Tracking Recent DDT Contamination in a Northern New England Watershed

Amanda May (amanda.may1796@gmail.com)
Plymouth State University Department of Environmental Science and Policy https://orcid.org/0000-0002-4798-3767

Lisa Doner
Plymouth State University Department of Environmental Science and Policy

Jeremiah Duncan
Plymouth State University Department of Atmospheric Science and Chemistry

Stephen Hill
Plymouth State University

Research Article

Keywords: DDT, DDD, DDE, United States, New Hampshire

Posted Date: December 3rd, 2021

DOI: https://doi.org/10.21203/rs.3.rs-373867/v3

Abstract

Research on declines in loon populations at Squam Lake, New Hampshire, U.S.A., point to multiple potential causes since 2005, including dichlorodiphenyltrichloroethane (DDT). This study narrows down sources of DDT in a small sub-watershed by focusing mainly on collecting and analyzing soil and sediment samples, achieving rapid source area determination of DDT. We find presence of p,p' isomers of DDT and DDE in the Bennett Brook sub-watershed arising from long-term soil and sediment storage of applications 60 years ago, plus a concentrated and current source area at a former barn. Highest concentrations, 723 µg/kg p,p'-DDT and 721 µg/kg p,p'-DDE, occur in the soils adjacent to the barn's foundation remnants. DDT exceeds that of the metabolite, DDE, in many soils around Bennett Brook, including but not limited to the barn site. In soils where DDT>DDE, we infer mechanisms that delayed breakdown of DDT over the last 60 years. A Pb-210 dated lake sediment core, collected near the outlet of Bennet Brook, shows continuous accumulation of p,p'-DDE and p,p-DDD after 1951. These residuals likely derived from multiple sources within the sub-watershed, including orchard soils, the barn site, and from mobilized sediment deposits following extreme floods in the watershed. Although the DDT residues fall below mandatory soil remediation levels for the State of New Hampshire, Bennett Brook sediments exceed sediment quality guidelines for protection of aquatic life. Crayfish collected in Bennett Brook have significantly higher concentrations of p,p'-DDE than crayfish collected elsewhere in Squam Lake.

Introduction

A popular pesticide, DDT, was banned in the United States in 1972, due to its adverse impacts on ecosystems and persistence in the environment (USEPA, 1975). Although the ban began almost 50 years ago, DDT is still detected in biota, sediments, and soils throughout the country (Feingold and Benoit, 2018; Kivenson et al. 2019). In 2004 to 2005, 44% of all resident loons died on Squam Lake, NH, U.S.A., followed by ongoing low reproductive successes (Vogel, 2010). Tests of loon eggshells revealed elevated levels of DDT residues, along with other contaminants including PCBs, PFOS, PBDEs, dioxins and furans (Vogel, 2010). Sediment samples collected in 2015 and 2016 from 14 tributary inlets to Squam Lake revealed elevated levels of DDT residues at the mouth of Bennett Brook (Vogel, 2017).

Sediment transport is the leading mechanism for environmental DDT dispersal, and sediments are a major sink for DDT residues (USDOI, 1998; Yang et al., 2013). DDT is a non-polar pesticide that does not easily dissolve in water but readily sorbs to organic matter, clay and silts in soils and sediments by hydrophobic bonding (Boul, 1995; Wohl, 2015). DDT often concentrates in the uppermost soil layers, which can be eroded by heavy rains and floods. Once transported to rivers and lakes, DDT becomes bioavailable to aquatic organisms. DDT readily dissolves, and is stored, in fatty tissues, resulting in bioaccumulation. Adverse impacts in piscivorous birds highest on the aquatic food chain include eggshell thinning, reproductive impairment, and low fledging success (Ames, 1966; Nygård, 1983; USDOI, 1998).

