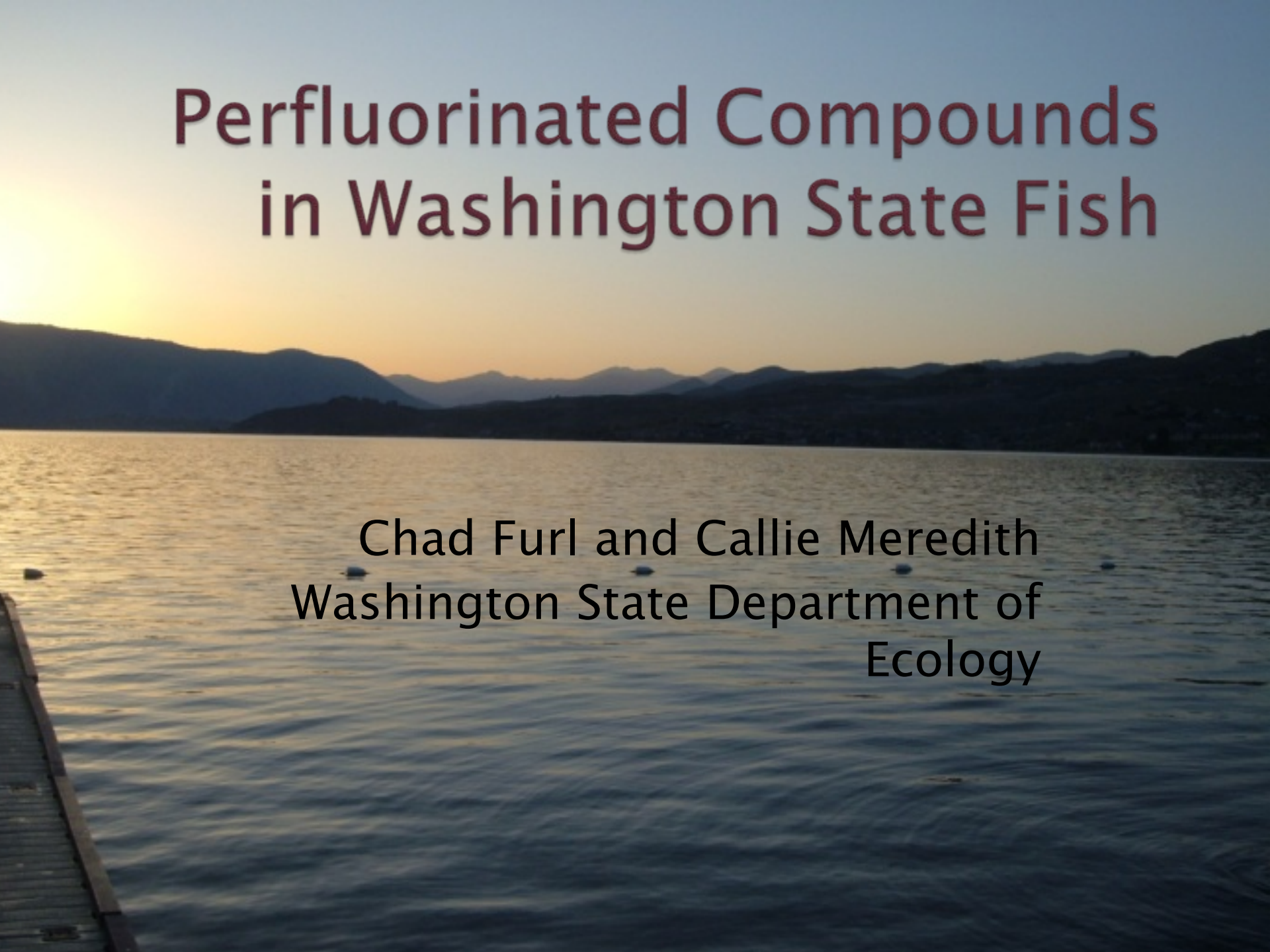
Perfluorinated Compounds in Washington State Fish



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Why study PFCs?

- Ecology PBT rule
  - Set forth criteria used to establish PBTs
  - List of 27 contaminants and metals of concern.
- Chemical Action Plans (CAPs)
  - Identify, characterize and evaluate all uses and releases of a specific PBT chemical.
  - Ultimate goal is to reduce and phase-out the use, release, and exposure to PBTs in Washington.
  - PBT chemicals eligibility for CAP development determined through a screening process.

