Contaminated Sediments in Squam Lake Tributaries, 2015-2016

Loon Preservation Committee
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Introduction

The Loon Preservation Committee (LPC) sampled sediments in tributaries flowing into Squam Lake in October 2015 and November 2016. Sampling was done to isolate potential sources of contaminants found at high levels in loon eggs that coincided with a dramatic (44%) decline in the Squam loon population in 2005 and subsequent poor breeding success of the remaining loons (45% of the statewide average from 2005-2016). Sampling of northern crayfish (*Oronectes virilis*) in Squam Lake and in tributaries flowing into Squam indicated areas of potential contaminant concerns, and LPC sampled sediments to further investigate these areas.

Materials and Methods

Sediments were sampled in October 2015 from the outflow from Kusumpe Pond (which flows into Squam Lake from the north), identified as having higher than background levels of certain contaminants in crayfish, as well as from 7 Squam Lake tributaries of concern based on contaminant levels in loon eggs. For the Kusumpe outflow, we sampled at 4 intervals along the length of the tributary (sampling sites labeled "K#" in Figure 1) to investigate if there was a point along the tributary where contaminant levels declined, indicating a potential contaminant source downstream of that portion of the rivershed. For the 7 other tributaries, we took a single sample near the outlets into Squam Lake to measure baseline contaminant loads flowing into the lake from that tributary (sampling sites labeled "SQ#" in Figure 1).

LPC conducted follow-up sampling in November 2016, sampling 3 additional tributaries lacking contaminant data (Ben 16, Car 16, Veer 16), re-sampling 2 sites (K1 and SQ3) tested in 2015 due to higher-than-background contaminant levels, and sampling 2 sites further up the SQ3 tributary. We re-sampled the K1 site after a beaver dam burst and culvert repair work was conducted upstream of the site subsequent to our October 2015 sampling.

LPC sampled the biologically-active sediment zone (the top 2-3 cm of substrate) from depositional zones in the tributaries (Shelton and Capel 1994, Chalmers et al. 2007). Samples were collected in chemically-clean jars rated for pesticides, PCB's, and semi-volatiles, stored, and shipped to SGS AXYS Analytical Services Ltd. (Sidney, BC) in accordance with standard practices (Shelton and Capel 1994, U.S. EPA 2001, Chalmers et al. 2007; Appendix A). SGS AXYS performed high resolution gas chromatography/mass spectrometry analysis to test sediment samples for PCB's, PCDD/F's, and OC pesticides, according to EPA methodologies (SGS AXYS Analytical Services Ltd., unpubl. report). The contaminants tested bind to organic matter in sediments, making sediments an appropriate matrix to sample (Van Metre et al. 2003). Results of 18 sediment samples, collected in 2015 and 2016, are included in this report.

Figure 1: Locations of sediment samples in the Squam Lake watershed, collected in the fall of 2015 and 2016 and submitted for contaminant testing. Sampling sites identified with a red marker indicate areas of elevated contaminant levels, as detailed in the text.

Results of Sediment Sampling and Discussion

Sediment sampling indicated three sites with contaminated sediments: K1, SQ3, and Ben 16 (Figure 1, red markers).

K1 site: The K1 site is located downstream of a gravel road passing over the outflow from Kusumpe Pond into Squam Lake. Total PCB levels in sediments in 2015 at this site (K1-15) were 12,541% of the geometric mean of total PCB levels of the other 10 sites sampled in 2015 (Table 1). Total PCB levels at K1-15 were 7,348% of those of the other three sites (K5, K9, and K10) sampled on the Kusumpe outflow upstream of the gravel road and 11,599% of the sampling site (K5) 139 m upstream from K1 (Table 1), indicating the road as the likely source. Sediments at the K1-15 site were also elevated for dioxins and furans. When combined with dioxin-like PCB's, K1-15 levels were 955% of the geometric mean of the other 10 tributaries sampled in 2015, 587% of the three other sites (K5, K9, K10) on the same tributary, and 1,139% of the sampling site (K5) 139 m upstream from K1 (Table 1), again suggesting the road as the likely source.