DDT breaks down into DDE and DDD under aerobic and anaerobic conditions, respectively (Boul, 1995; Quensen et al., 1998; Gao et al., 2013). Therefore, in upper, aerobic layers of soils, DDE is the main residue, whereas in anoxic lake bottoms and wetlands, DDD is the main residue and most easily microbially degraded (Pham et al., 1993; Boul 1995). DDT is composed of two isomers of about 85% p,p'-DDT and 15% o,p'-DDT (ATSDR, 2002). The half-life of DDT is variable, generally 2 to 35 years depending on local environmental conditions (Nash and Woolson, 1967; Lichtenstein et al., 1971; Dimond and Owen, 1996, Qu et al., 2019). The rate of degradation may vary continuously, often with faster rates immediately after application or introduction into the environment (Lichtenstein et al., 1971). The half-life in soil varies with soil type, organic carbon content, soil pH, temperature, susceptibility to volatilization, microbial activity, tilling, and flooding (Nash and Woolson, 1967; Pham et al., 1993; Boul et al., 1994; Boul, 1995; Dimond and Owen, 1996; USDOI, 1998). Since the ban of DDT in 1972, the ratio of DDE and DDD to DDT has increased in soils, sediments, and biota (USEPA, 2017). However, some recent studies report higher concentrations of DDT relative to its breakdown products in sediments and soils (Bailey et al., 2005; Kurt-Karakus et al., 2006, Hu et al., 2010). The persistence of DDT and its breakdown products makes the pesticide a long-term threat to aquatic life.

The aim of this study is to better understand the fate and impact of DDT, including transportation pathways of DDT residues from soils to aquatic sediments to aquatic life via an array of processes. Although DDT has ultimate impacts on ecosystems, the pathways for introduction to the ecosystem begin with sedimentary processes. This interdisciplinary systems approach guides the objectives of this study, which are to: 1) identify source(s) of DDT residues in an affected watershed; 2) determine the duration and triggers for mobilization of the contaminants; and 3) determine if DDT from the Bennett Brook sub-watershed is entering the aquatic food chain at detectable concentrations.

Materials And Methods

2.1 Study area

Squam Lake, New Hampshire (NH), U.S., located at 43.76, -71.53 within the Merrimac River Watershed, is oligotrophic, and morphologically complex. Bennett Brook is a second order tributary to Squam Lake. Its 2.6 km^2 watershed comprises 2% of the 172 km^2 Squam Lake watershed.

In 2017, a high concentration of DDT residues (60 µg/kg) was reported in a sediment sample collected in 2016 at the mouth of Bennett Brook, on the northwest end of Squam Lake (Vogel, 2017). Within this watershed, a 0.25 km^2 orchard of 2300 apple trees surrounding Bennett Brook was actively managed from the early 1920s until 1961, at the latest. Commercial agriculture has not occurred on those lands since, so it has been almost 60 years since the last likely DDT application, making the maximum duration of applications 15 years, based on the first availability of DDT in the U.S. around 1946. In the U.S., DDT use on orchards was common, especially to control codling moths (Glass and Fiori, 1955). Today, remnants of the orchard operation include two dump sites and a barn. The barn was destroyed in a controlled burn around 1967 and, based on site observations today, the area was likely bulldozed

afterwards, disrupting the barn's foundation. Today, the Bennett Brook watershed is mostly reforested land, along with a clearcut north of Bennett Brook, upgradient of NH RTE 113 (New Hampshire Route 113), and hay fields south of the brook, downgradient of the road.

2.2 Soil and sediment collection

Historic data on land uses and watershed characteristics guided strategic selection of sampling locations to determine DDT source area(s) (Fig. 1). Surficial sediments were collected from the upper few centimeters of Bennet Brook's streambed deposits by scooping the material directly into clean, borosilicate glass jars lined with PTFE-lined caps (USEPA, 2001). Outside the stream channel, a stainless-steel probe was used to collect the upper few centimeters of the soil horizon, dropped directly into sample jars. Samples were refrigerated until processing, then air dried for 48 hours and passed through a 250 µm sieve, retaining the finer fraction. All soil and sediment concentrations are expressed in dry weight.