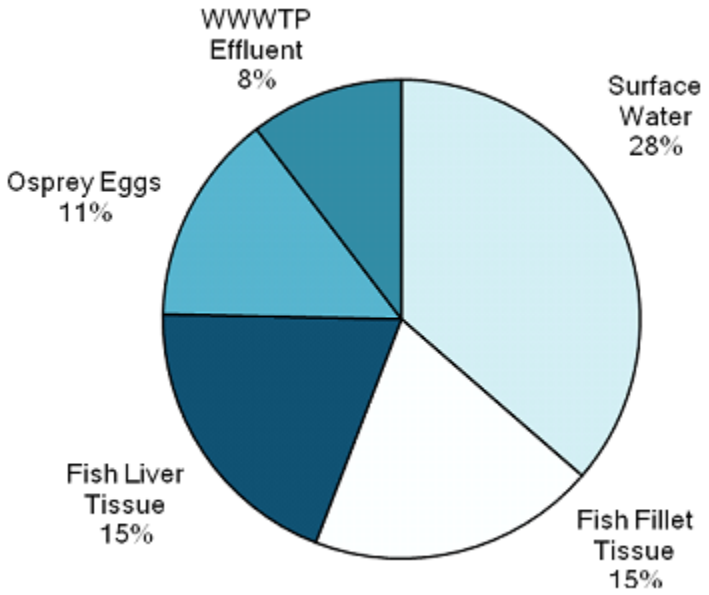
Why study PFCs?

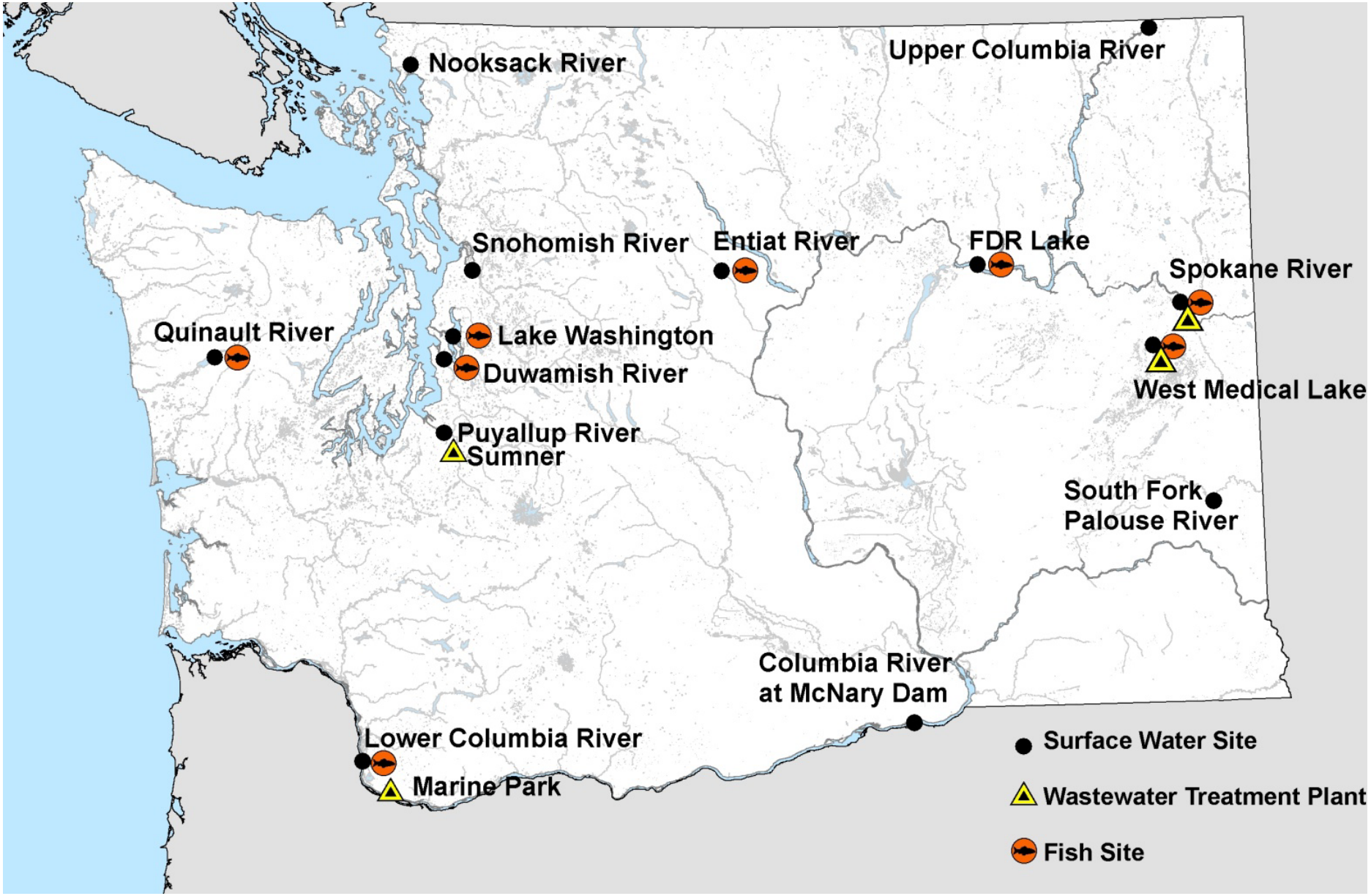
PBT List			
Metals	**Flame Retardants**	**Banned Pesticides**	**Organic Chemicals**
Methyl-mercury	***PBDEs***	Aldrin/Dieldrin	1,2,4,5-TCB
	Tetrabromobisphenol A	Chlordane	**Perfluoro-octane sulfonate**
	Hexabromocyclododecane	DDT/DDD/DDE	Hexachlorobenzene
	Pentachlorobenzene	Heptachlor Epoxide	Hexachlorobutadiene
		Toxaphene	Short-chain chlor parraffin
		Chlordecone	Polychlorinated Naphthalenes
		Endrin	
		Mirex	
Combustion By-Products	**Banned Flame Retardants**	**Banned Organic Chemicals**	**Metals of Concern**
PAHs	Hexabromobiphenyl	PCBs	Cadmium
PCDD			***Lead***
PCDF			
PBDD/PBDF			

