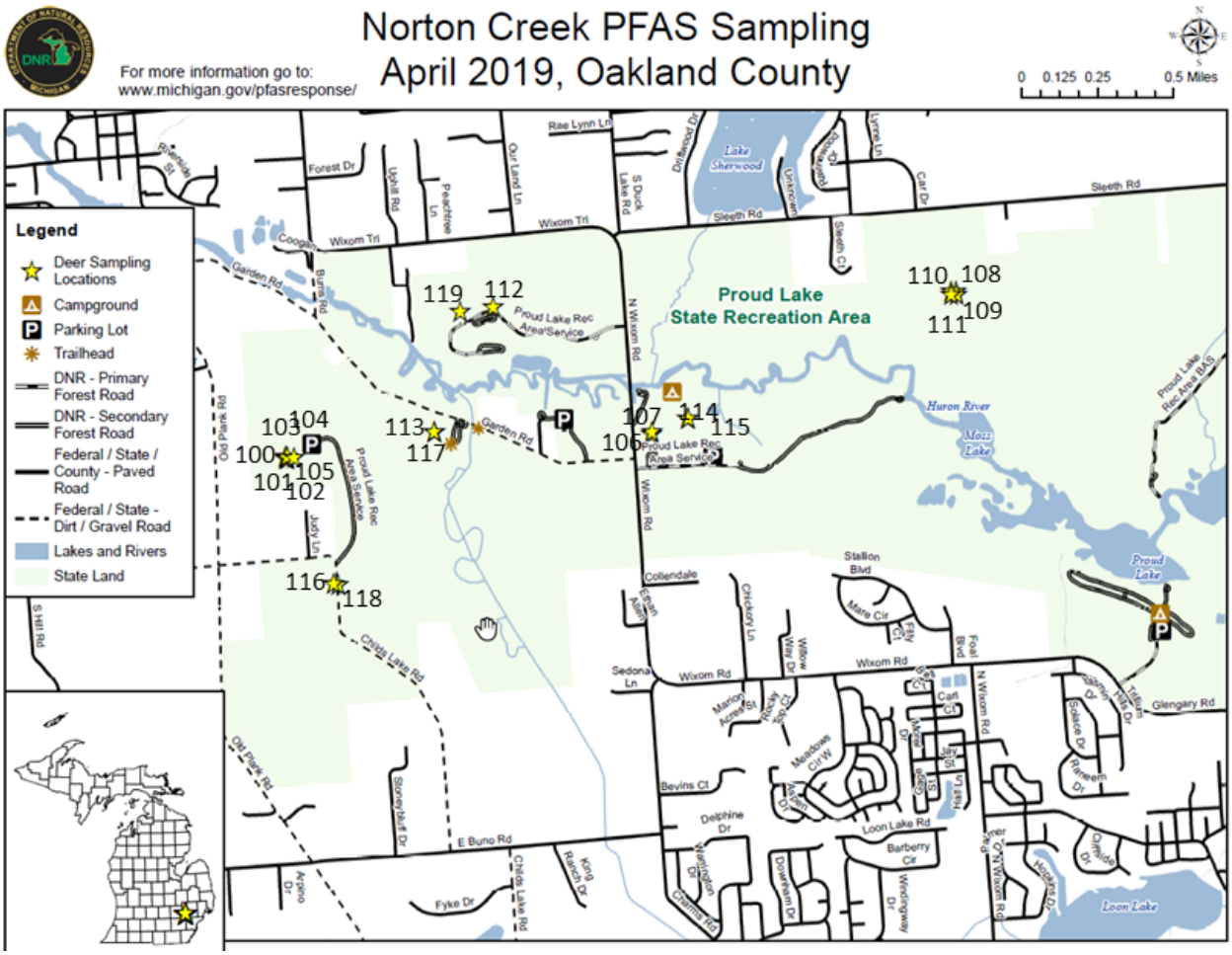

Figure 2: Locations for deer harvested for PFAS sampling within 5 miles of Norton Creek.

Disease testing after harvest

Field and laboratory assessments for bovine tuberculosis (bTB)[1,2] and Chronic Wasting Disease (CWD) were conducted based on existing protocols through the MDNR's Wildlife Disease Laboratory analysis to

[1] O'Brien DJ, Fitzgerald SD, Lyon TJ, et al. 2001. Tuberculous lesions in free-ranging white-tailed deer in Michigan. J Wildl Dis. 37(3):608-13.

[2] O'Brien DJ, Schmitt SM, Fierke JS, et al. 2002. Epidemiology of Mycobacterium bovis in free-ranging white-tailed deer, Michigan, USA, 1995–2000. Prev Vet Med. 54(1):47-63.

prevent exposure of MDHHS Analytical Chemistry Lab personnel. All deer were tested and found negative for bTB and CWD. Samples were then processed and analyzed for PFAS, PCBs, and other selected contaminants.