Samples were processed largely following U.S. EPA method 3546, using a microwave digestor (CEM MARS 5), 14 mL vessels, and 1.25 g of sample mixed with 10 mL acetone/hexane (50/50 v/v) extraction solvent in each vessel. During extraction, the vessels were heated to 120°C in 10 minutes, followed by a 20 minute hold time and 15 minute cooling time. Because the vessels were smaller than the desired sample size, each sample was split across three vessels for extraction and recombined for analysis. For each sample, the liquid extract was collected and combined by passing the contents of the three vessels through a glass column with a fritted disc. Afterwards the samples were dried through a column with sodium sulfate, concentrated in a Kuderna-Danish (K-D) concentrator, and cleaned with florisil (1 g, 6 mL).

2.3 Lake core collection

Freeze-coring samples surface lake sediments and preserves the chronological sequence of the uppermost, flocculant material (Last and Smol, 2001). Such sediments, when analyzed for Pb-210 activity and DDT residues provides time-series of historical and current DDT inputs. This has been demonstrated in both freshwater and marine settings (Oliver et al., 1989; Muir et al., 1995; Olsson et al., 2000; Hu et al., 2010; Kurek et al., 2019). Analyses of Squam Lake sediment cores, therefore, can provide insight for 1) the duration of DDT inputs to the Bennett Cove area of Squam Lake, 2) the dominant DDT products held in the lake sediments, and 3) possible evidence of DDT mobilization from the Bennett Brook watershed.

We identified suitable lake coring locations with the help of ground penetrating radar (GPR), in collaboration with engineer Dr. Steven Arcone, Dartmouth College. GPR images of subsurface deposits

show offshore locations containing layered, and therefore sequentially deposited, sediments. In February and March 2019, we collected GPR data along three, 130 m-long, over-ice transects, radiating lakeward from the mouth of Bennett Brook. From these, we identified the edge of the littoral slope, at 10-12 meters water depth, where offshore sediment deposition is most likely. From this depth, working from the ice surface, we collected three freeze cores spaced less than 5 meters apart. These locations, proximal to the outflow of Bennett Brook, should contain sediments predominantly sourced from the Bennett Brook sub-watershed (Fig. 1).

After removal of non-*in situ* sediments, we took close-up, high resolution photographs of the core surface, with a meter-tape for scale, and created a core log of significant features and color changes using a Muncel color chart. Working in sub-freezing conditions with a band saw, we subsampled the frozen core at 1-cm intervals. We further cleaned all surfaces of each sample using sterile razor blades prior to allowing the samples to thaw. Samples from SQ2019-2 (41 cm length, 43.774750, -71.548517) provided dried, homogenized material for ^{210}Pb and ^{214}Pb analyses on a germanium gamma detector at Woods Hole Oceanographic Institution. Samples from SQ2019-3 (56 cm length, 43.774867, -71.548450) provided material for DDT residue analysis. The third core collected was not processed, and is archived at Plymouth State University.

2.4 Crayfish collection

Northern crayfish (*Faxonius virilis*) collections, obtained using beef liver lures at three locations in 2019, come from 1) the mouth of Bennett Brook (43.77698167, -71.54922819); 2) a connecting channel from Squam Lake to Little Squam Lake (43.73230127, -71.58728496); and 3) Mirror Lake, Woodstock, NH (43.94283783, -71.69436269) (Fig. 1). Mirror Lake is a regional reference site, chosen for its proximity to Squam Lake and watershed with relatively low development. This study also includes extraction and analyses of six crayfish collected by the Loon Preservation Committee (LPC) in 2013, approximately 2.3 km and 1.9 km distant from the mouth of Bennett Brook (43.769722, -71.528611 and 43.758611, -71.545278, respectively). Crayfish sample processing follows a methodological variation of Tsygankov and Boyarova (2015), with Soxhlet extraction, rotary evaporation, purification with concentrated sulfuric acid, drying through a sodium sulfate column, another rotary evaporation, reconstitution, and cleaning with florisil (1 g, 6 mL). All samples are of single crayfish, except one composite sample of three small crayfish collected in Bennett Brook (Table 1).

Table 1 p,p'-DDE (µg/kg wet weight) concentrations in crayfish collected in Bennett Brook and in Squam Lake.