Monitoring is conducted through Ecology's PBT program which receives funds from the State Toxics Account.

Study Design

- Exploratory survey characterizing surface water, wastewater, fish tissues (fillet and liver), and osprey eggs.
- Broad spatial coverage and contamination potential.

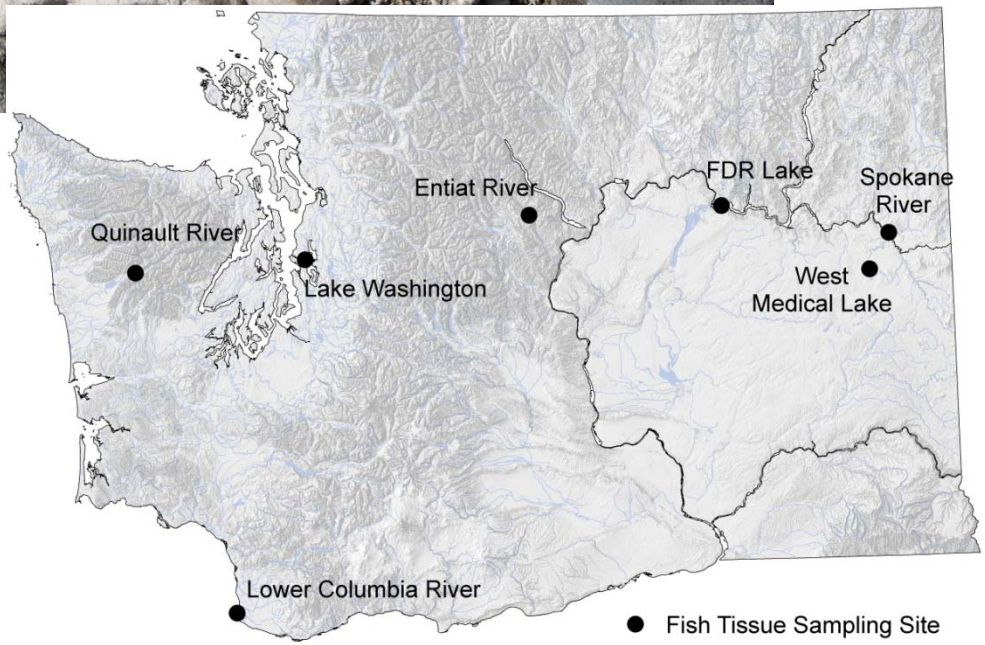




PFC Sampling Sites in Washington State.

Fish Tissue Sites

- Background sites
  - Quinault River
  - Entiat River
- Dense urban
  - Lake Washington
  - Spokane River
  - Lower Columbia River
- Other
  - FDR Reservoir
  - West Medical Lake



Sample Collection and Processing

- Collected fish during Fall 2008.
- Targeted 2 species from each waterbody ideally a predator and a bottom dweller.
- Analyzed skin-off fillet and liver composites of 3-5 fish.
- Homogenized fish with stainless steel sonicator.