Upon collection, individual deer were uniquely identified, and all samples were labeled. (See Appendix A for a list of identifiers). Additional data collected for targeted deer testing included:

- the location (GPS preferred) of collection;
- results of TB field assessment (i.e., presence or absence of pleural lesions in the chest cavity suggestive of bTB);
- date and time of collection;
- position of the bullet entry hole, exit wound, and bullet/broadhead type;
- sex of the animal; and
- health description of the animal.

MDNR communicated the results of the bTB and CWD testing to the MDHHS lab to commence testing for PFAS, PCBs, and other chemicals.

All deer were also aged by MDNR. Tooth eruption and wear is a widely used, accepted, and reliable method for estimating age in white-tailed deer, particularly in younger animals, which comprise most of the population. Ages of the deer are estimated based on eruption of the teeth through the gums and wear of the cheek teeth (premolars and molars).[3]

Sample Collection for Contaminant Analyses

The following samples were collected:

- Muscle tissue –100-200 grams, without connective tissue or tendons
- Liver – 100-200 grams
- Kidney – 100-200 grams
- Heart – 100-200 grams

Muscle was collected from the hamstring, or large muscle mass in the hind quarters of the deer. No specific area of the liver or kidney was targeted for sampling during field collection of the samples. Sample amounts in excess of 100-200 grams (g) may have been collected, but there needed to be at least 50 g. No more than 250 g was needed for laboratory analysis.

Tissue samples were placed in sealable plastic bags and labeled. All samples were stored in the freezer until processing for analysis at the MDHHS Analytical Chemistry Laboratory.

PFAS analysis in deer tissue

The MDHHS Analytical Chemistry Laboratory homogenized, extracted, and analyzed all samples for PFAS. The laboratory's method for PFAS uses reversed-phase high-performance liquid chromatography with multiple reaction monitoring tandem mass spectrometry (HPLC-MRM-MS/MS) following their

[3] Severinghous, CW 1949. Tooth development and wear as criteria of age in white-tailed deer. J Wildl Manage 13:195–216.

standard operating procedures. The list of PFAS analyzed for in deer tissues can be found in Table 1. Only 11 PFAS are quantified.[4]

Table 1: PFAS measured in deer muscle, liver, kidney, and heart tissue harvested in Michigan and analyzed in the MDHHS Analytical Chemistry Laboratory.

Abbreviation	Name
PFHxA[1]	Perfluorohexanoic acid
PFHpA[1]	Perfluoroheptanoic acid
PFOA	Perfluorooctanoic acid (branched and linear)
PFNA	Perfluorononanoic acid
PFDA	Perfluorodecanoic acid
PFUnA	Perfluoroundecanoic acid
PFDoA	Perfluorododecanoic acid
PFTriA	Perfluorotridecanoic acid
PFTeA	Perfluorotetradecanoic acid
PFHxDA[1]	Perfluoro-n-hexadecanoic acid
PFODA[1]	Perfluoro-n-octadecanoic acid
PFBS[1]	Perfluorobutanesulfonic acid
PFHxS	Perfluorohexane sulfonate (branched and linear)
PFOS	Perfluorooctane sulfonate (branched and linear)
PFDS	Perfluorodecanesulfonic acid
PFOSA	Perfluorooctane sulfonamide
1 = This is not quantified in tissue samples although it is included in the method.	

PCB and other chemical analysis in deer tissue

The MDHHS Analytical Chemistry Laboratory homogenized, extracted, and analyzed all samples for PCBs and other chemicals. The laboratory's method for PCB congeners and pesticides uses a gas chromatography with electron capture detection following their standard operating procedures.[5] Along with 100 PCB congeners, aldrin, heptachlor, and polybrominated biphenyl 153 were measured in deer tissue. The list of PCB congeners analyzed for in deer tissues can be found in Appendix B.

PFAS levels in muscle, liver, kidney, and heart

Muscle, liver, kidney, and heart samples were collected from 20 deer (5 male, 15 female) in April 2019 and analyzed for PFAS. The only PFAS detected in any tissue type was PFOS, and no PFAS were detected in any muscle or heart sample (Table 2). PFOS was detected in liver samples from 10 deer (samples from

[4] This is the same method that the MDHHS Analytical Chemistry Laboratory developed for fish tissue analysis. Five additional PFAS are included in the method, but not quantified as they are not found in tissue samples.
[5] This is the same method that the MDHHS Analytical Chemistry Laboratory developed for fish tissue analysis.

two males [deer #101, 106] and eight females [deer #102, 103, 104, 105, 107, 112, 113, and 117]). PFOS was detected in kidney samples from six deer (samples from three males [deer #100, 101, and 116] and three females [deer #102, 104, and 112]).