Location	Sample ID	Year collected	Carapace Length (mm)	p,p'-DDE (µg/kg wet weight)
Bennett Brook	BC1	2019	44	12.5
	BC2	2019	40	2.3
	BC3	2019	44	10.3
	BC4	2019	36*	2.4
	BC5-1	2019	33	1.2
	BC6-1	2019	18	12.6
	BC7-1	2019	34	0.7
	BC7-2	2019	25	2.5
	BC7-3	2019	38	0.8
Squam Lake	SC1-1	2019	37	0.6
	SC2-1	2019	35	ND
	SC2-2	2019	30	BRL
	SC2-3	2019	32	0.8
	MPC1	2013	34	ND
	MPC2	2013	23	ND
	MPC3	2013	35	1.1
	FFC1	2013	35	0.9
	FFC2	2013	36	1.2
	FFC3	2013	30	1.7

ND No Detection; *BRL* Below the Reporting Limit; * denotes average carapace length (composite sample of three crayfish); see Figure 1 for sample locations

2.5 Analytical method and quantification

DDTs in soils, sediment, and crayfish samples analyzed at Plymouth State University used a gas chromatography-electron capture detector (Agilent 7820a GC-ECD) instrument, with helium as the carrier gas and nitrogen as the makeup gas. Samples injected into the capillary column DB-608 (30 m x 0.25 mm ID x 0.25 µm), and a subsequent DB-1701P column of the same dimensions, confirm presence of analytes and their respective concentrations. Two µL of sample was injected into one column at a time, with a 10:1 split for soil and sediment analysis and 5:1 for crayfish analysis. During the runs, temperatures of the detector and inlet were 280°C and 200°C, respectively. The oven was held at 150 ºC for 0.5 minutes and heated to 270ºC at a rate of 6 ºC/min, then held at 270ºC for 10 minutes.

Samples were quantified using an external standard calibration with a minimum of four standard concentrations per isomer: p,p'-DDT, p,p'-DDE, and p,p'-DDD, collectively referred to as ΣDDT. ΣDDT is reported with molecular weight adjustment, expressed in terms of the parent compound, p,p'-DDT (FAO, 2016). Our reporting limit is equivalent to the concentration of the lowest calibration standard which is 7 µg/kg for soil and sediment samples, and 2 µg/kg for crayfish samples. Detections below these values

are reported as below the reporting limit (BRL). Samples with no measurable detections are reported as non-detects (ND). We acknowledge that our reporting limits are high compared to modern methods, which is due to funding limitations and available analytical equipment.

2.6 Quality Control and Cleanup

To confirm the absence of analytes in the solvent, a solvent blank was analyzed at the start and end of each batch of samples. Each analytical batch contained a split sample, with known amounts of p,p'-DDT, p,p'-DDE, and p,p'-DDD added to one half before extraction. Based on this, extraction efficiencies for p,p'-DDT, p,p'-DDE, and p,p'-DDD were 42.4% - 159.7%, 52.6% - 140.0%, and 137.6% - 189.9%, respectively. This variability may in part be due to the heterogenous nature of the soil and sediment samples. Extraction efficiencies for p,p'-DDD were always greater than 100%, because of DDT degradation into DDD within the GC-ECD instrument. From the beginning of the analytical work, this within-instrument degradation was observed, but only when DDT was present in the sample, such as with each spiked sample. Recommended solutions were followed to resolve these degradation issues, including addition of a clean-up step with florisil, a Restek Siltek guard column (5 m x 0.25 mm ID), and ultra-inert liners. The guard column was inserted into the inlet, and the other end into a connector piece that joins it with the analytical column. After each run, 6 inches of the guard column was trimmed at the inlet end, and if necessary, a new ultra-inert liner was installed. DDT standards were placed as quality control checks throughout the sample sequence to monitor DDT degradation; these confirmed the added cleanup steps greatly reduced degradation, but did not entirely eliminate it. One soil sample was split into two, with half analyzed at Alpha Analytical, Westborough, MA, U.S., a commercial environmental testing laboratory, and half analyzed at our lab.