Analytical Methods

- EPA Office of Research and Development – RTP, NC
- 10 PFCs, 3 sulfonates (PFBS, PFHS, PFOS), 7 carboxylics (C6 – C12)
- SPE LC/MS/MS
- Delinsky et al. 2009

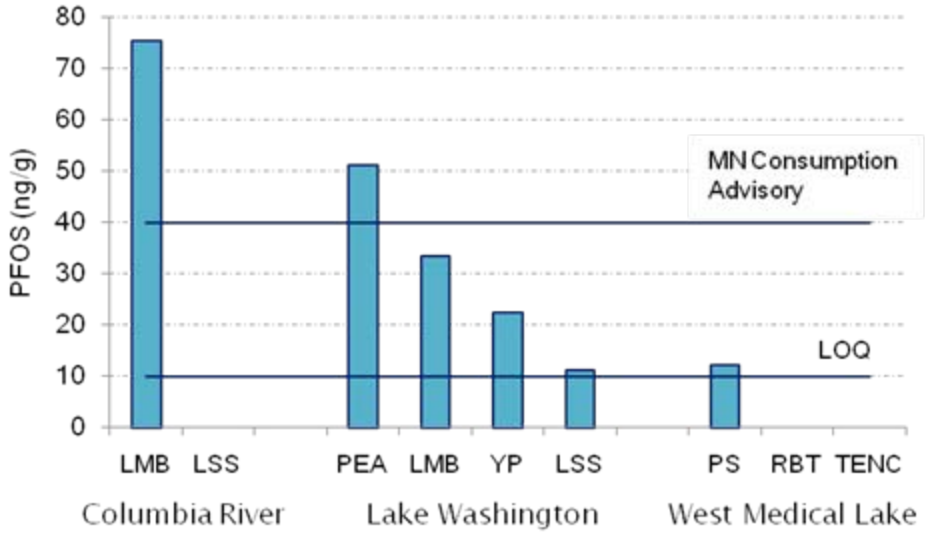
Results

LOQ (ng/g)		5	5	5	5	5	5	5	10	5	5
Waterbody	Species	C12	C11	C10	C9	PFOA	C7	C6	PFOS	PFHS	PFBS
Quinault R.	Cutthroat trout	< LOQ	ND	ND	< LOQ	ND	ND	< LOQ	< LOQ	< LOQ	< LOQ
Entiat R.	Rainbow trout	ND	ND	ND	< LOQ	ND	ND	< LOQ	< LOQ	ND	ND
"	Brook trout	ND	ND	ND	< LOQ	ND	ND	< LOQ	ND	< LOQ	ND
Spokane R.	Largescale sucker	ND	ND	< LOQ	< LOQ	ND	ND	< LOQ	< LOQ	< LOQ	< LOQ
Lower Columbia R.	Largemouth bass	ND	ND	< LOQ	< LOQ	ND	ND	< LOQ	**75.54**	< LOQ	< LOQ
"	Largescale sucker	< LOQ	ND	< LOQ	< LOQ	ND	ND	< LOQ	< LOQ	< LOQ	ND
L. Washington	Largemouth bass	< LOQ	< LOQ	< LOQ	< LOQ	ND	ND	< LOQ	**33.58**	< LOQ	< LOQ
"	Yellow perch	< LOQ	< LOQ	< LOQ	< LOQ	ND	ND	< LOQ	**22.45**	< LOQ	< LOQ
"	Peamouth	**5.5**	**7.15**	< LOQ	< LOQ	ND	ND	< LOQ	**51.21**	< LOQ	< LOQ
"	Largescale sucker	< LOQ	< LOQ	< LOQ	< LOQ	ND	ND	< LOQ	**11.14**	< LOQ	< LOQ
West Medical L.	Pumpkinseed	< LOQ	< LOQ	**7.5**	< LOQ	ND	ND	< LOQ	**12.29**	< LOQ	< LOQ
"	Rainbow trout	ND	ND	< LOQ	< LOQ	ND	ND	< LOQ	< LOQ	ND	< LOQ
"	Tench	ND	ND	< LOQ	< LOQ	ND	ND	< LOQ	< LOQ	< LOQ	< LOQ
FDR Reservoir	Smallmouth bass	ND	ND	< LOQ	< LOQ	ND	ND	< LOQ	< LOQ	< LOQ	< LOQ
"	Walleye	ND	ND	< LOQ	< LOQ	ND	ND	< LOQ	< LOQ	< LOQ	ND

- 15 samples from 11 species
- PFOS and C10 – C12 and were the only PFCs quantified
- Of 150 assays 9 (6%) > LOQ