Table 2: PFOS levels in muscle, liver, kidney, and heart samples (in nanograms per gram [ng/g] or parts per billion [ppb]) from deer harvested in the Norton Creek area. No other PFAS were detected in any of the samples.

PFAS	Deer tissue	Number of samples with detections	Range (minimum to maximum in parts per billion [ppb])
PFOS	Muscle	0/20	<0.25 ppb
	Liver	10/20	<0.25 to 4.48 ppb
	Kidney	6/20	<0.25 to 0.54 ppb
	Heart	0/20	<0.25 ppb

PCB and other chemical levels in muscle and liver

Muscle and liver samples from twenty deer (5 male, 15 female), collected in April 2019, were analyzed for 100 PCB congeners (Table 3). Percent lipid (fat) was also measured in the liver and muscle samples. In the liver samples, the percent lipid ranged from 1.37 to 4.49%. In the muscle samples, the percent lipid ranged from 0.19 to 0.98%.

Other chemicals (aldrin, heptachlor, and polybrominated biphenyl 153) were also measured with the PCB congener analyses. There were no detections of these three chemicals in either liver or muscle samples.

Table 3: PCB levels in muscle and liver samples (in nanograms per gram [ng/g] or parts per billion [ppb]) from deer harvested in the Norton Creek area.

Chemical	Deer tissue	Number of samples with detections	Range (minimum to maximum in parts per billion [ppb])
Total PCBs	Muscle	0/20	<1 ppb
	Liver	11/21 (1 duplicate)[1]	<1 to 2 ppb
1 = PCB 153, 118, 170, 180, 199, and 40 were detected in liver samples. Only two deer (deer #106 [2 ppb] and deer #113 [1.5 ppb]) had detections of total PCBs above 1 ppb.			

Appendix A: Age and sex for deer harvested in Oakland County within five miles of Norton Creek.

Sample ID	CWD Tag #	Date	GPS Location	Sex	Age Class	Age	Health Notes	TB Field Assessment and CWD results
Deer 100	675751	4/10/2019	N 42.57124, W - 83.58210	Male	Adult	1	Healthy	Negative
Deer 101	675752	4/10/2019	N 42.57126, W - 83.58200	Male	Adult	1	Healthy	Negative
Deer 102	675753	4/10/2019	N 42.57135, W - 83.58214	Female	Adult	1	Healthy	Negative
Deer 103	675754	4/10/2019	N 42.57132, W - 83.58209	Female	Adult	1	Healthy	Negative
Deer 104	675755	4/10/2019	N 42.57137, W - 83.58201	Female	Adult	2	Healthy	Negative
Deer 105	675756	4/10/2019	N 42.57131, W - 83.58160	Female	Adult	4	Healthy	Negative
Deer 106	675757	4/10/2019	N 42.57192, W - 83.55854	Male	Adult	1	Healthy	Negative
Deer 107	675758	4/10/2019	N 42.57202, W - 83.55851	Female	Adult	6	Healthy	Negative
Deer 108	675759	4/10/2019	N 42.57825, W - 83.53868	Female	Adult	3	Healthy	Negative
Deer 109	675760	4/10/2019	N 42.57825, W - 83.53900	Female	Adult	4	Healthy	Negative
Deer 110	675761	4/10/2019	N 42.57810, W - 83.53864	Female	Adult	7	Healthy	Negative
Deer 111	675762	4/10/2019	N 42.57811, W - 83.53899	Male	Adult	1	Healthy	Negative
Deer 112	675763	4/18/2019	N 42.57815, W - 83.56851	Female	Adult	3	Healthy	Negative
Deer 113	675764	4/18/2019	N 42.57233, W - 83.57248	Female	Adult	6	Healthy	Negative
Deer 114	675765	4/18/2019	N 42.57261, W - 83.55619	Female	Adult	5	Healthy	Negative
Deer 115	675766	4/18/2019	N 42.57262, W - 83.55615	Female	Adult	1	Healthy	Negative
Deer 116	675767	4/18/2019	N 42.56520, W - 83.57899	Male	Adult	1	Healthy	Negative
Deer 117	675768	4/18/2019	N 42.57231, W - 83.57252	Female	Adult	1	Healthy	Negative
Deer 118	675769	4/18/2019	N 42.56524, W - 83.57926	Female	Adult	5	Healthy	Negative
Deer 119	675770	4/18/2019	N 42.57802, W - 83.57063	Female	Adult	2	Healthy	Negative

Appendix B: List of polychlorinated biphenyl congeners measured in deer tissue.