Results

3.1 Bennett Brook watershed soils and sediments

The analyses reveal measurable amounts of p,p'-DDT and p,p'-DDE but not p,p'-DDD, in soil and stream sediment samples from the Bennett Brook watershed (Fig. 2, Table 2). While no stream sediments have more p,p'-DDT than p,p'-DDE, 75% of soil samples with detections above the reporting limit have a preponderance of p,p'-DDT. Of those samples, the ratio of p,p'-DDT:(p,p'-DDT + p,p'-DDE), is from 0.57 to 0.74. We also find that DDT residues are widely distributed within the relict apple orchard. For soil samples collected outside the apple orchard along NH RTE 113, 90% contain no detectable DDT residues. Areas downgradient of dump sites and at tributary confluences, showed low or no detections of ΣDDT. No detections in some instances may also be due to our high reporting limits. Detailed soil and sediment concentrations from each sampling location is available in Table A.1 and May (2020).

Elevated p,p'-DDE concentrations (up to 37.9 µg/kg) occur in a NH RTE 113 gulley receiving runoff from the northern orchard area (the upper orchard). Of special note, soil samples from material overlying a bulldozed barn foundation have low detections, but soil samples B42, B53, and B54 contain DDT residues up to 53x higher than any other sample collected in the watershed (Fig. 2). These high-value samples are from a location just 2 meters east and downgradient of the bulldozed barn foundation (the barn site). Half of one sample at this location, sample B53, was analyzed at Alpha Analytical, reporting 290 µg/kg p,p'-DDT, 191 µg/kg p,p'-DDE, 5.40 µg/kg p,p'-DDD, 69.8 µg/kg o,p'-DDT, and no detections of o,p'-DDE and o,p'-DDD. Alpha Analytical results for sample B53 were 1.76 times higher than our lab's for p,p'-DDT, and 1.73 times higher for p,p'-DDE, and we did not detect any p,p'-DDD, nor analyze for the o,p' isomers. No detection by our lab of p,p-DDD in the Bennett Brook sediments and watershed soils may be due to our lab's high reporting limits.

The barn site values range from 165.1 to 723.2 µg/kg p,p'-DDT and 57.8 to 721.1 µg/kg p,p'-DDE, with averages of 336.5 µg/kg and 270.1 µg/kg, respectively. ΣDDT levels are 232.1 to 1527.0 µg/kg and average 637.5 µg/kg. The barn site's samples are significantly different from all other samples in the Bennett Brook watershed, based on a Mann-Whitney U test ($W = 406.00$, $p = 0.006$). A point source is a highly concentrated area of contamination, at an explicit location. We conclude that the barn site meets the criteria for a point source.

3.2 Lake sediments

The ^{210}Pb results, completed on core SQ2019-2, show a clear extinction tail in excess ^{210}Pb activity, with excess calculated by subtracting ^{214}Pb from ^{210}Pb concentrations. We assume a constant rate of ^{210}Pb supply from atmospheric sources (Appleby, 2008; Zhang et al., 2021). ^{210}Pb dating enables development of a high-resolution sediment depth-age model based on the relationship of radioactive decay to sediment accumulation rate. The two analyzed cores contain clear marker horizons, occurring at identical sediment depths, that support correlation with the age model. By comparing close-up photographs of the cores, and the descriptive core logs, we have high confidence in applying the age model from SQ2019-2 to SQ2019-3.

In Squam Lake sediment core SQ2019-3, we find p,p'-DDE at 16 cm (A.D. 1951) and p,p'-DDD at 15 cm (A.D. 1957), very soon after DDT became commercially available. Below 16 cm, we detect no DDT residues. Above 16 cm, concentrations range from 7.7 – 42.3 µg/kg p,p'-DDE and 10.8 – 101.0 µg/kg p,p'-DDD, with p,p'-DDD concentrations consistently above those for p,p'-DDE. After their first occurrence in the lake sediments, concentrations of these residues increase until A.D. 1982, after which p,p'-DDD levels decrease but p,p'-DDE levels rise to the top of the core. Overall, ΣDDT levels decrease after 1982 (Fig. 3). DDT residue levels in Bennett Brook and Squam Lake sediments compare in magnitude to those elsewhere in the world (Table 3). P,p'-DDT was not detected in the sediment core, however, there may be p,p'-DDT at concentrations below our lab's reporting limits.