Total PCB levels at K1-15 were 92% of the levels identified by the Canadian government as posing potential risk to aquatic life (see Appendix B for definitions of effects levels). Levels of dioxins and dioxin-like compounds exceeded the threshold effects levels for aquatic biota set by the Canadian government and the New York State Department of Environmental Conservation (Table 1; Canadian Council of Ministers of the Environment [CCME] 2001; New York State Department of Environmental Conservation [NYSDEC] 2014).

There was a reported beaver dam washout in late fall 2015 with resulting work in spring 2016 to repair the gravel road and culvert upstream of the K1 site. LPC re-sampled the site in November 2016 (K1-16) and found total PCB levels that were 2,311% of levels in 2015 and were nearly 290,000% of the geometric mean of the other 10 sites sampled in 2015 (Table 1). Levels of dioxins and dioxin-like compounds increased to 1,490% of 2015 levels and were over 14,000% of the geometric mean of the other sites tested in 2015.

In 2016, total PCB levels at the K1 site exceeded both the Canadian Probable Effects Level and the Probable Effects Concentration identified by MacDonald et al. (2000), above which harmful biological effects are likely to occur (MacDonald et al. 2000, CCME 2001). The level of dioxins and dioxin-like compounds in 2016 was 90% of the Probable Effects Level identified by the Canadian Government (CCME 2001, Table 1).

Table 1: Sediment contaminant levels as a percentage of background levels and effects levels. Values in bold print indicate levels exceeding 100% of effects levels. Cells with "--" indicate no effects levels are available. Appendix B provides definitions of the effects levels categories.

			% Threshold effects levels					**% Probable effects levels**			
Site	**Contaminant**	**% of background levels**	**Canadian Threshold Effects Level**	**Threshold Effects Concentration (MacDonald et al. 2000)**	**NY Sediment Guidance Values Class A**	**NY Bioaccumulation-based Sediment Guidance Values**	**US Dept. of Interior Effects Range Low**	**Canadian Probable Effects Level**	**Probable Effects Concentration (MacDonald et al. 2000)**	**NY Sediment Guidance Values Class C**	**US Dept. of Interior Effects Range Median**
K1 2015	Total PCB's	12,541%	92%	52%	31%	**761%**	--	11%	5%	3%	--
	Dioxins/dioxin-like compounds	955%	**153%**	--	**260%**	**260%**	--	6%	--	--	--
K1 2016	Total PCB's	289,812%	**2,114%**	**1,206%**	**721%**	**17,585%**	--	**260%**	**107%**	72%	--
	Dioxins/dioxin-like compounds	14,233%	**2,275%**	--	**3,868%**	**3,868%**	--	90%	--	--	--
SQ3 2015	Total DDT	1,293%	--	34%	4%	**377%**	**114%**	--	<1%	<1%	4%
	DDT isomers	2,286%	**122%**	35%	--	--	--	30%	2%	--	--
	DDE isomers	470%	13%	6%	--	--	--	3%	1%	--	--
	DDD isomers	840%	5%	4%	--	--	--	2%	1%	--	--
SQ3 2016	Total DDT	1,582%	--	42%	5%	**460%**	**140%**	--	<1%	<1%	5%
	DDT isomers	2,113%	**113%**	32%	--	--	--	28%	2%	--	--
	DDE isomers	1,077%	29%	13%	--	--	--	6%	1%	--	--
	DDD isomers	2,181%	13%	9%	--	--	--	5%	2%	--	--
Ben 16 (2016)	Total DDT	42,986%	--	**1,138%**	**137%**	**12,515%**	**3,802%**	--	11%	<1%	**130%**
	DDT isomers	66,603%	**3,553%**	**1,016%**	--	--	--	**886%**	67%	--	--
	DDE isomers	32,987%	**899%**	**404%**	--	--	--	**189%**	41%	--	--
	DDD isomers	24,227%	**142%**	**103%**	--	--	--	59%	18%	--	--