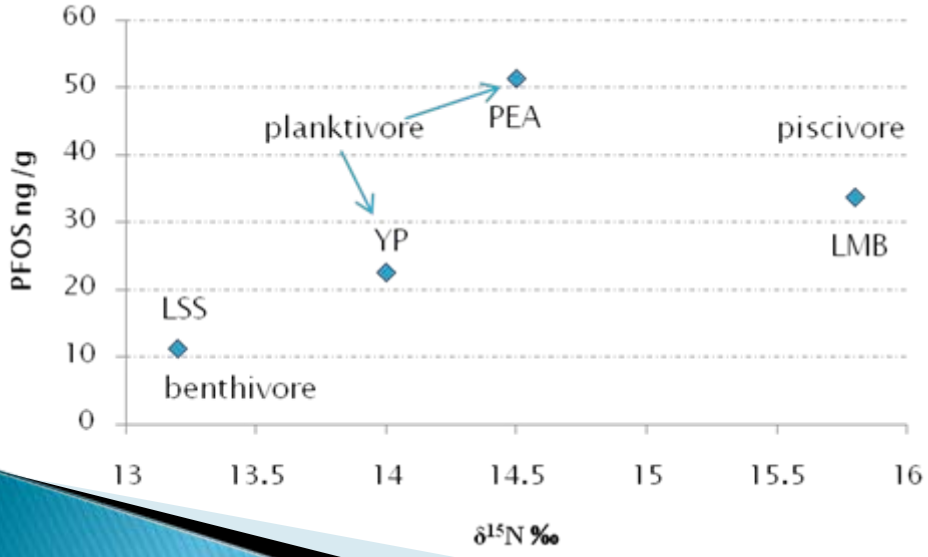
Results

- PFOS > LOQ (10 ng/g) in 6 of 15 (40%) samples representing 3 waterbodies (Lower Columbia R., L. Washington, West Medical L.)
- No PFCs found at background sites, Spokane R., or FDR Reservoir
- Not expected to efficiently bioaccumulate in piscivorous food web.
- Bioconcentration factors > 1,000 for blood, carcass, and liver.



Lake Washington

- Dense urban landscape. Likely sources include stormwater, CSOs, atmospheric transport
- Well studied food web
- PFOS = 5.27 ng/L in fall sampling
- BCF range from 2,000 – 10,000



Osprey Eggs

- 11 eggs collected from nests upstream and downstream of Willamette R.
- Osprey diet consists of ≈ 85% LSS by weight
- Birds winter in rural Mexico and Central America
- LSS fillet and liver sample from study area < LOQ.

Columbia River Osprey Egg PFOS Concentrations (ng/g, ww)