Table 2: Summary data of DDT isomers in the Bennett Brook watershed

Sample Type	p,p'-DDT	p,p'-DDE	p,p'-DDD
	Range (average ± standard deviation) µg/kg		
Bennett Brook stream sediments (n = 18)	ND - 6.8 (1.5 ±2.1)	ND - 37.9 (13.2 ±10.2)	ND
Bennett Brook watershed soils (n = 25)	ND - 723.2 (58.2 ±155.4)	ND - 721.1 (46.5 ±147.0)	ND

n number of samples; *ND* No Detection

Table 3 Comparison of ΣDDT (µg/kg) levels in sediments with recent studies

Location	ΣDDT (µg/kg)	Reference
Squam Lake, New Hampshire	ND – 152.02	This study
Hooghly River, India	0.46 - 41.2	Khuman et al., 2019
Pine River, Michigan	7.9 - 154.1	Harwood et al., 2019
Lake Como, Italy	50 - 63	Bettinetti et al., 2016
Lake Chaohu, China	0.31 - 25.41	Kang et al., 2016
Northwest Mexico	0.21 - 55.0	Sánchez-Osorio et al., 2017
New Brunswick, Canada	<MDL - 4500	Kurek et al., 2019
Poland	0.4 – 602.9	Bojakowska et al., 2012
Northwest Mexico	0.21 - 55.0	Sánchez-Osorio et al., 2017

ND No Detection; *MDL* Method Detection Limit

3.3 Crayfish

Crayfish results are shown in Table 1. In Mirror Lake, the reference site, crayfish contain no detectable DDT residues. Crayfish from Bennett Brook have p,p'-DDE levels of 0.7 to 12.6 µg/kg wet weight (ww) but neither p,p'-DDT or p,p'-DDD were detected. The p,p'-DDE values in crayfish collected in 2013 and 2019 at Squam Lake, distant from Bennett Brook, range from no detection to 1.7 µg/kg ww. A 2013 crayfish study in Squam Lake found p,p'-DDE concentrations ranged from 0.29 – 1.1 µg/kg ww (Loon Preservation Committee, unpublished data). The levels of p,p'-DDE in Bennett Brook crayfish (mean = 5.03) are statistically different than the other Squam Lake crayfish we analyzed (mean = 0.83), based on a 2

sample t-test (df = 8, t = 2.42, p = 0.042). Residues in samples that were below the reporting limit were assigned the lowest standard value of 2 µg/kg in the statistical analysis. Regression analyses reveal no relationship between carapace length and p,p'-DDE levels (df = 12, F = 3.82, p = 0.076).

Discussion

4.1 Sources of DDT

DDT residues in Bennett Brook sediments likely derive from multiple sources. DDT can remain in soil for years after initial application (Gao et al., 2013), supporting our findings of DDT residues throughout the orchard area. The historic orchard surrounds Bennett Brook, meaning that, as the soils erode and are transported within the watershed, the orchard's soils may be nonpoint sources to Bennett Brook and, eventually, to Squam Lake. Furthermore, DDT contamination is largely constrained to the former orchard operation, with 90% of samples collected outside the orchard showing no detection of residues. Therefore, DDT residues detected in Bennett Brook are most likely sourced from legacy contamination from past DDT use on the orchard.

The high DDT levels detected at the barn site indicate probable storage there during the orchard operation, and possible failure to remove stored DDT prior to destruction of the barn, or spills of DDT during its use on the orchard. Of the barn site samples, B42 has the highest levels of residues (1,527.0 µg/kg ΣDDT). This sample included the deepest material collected (0 to 6 cm depth). The vertical extent of the contamination is as yet unknown but could be determined by collecting successively deeper samples until detections diminish. However, due to low mobility of DDT and potentially low soil invertebrate activity, vertical movement may be limited (Boul et al., 1994; Dimond and Owen, 1996; Kaste et al., 2007). Our study included only six samples in and around the barn. More intensive sampling of the site is needed to assess the spatial distribution and range of levels at the location, and overall threat of this site as a point source.