Ben 16 and SQ3 sites: LPC identified two sites with elevated levels of DDT, Ben 16 and SQ3 (Figure 1). Total DDT at Ben 16 was nearly 43,000% of the background level of the 14 other sites sampled in 2015-2016, excluding SQ3-15 and SQ3-16 (Table 1). Levels of total DDT at SQ3 were lower than Ben 16 but 1,300-1,600% of background levels (Table 1). Total DDT at Ben 16 was 130% of the U.S. Department of the Interior effects-range-median, above which harmful biological effects are likely (Table 1; US Department of the Interior 1998). The SQ3 site exceeded threshold effects levels identified by the U.S. Department of the Interior for total DDT and the potential risk of bioaccumulation in the food web from total DDT identified by New York State (Table 1). Total DDT is made up of chemically-related compounds (isomers), with the primary constituent isomers being DDT and breakdown products (DDE and DDD). The SQ3 site exceeded threshold effects levels identified by the Canadian government for DDT isomers, and Ben 16 exceeded multiple threshold and probable effects levels identified by the Canadian government for DDT, DDE, and DDD isomers (Table 1).

At both sites, a contaminant profile of total DDT suggests either the presence of undegraded DDT or recent inputs of DDT into the system (<20 years). The half-life of DDT in soil in New England is approximately 20-30 years (Dimond and Owen 1996). Over 40 years after use of DDT was banned in the United States, we would expect to see a preponderance of breakdown products (DDE and DDD) in the contaminant profile (Gewurtz et al. 2008, Johnson et al. 1988, Agee 1986). Instead, at both sites, the sum of DDT isomers was greater than those of DDD and DDE (Figure 2), with the percentage of DDT isomers ranging from 61-79% (Figure 2).

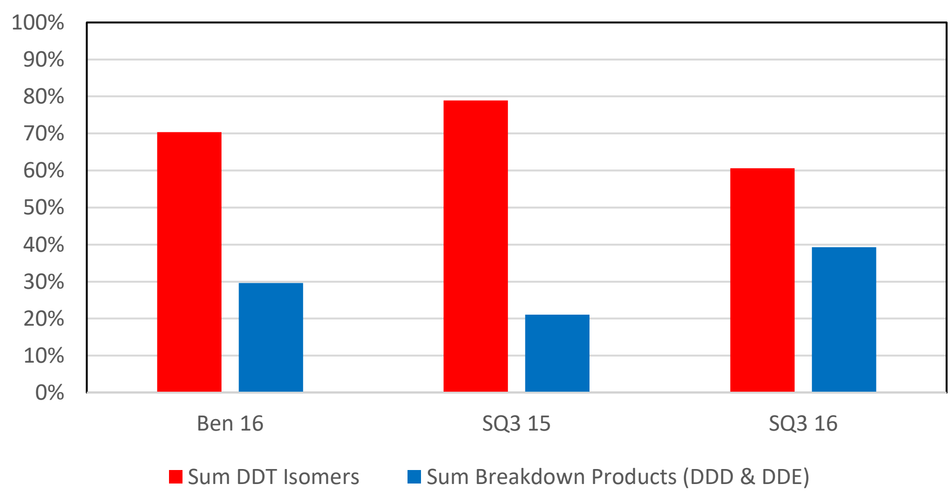

Figure 2: The preponderance of DDT isomers at the Ben 16 and SQ3 sites over the breakdown products DDD and DDE suggests recent inputs of DDT into the system (<20 years) or recent mobilization of the contaminants (Gewurtz et al. 2008, Johnson et al. 1988, Agee 1986).

Contaminants in Squam loon eggs

Sediment guidelines emphasize the need to interpret sediment contaminant levels in conjunction with other sources of information, including biological assessments (CCME 2001, NYSDEC 2014), to determine the degree of threat to the environment. Levels of contaminants found in inviable Squam loon eggs from failed nests suggest reason for concern. Farmahin et al. (2013)

found that loons have a low sensitivity to dioxins and dioxin-like compounds. One of 41 Squam eggs tested contained total PCB levels above levels that produce negative effects for all but the most sensitive species. However, Schmutz et al. (2009) pointed out that the use of toxic equivalency factors (TEF's) for dioxin-like PCB's better reflects toxicity of PCB's in biota.