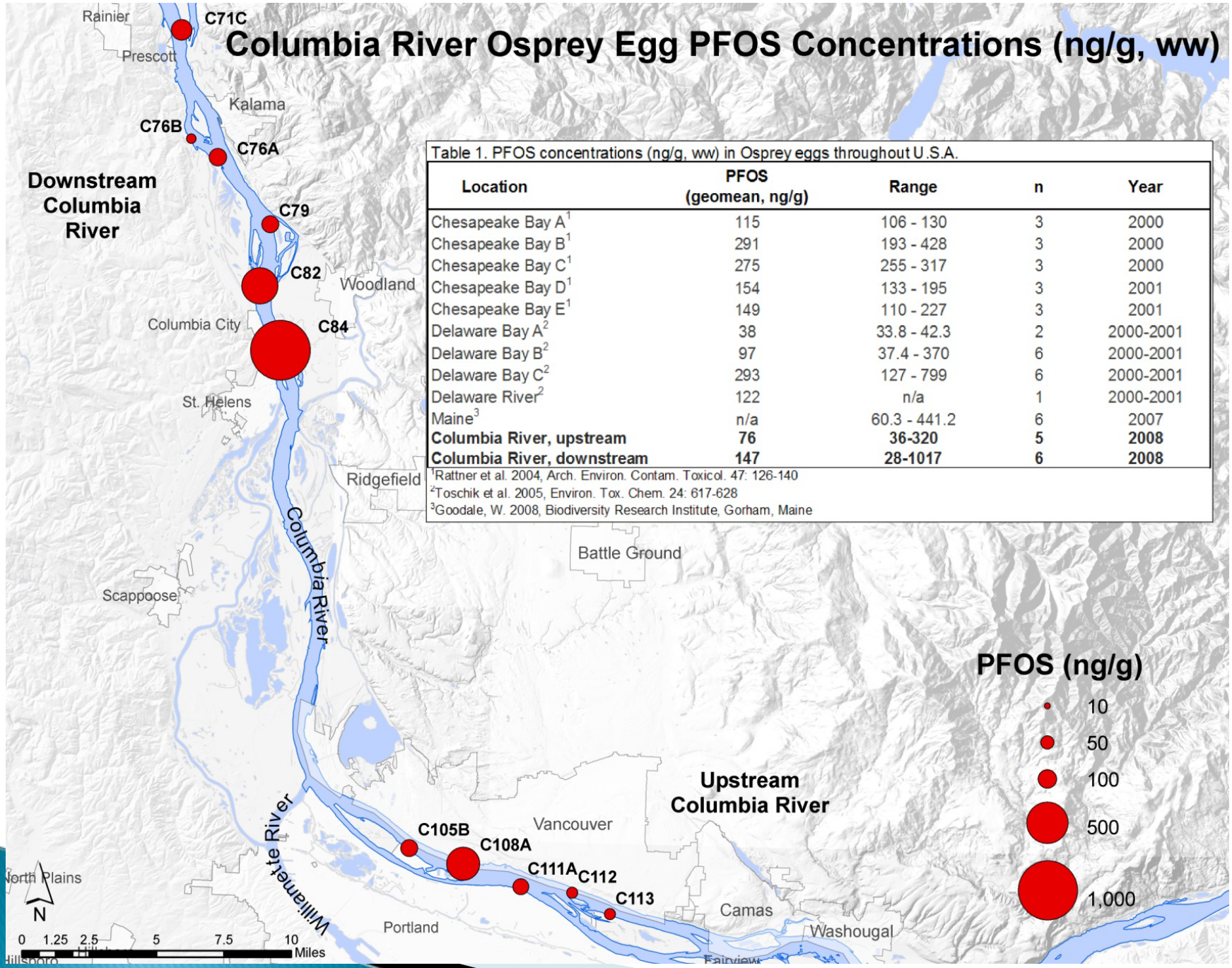


Table 1. PFOS concentrations (ng/g, ww) in Osprey eggs throughout U.S.A.

Location	PFOS (geomean, ng/g)	Range	n	Year
Chesapeake Bay A[1]	115	106 - 130	3	2000
Chesapeake Bay B[1]	291	193 - 428	3	2000
Chesapeake Bay C[1]	275	255 - 317	3	2000
Chesapeake Bay D[1]	154	133 - 195	3	2001
Chesapeake Bay E[1]	149	110 - 227	3	2001
Delaware Bay A[2]	38	33.8 - 42.3	2	2000-2001
Delaware Bay B[2]	97	37.4 - 370	6	2000-2001
Delaware Bay C[2]	293	127 - 799	6	2000-2001
Delaware River[2]	122	n/a	1	2000-2001
Maine[3]	n/a	60.3 - 441.2	6	2007
Columbia River, upstream	**76**	**36-320**	**5**	**2008**
Columbia River, downstream	**147**	**28-1017**	**6**	**2008**

[1]Rattner et al. 2004, Arch. Environ. Contam. Toxicol. 47: 126-140
[2]Toschik et al. 2005, Environ. Tox. Chem. 24: 617-628
[3]Goodale, W. 2008, Biodiversity Research Institute, Gorham, Maine

Additional information

- Report out spring 2010.
- PFC CAP construction begins in 2010.
- For more information on toxics monitoring by Ecology visit: http://www.ecy.wa.gov/programs/eap/toxics/toxicsmonitoring_by_Ecology.htm

Fish Size and Age

	Length	Weight	Age	n
QUINRCTTL	276	175	3.25	4
ENTRRBTL	216	107	4.67	3
ENTRBKTL	143	75	3.5	2
SPKRLSSL	530	1614	10.25	4
COLRLMBL	208	128	0	5
COLRLSSL	469	1008	10.75	4
WASHLLMBL	215	131	1	5
WASHLYPL	198	82	2	3
WASHLPEAL	297	241	7.6	5
WASHLLSSL	473	1186	9	4
WMLPSL	149	79	3	5
WMLRBTL	377	520	1	4
WMLTENCL	325	519	3.3	3
FDRSMBL	266	273	2	5
FDRWAL	342	306	2	5