Structure	Congener number
CHLOROBIPHENYL	
2	PCB 1
4	PCB 3
DICHLOROBIPHENYL	
2,4'	PCB 8
3,3'	PCB 11
TRICHLOROBIPHENYLS	
2,2',3	PCB 16
2,2',4	PCB 17
2,2',5	PCB 18
2,3,4'	PCB 22
2,3',4	PCB 25
2,3',5	PCB 26
2,3',6	PCB 27
2,4,4'	PCB 28
2,4',5	PCB 31
2,4',6	PCB 32
2',3,4	PCB 33
3,4,4'	PCB 37
TETRACHLOROBIPHENYLS	
2,2',3,3'	PCB 40
2,2',3,4'	PCB 42
2,2',3,5'	PCB 44
2,2',3,6	PCB 45
2,2',4,4'	PCB 47
2,2',4,5	PCB 48
2,2',4,5'	PCB 49
2,2',5,5'	PCB 52
2,3,3',4'	PCB 56
2,3,4,4'	PCB 60
2,3',4',5	PCB 63
2,3,4',6	PCB 64
2,3',4,4'	PCB 66
2,3',4',5	PCB 70
2,3',4',6	PCB 71

Structure	Congener number
2,4,4',5	PCB 74
3,3',4,4'	PCB 77
3,4,4',5	PCB 81
PENTACHLOROBIPHENYLS	
2,2',3,3',4	PCB 82
2,2',3,3',5	PCB 83
2,2',3,3',6	PCB 84
2,2',3,4,5'	PCB 87
2,2',3,4',5	PCB 90
2,2',3,4',6	PCB 91
2,2',3,5,5'	PCB 92
2,2',3,5',6	PCB 95
2,2',3',4,5	PCB 97
2,2',4,4',5	PCB 99
2,2',4,4',6	PCB 100
2,2',4,5,5'	PCB 101
2,3,3',4,4'	PCB 105
2,3,3',4',6	PCB 110
2,3,4,4',5	PCB 114
2,3',4,4',5	PCB 118
2,3',4,4',5'	PCB 123
3,3',4,4',5	PCB 126
HEXACHLOROBIPHENYLS	
2,2',3,3',4,4'	PCB 128
2,2',3,3',4,5'	PCB 130
2,2',3,3',4,6'	PCB 132
2,2',3,3',5,6	PCB 134
2,2',3,3',5,6'	PCB 135
2,2',3,3',6,6'	PCB 136
2,2',3,4,4',5	PCB 137
2,2',3,4,4',5'	PCB 138
2,2',3,4,5,5'	PCB 141
2,2',3,4,5',6	PCB 144
2,2',3,4',5,5'	PCB 146
2,2',3,4',5',6	PCB 149
2,2',3,5,5',6	PCB 151
2,2',4,4',5,5'	PCB 153
2,3,3',4,4',5	PCB 156

Structure	Congener number
2,3,3',4,4',5'	PCB 157
2,3,3',4,4',6	PCB 158
2,3,3',4,5,6	PCB 160
2,3,3',4',5,6	PCB 163
2,3',4,4',5,5'	PCB 167
3,3',4,4',5,5'	PCB 169
HEPTACHLOROBIPHENYLS	
2,2',3,3',4,4',5	PCB 170
2,2',3,3',4,4',6	PCB 171
2,2',3,3',4,5,5'	PCB 172
2,2',3,3',4,5,6'	PCB 174
2,2',3,3',4,5',6	PCB 175
2,2',3,3',4',5,6	PCB 177
2,2',3,3',5,5',6	PCB 178
2,2',3,3',5,6,6'	PCB 179
2,2',3,4,4',5,5'	PCB 180
2,2',3,4,4',5,6'	PCB 182
2,2',3,4,4',5',6	PCB 183
2,2',3,4,5,5',6	PCB 185
2,2’,3,4’,5,5’,6	PCB 187
2,3,3',4,4',5,5'	PCB 189
2,3,3',4,4',5,6	PCB 190
2,3,3',4',5,5',6	PCB 193
OCTACHLOROBIPHENYLS	
2,2',3,3',4,4',5,5'	PCB 194
2,2',3,3',4,4',5,6	PCB 195
2,2',3,3',4,4',5,6'	PCB 196
2,2’,3,3’,4,5,5’,6	PCB 198
2,2',3,3',4,5,6,6'	PCB 199
2,2',3,3',4,5,6,6'	PCB 200
2,2',3,3',4,5,5',6'	PCB 201
2,2',3,4,4',5,5',6	PCB 203
2,3,3',4,4',5,5',6	PCB 205
NONACHLOROBIPHENYLS	
2,2',3,3',4,4',5,5',6	PCB 206
2,2',3,3',4,4',5,6,6'	PCB 207

PCB 104 and PCB 209 are used as surrogate spikes