TEF's are calculated differently in different studies; we calculated TEF's for dioxins and dioxin-like PCB's for 24 Squam loon eggs according to methods suggested for avian species in Van den Berg et al. (1998) and compared levels in Squam loon eggs with other species exhibiting low-sensitivity to dioxins (Farmahin et al. 2013). In double-crested cormorants, embryonic deformities or mortality resulted from TEF levels ranging from 350-1,300 ppt (summarized in Hoffman et al. 1996). Twenty of 24 Squam eggs exceeded the 350 ppt level. Twenty-three Squam eggs exceeded levels shown to result in embryonic health effects in great blue herons (summarized in Hoffman et al. 1996) and levels that Schmutz et al. (2009) suggested may be resulting in decreased reproductive success and population declines in red-throated loons. All 24 Squam eggs exceeded levels resulting in reduced productivity and embryo deformities in wood ducks (White and Hoffman 1995, Hoffman et al. 1996).

The geometric mean of total DDT levels in Squam loon eggs was 94% of a "no observed effects level" identified for brown pelicans (Bouwman et al. 2013); however, interpretation of DDT levels is limited by lack of knowledge of its effects in loons. LPC's finding of recent mobilization or inputs of DDT into the Squam system is concerning. Water flow on Squam is from the northeast to the southwest, and a recent input/mobilization incident may have been reflected in a spike of DDT isomers (versus DDE/DDD) in loon eggs in 2007 at two nest sites southwest of the Ben16 site, but not at a nest site northeast of it.

Stable isotope testing (which measures the origin of nutrients in food webs) conducted on Squam loon eggs indicated that the majority of nutrients and, thus, contaminants found in eggs came from a freshwater source (LPC, unpubl. data). Given this evidence, the fact that nutrients and contaminants deposited by female birds into their eggs generally come from prey consumed during the 4 weeks prior to egg-laying, and that loons are on their territories 4 or more weeks prior to nesting, it is clear that the majority of contaminants identified in Squam loon eggs were acquired on Squam Lake.

The individual, additive, or synergistic effects on loons of the contaminants identified in Squam tributary sediments and in Squam loon eggs are not well understood, but the presence of these contaminants at elevated levels in eggs of a top-level predator demonstrates the risks sustained by both loons and other species from these contaminants in Squam's watershed. LPC will continue monitoring loon eggs for possible future spikes in contaminant levels or indications of fresh inputs.

Conclusion

LPC's sediment sampling identified three sites (K1, Ben 16, and SQ3) of contaminated sediments in tributaries flowing into Squam Lake. Contaminants are one of many factors that may have contributed to the declines of Squam's loons, and LPC recognizes that the contaminant levels reported here in sediments (and in Squam loon eggs) are below Superfund site levels. Nevertheless, given that sediment levels exceed established thresholds for potential or likely harm to aquatic life and levels in Squam loon eggs approach or exceed possible effects levels, we believe there is cause for concern. A systems dynamics model investigating the decline of loons on Squam indicated contaminants were likely one of the factors contributing to reduced survivorship and breeding success (L. Siegel, unpublished data). The evidence that three or more tributaries seem to have flushed contaminants into the lake at the same time suggests that a storm/runoff event may have pushed contaminant-laden sediments in tributaries into the lake some years prior to the decline of loons on Squam.

Given that the three sites identified contain levels of contaminants that represent potential or likely harm to wildlife and LPC has identified these contaminants at elevated levels in Squam loon eggs, we request that DES address this issue as soon as possible with options and plans for mitigation.