Liver

LOQ (ng/L)			10	10	25	10	10	10	10	10	10	10
Sample	Actual Mass liver	conversion factor	C12	C11	C10	C9	PFOA	C7	C6	PFOS	PFHS	PFBS
QUINRCTTL	0.1208	0.966										
ENTRRBTL	0.122	0.9762										
ENTRBKTL	0.1201	0.961										
SPKRLSSL	0.1204	0.9628								20.79		
COLRLMBL	0.1175	0.9398								527.25		
COLRLSSL	0.1212	0.9694										
WASHLLMBL	0.1254	1.0028		10.32						257.1		
WASHLYPL	0.1203	0.962								118.54		
WASHLPEAL	0.1217	0.9736	20.99	46.06						363.17		
WASHLLSSL	0.1192	0.9538		15.5						100.34		
WMLPSL	0.1201	0.9604			21.03					47.5		
WMLRBTL	0.126	1.0078								65.19		
WMLTENCL	0.1194	0.955								35.26		
FDRSMBL	0.11955	0.9564										
FDRWAL	0.1224	0.9792								47.62		

Water Spring – (ng/L)

Sample ID	Waterbody	Collection Date	PFDoDA	PFUnDA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA	PFDS	PFOS	PFHS	PFBS
08190011	Columbia River at McNary Dam	5/8/2008	< 1	< 1	< 1	< 1	**1.06**	**2.33**	< 1	ND	< 0.2	< 1	< 0.2	< 1	< 0.2
08190008	Duwamish River	5/7/2008	< 1	< 1	< 1	ND	< 1	**1.44**	< 1	ND	< 0.2	ND	ND	< 1	ND
08190009	Entiat River	5/7/2008	< 1	< 1	< 1	< 1	**1.41**	**3.77**	**1.06**	ND	ND	< 1	< 0.2	< 1	ND
08190005	F.D.R. Lake	5/6/2008	**1.07**	< 1	< 1	< 1	< 1	**1.66**	< 1	ND	ND	< 1	< 0.2	< 1	ND
08190007	Lake Washington	5/12/2008	ND	< 1	**1.50**	**1.06**	**6.85**	**4.31**	**4.27**	**1.47**	< 0.2	< 1	**5.93**	**2.45**	**1.09**
08190002	Lower Columbia River	5/5/2008	< 1	< 1	< 1	< 1	< 1	< 1	< 1	ND	ND	< 1	< 0.2	< 1	ND
08190003	Marine Park WWTP	5/5/2008	< 1	**1.18**	**5.99**	**3.50**	**20.6**	**4.12**	**14.2**	**3.55**	< 0.2	ND	**9.86**	**3.65**	**1.31**
08190001	Nooksack River	5/12/2008	< 1	< 1	< 1	< 1	**2.93**	**4.13**	< 1	ND	ND	< 1	< 0.2	< 1	ND
08190017	Puyallup River	5/12/2008	< 1	< 1	< 1	< 1	**1.25**	**3.14**	**1.39**	ND	< 0.2	< 1	< 0.2	< 1	ND
08190004	Quinault River	5/6/2008	< 1	< 1	< 1	< 1	< 1	**1.86**	< 1	ND	< 0.2	ND	< 0.2	< 1	ND
08190016	S. Fork Palouse River	5/9/2008	< 1	< 1	**1.46**	**1.23**	**9.07**	**3.84**	**9.91**	**2.52**	**4.27**	< 1	**1.67**	**1.31**	**1.15**
08190006	Snohomish River	5/7/2008	< 1	< 1	< 1	< 1	< 1	**1.14**	< 1	ND	ND	< 1	ND	< 1	ND
08190015	Spokane River at Ninemile Dam	5/9/2008	< 1	< 1	< 1	< 1	**1.84**	**3.56**	**3.95**	ND	< 0.2	< 1	< 0.2	< 1	< 0.2
08190014	Spokane WWTP	5/8/2008	< 1	< 1	**13.3**	**18.5**	**136**	**35.6**	**137**	**30.6**	**3.99**	< 1	**36.2**	**20.2**	**3.00**
082000017	Sumner WWTP	5/12/2008	< 1	**1.27**	**12.0**	**10.5**	**88.2**	**7.37**	**44.8**	**20.7**	**3.04**	< 1	**5.56**	**1.63**	**1.71**
08190010	Upper Columbia River	5/7/2008	< 1	< 1	< 1	< 1	**1.47**	**4.00**	**1.38**	ND	ND	< 1	< 0.2	< 1	ND
08190012	West Medical Lake	5/8/2008	< 1	< 1	**4.63**	**18.2**	**107**	**27.3**	**79.8**	**25.7**	**3.90**	**1.65**	**11.6**	**5.03**	**1.71**
08190013	West Medical Lake WWTP	5/8/2008	< 1	< 1	**3.37**	**6.84**	**83.3**	**12.9**	**58.7**	**28.5**	**2.70**	< 1	**4.35**	**3.21**	**5.46**

Water Fall – (ng/L)

Sample ID	Waterbody	Collection Date	PFDoDA	PFUnDA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA	PFDS	PFOS	PFHS	PFBS
083700029	Columbia River at McNary Dam	9/9/2008	< 5	< 0.5	**0.53**	< 0.5	**0.74**	**4.95**	< 0.5	< 0.5	< 0.5	< 0.5	**0.53**	< 0.5	< 0.5
083700026	Duwamish River	9/11/2008	< 5	< 0.5	**0.78**	**1.12**	**1.90**	**3.21**	**1.19**	**0.57**	< 0.5	< 0.5	**1.01**	**0.84**	**0.74**
083700027	Entiat River	9/8/2008	< 5	< 0.5	< 0.5	< 0.5	< 0.5	**0.95**	**0.64**	< 0.5	< 0.5	< 0.5	**0.66**	< 0.5	< 0.5
083700023	F.D.R. Lake	9/9/2008	< 5	< 0.5	< 0.5	< 0.5	< 0.5	**1.31**	**1.87**	**0.55**	**0.81**	< 0.5	**0.54**	< 0.5	< 0.5
083700025	Lake Washington	9/11/2008	< 5	< 0.5	**0.69**	< 0.5	**2.19**	**2.06**	**1.42**	**1.23**	< 0.5	< 0.5	**5.27**	**1.63**	**0.78**
083700020	Lower Columbia River	9/12/2008	< 5	< 0.5	< 0.5	< 0.5	**0.81**	**0.86**	**1.59**	< 0.5	< 0.5	< 0.5	**1.04**	< 0.5	**0.54**
083700021	Marine Park WWTP	9/12/2008	< 5	< 0.5	**4.42**	**5.7**	**22.1**	**3.52**	**10.9**	**12.6**	**1.91**	< 0.5	**11.7**	**3.97**	< 0.5
083700019	Nooksack River	9/12/2008	< 5	< 0.5	< 0.5	< 0.5	< 0.5	**1.19**	**1.19**	< 0.5	< 0.5	< 0.5	**0.66**	< 0.5	**0.52**
083700035	Puyallup River	9/12/2008	< 5	< 0.5	**0.58**	< 0.5	< 0.5	**2.02**	< 0.5	< 0.5	< 0.5	< 0.5	**0.50**	< 0.5	< 0.5
083700022	Quinault River	9/8/2008	< 5	< 0.5	< 0.5	< 0.5	< 0.5	**1.54**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	**0.63**
083700034	S. Fork Palouse	9/10/2008	< 5	< 0.5	**3.14**	**2.46**	**24.0**	**6.88**	**12.4**	**13.0**	**2.70**	< 0.5	**6.36**	**1.93**	**1.98**
083700024	Snohomish River	9/11/2008	< 5	< 0.5	< 0.5	< 0.5	< 0.5	**0.97**	< 0.5	< 0.5	< 0.5	< 0.5	**0.55**	< 0.5	< 0.5
083700033	Spokane River at Nine Mile	9/10/2008	< 5	< 0.5	**0.63**	< 0.5	**1.82**	**3.30**	**1.43**	**1.40**	< 0.5	< 0.5	**3.25**	**1.26**	**0.62**
083700032	Spokane WWTP	9/10/2008	< 5	< 0.5	**3.67**	**7.72**	**36.6**	**12.9**	**29.8**	**16.0**	**2.80**	< 0.5	**18.1**	**11.9**	**2.40**
083700036	Sumner WWTP	9/12/2008	< 5	**0.68**	**13.2**	**13.8**	**59.9**	**9.74**	**17.1**	**21.7**	**4.25**	< 0.5	< 0.5	**2.72**	**3.15**
083700028	Upper Columbia River	9/9/2008	< 5	< 0.5	< 0.5	< 0.5	< 0.5	**0.90**	< 0.5	< 0.5	< 0.5	< 0.5	**0.67**	< 0.5	< 0.5
083700030	West Medical Lake	9/10/2008	< 5	< 0.5	**3.72**	**6.83**	**47.3**	**21.9**	**36.1**	**31.0**	**5.40**	**1.27**	**7.44**	**4.40**	**1.54**
083700031	West Medical Lake WWTP	9/10/2008	< 5	< 0.5	**6.08**	**5.89**	**63.1**	**12.8**	**29.4**	**46.7**	**5.43**	< 0.5	**10.2**	**2.19**	**6.58**

WWTP effluent