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Appendix A: Sampling Methodology

LPC sampled the biologically-active sediment zone (the top 2-3 cm of substrate; Shelton and Capel 1994; Chalmers *et al.* 2007) from depositional zones in the tributaries (Shelton and Capel 1994), per the recommendation of sediment researchers from U.S. Fish and Wildlife Service (D. Major, pers. comm.) and Plymouth State University (L. Doner, pers. comm.) and in consultation with SGS AXYS Analytical Services Ltd. in Sidney, BC. We used a stainless steel trowel and poured the collected material through a 2-millimeter mesh stainless steel sieve (Shelton and Capel 1994; Chalmers *et al.* 2007) to separate the particles of silt and clay from the coarse organic matter. Samples were collected in chemically-clean jars rated for pesticides, PCB's, and semi-volatiles, placed on ice in the field, and then refrigerated at 4 degrees C. Within two weeks of collection, all samples were shipped overnight to AXYS, to minimize loss of contaminants (U.S. EPA 2001). This sampling protocol was approved by representatives from U.S. Fish and Wildlife Services, SGS AXYS Analytical Services, and Plymouth State University. SGS AXYS performed high resolution gas chromatography/mass spectrometry analysis on the samples for PBDE's, PCB's, PCDD/F's, PFC's, and OC pesticides, according to EPA methodologies (AXYS, unpubl. report).

Appendix B: Sediment Quality Guidelines

Source	Effects category	Definition	Total PCB's (ng/g dw)	PCDD/F (TEQ pg/g dw)	DDT (ng/g dw)	Citation
Canadian Council of Ministers of the Environment	Threshold Effect Level (TEL)	"The minimal effect range within which adverse effects rarely occur (i.e., fewer than 25% adverse effects occur below the TEL)"	34.1	0.85	DDD: 3.54 DDE: 1.42 DDT: 1.19	Canadian Council of Ministers of the Environment (2001)
	(unnamed intermediate category)	"The possible effect range within which adverse effect occasionally occur (i.e., the range between the TEL and PEL)"	Between TEL and PEL	Between TEL and PEL	Between TEL and PEL	
	Probable Effect Level (PEL)	"The probable effect range within which adverse biological effects frequently occur (i.e, more than 50% adverse effects occur above the PEL)"	277	21.5	DDD: 8.51 DDE: 6.75 DDT: 4.77	
MacDonald et al. study	Threshold Effects Concentration (TEC)	"Below which harmful effects are unlikely to be observed"	59.8	Not included in study	DDD: 4.88 DDE: 3.16 DDT: 4.16 Total DDT: 5.28	MacDonald et al. (2000)
	Probable Effects Concentration (PEC)	"Above which harmful effects are likely to be observed"	676	Not included in study	DDD: 28.0 DDE: 31.3 DDT: 62.9 Total DDT: 572	
New York State Department of Environmental Conservation	Class A	"Class A sediments are considered to be of low risk to aquatic life."	< 100	< 0.5	Total DDT: < 44	New York State Department of Environmental Conservation (2014)
	Class B	"Class B sediments are slightly to moderately contaminated and additional testing is required to evaluate the potential risks to aquatic life."	100 – 1,000	> 0.5	Total DDT: 44 – 48,000	
	Class C	"Class C sediments are considered to be highly contaminated and likely to pose a risk to aquatic life."	> 1,000		Total DDT: > 48,000	
	Bioaccumulation-based Sediment Guidance Values (BSGV)	"BSGVs are *not* used to classify sediments. Exceedances of BSGVs are intended to serve only as flags; that is, to identify a risk from food chain bioaccumulation *might* be present."	4.1	0.5	Total DDT: 0.48	
U.S. Department of the Interior	Effects-range-low (ERL)	"Concentrations below the ERL typically represent conditions where adverse effects would rarely occur."	Not included	Not included	Total DDT: 1.58	U.S. Department of the Interior (1998) citing a study by Long et al. (1995)
	(unnamed intermediate category)	"Concentrations between the ERL and the ERM represent conditions in which adverse effects may occur."	Not included	Not included	Total DDT: 1.58 – 46.1	
	Effects-range-median (ERM)	"Concentrations above the ERM represent conditions in which adverse effects are likely to occur."	Not included	Not included	Total DDT: 46.1	