Within the study area, roadside gullies along NH RTE 113 carry runoff, including any DDT-laden sediments eroded from upslope locations, directly into Bennett Brook. We find p,p'-DDE in the gully samples along the stretch of NH RTE 113 immediately downgradient of the orchard area, upgradient from the barn site. We find no detection in roadside gullies in the study area that are not adjacent to the orchard lands or barn. This finding supports the idea that DDT is not just from a single point source at the barn but is also transported to Bennett Brook by runoff from DDT-treated soils. It also excludes the road itself as a source. The upper orchard is steeply sloped and was recently logged. Steep slopes have higher runoff and greater potential for erosion, even without the soil destabilization caused by logging (Tang et al., 2014). Soils eroded from the upper orchard may be nonpoint sources of residues adsorbed to the soils from historic applications, perhaps even more so because of their vulnerability to erosion (Munn and Gruber, 1997). Since samples were not collected from the soils within the upper orchard, we cannot rule out the possibility that additional point sources may contribute to p,p'-DDE in the gullies.

4.2 Transportation potential

The peak values for p,p'-DDD and p,p'-DDE in the lake core sediments occurs in those dated to 1982, ten years after the U.S. ban. This lag in peak concentrations implies retention of DDT-laden particles in the watershed soils or in Bennett Brook's channel deposits. We hypothesized that watershed erosion events would produce spikes of ΣDDT in the lake sediments, associated with floods and other sediment disturbances. The freeze core was subsampled at 0.5 cm increments to enable this kind of event identification. However, none of the extreme floods and sediment transport events associated with beaver dam breaches in 2002, the Mother's Day Storm in 2006, or Tropical Storm Irene in 2011 leave a distinct DDT signature in the lake core collected in 2019. Higher resolution core subsampling, for instance at 0.25 cm intervals, may provide more information on impacts from individual storms. The destruction of the barn in a controlled burn in about 1967 likely destabilized soils, potentially allowing DDT-laden soils to mobilize from the barn and into Bennett Brook.

The lake core results show that DDT residues have consistently entered Squam Lake for several decades, from a seemingly constant source, or sources, in the Bennett Brook watershed. Weathered soils can release persistent contaminants for years after last application (Santschi et al., 2001; Hu et al., 2010; Bettinetti et al., 2016). Kaste et al. (2007) finds that New England soils are not easily eroded and, for soil mobilization to occur, the source soils must be especially vulnerable to erosion, such as stream banks, logged land, and steep slopes. Transportation of erodible sources can occur even at low rain intensities if the soils are unstable. The constant supply observed in the lake core is likely transported from multiple sources, including erodible orchard soils, the barn site, at culverts and behind beaver dams, and perhaps another unidentified point source in the upper orchard.

High levels of p,p-DDT and p,p'-DDE in the barn site samples (max = 1,527.0 µg/kg ΣDDT), but not in samples downgradient of the barn (max = 34.8 µg/kg ΣDDT) may suggest stable DDT-laden soils at the barn site or a relatively slow transportation rate. However, as previously mentioned, more sampling around and downgradient of the barn is needed to better understand stability of the soils and transportation rates.

4.3 Persistence

Historically, when higher levels of DDT than DDE occur in soil, it serves as a possible indicator of illegal usage or dumping (Hitch and Day, 1992). However, as recent use cannot be completely ruled out, we have no reason to suspect illegal DDT usage in the study area. Supporting this, another study investigating the cause of unusually high DDT:DDE in soils concluded the cause was slow conversion of old DDT, applied

before the ban, to DDE (Hitch and Day, 1992). Yang et al. (2013) and Sánchez-Osorio et al. (2017) find p,p'-DDT as the dominant isomer in soil samples, and the latter study concluded the lack of microbial degradation of p,p'-DDT might account for its dominance in some soil samples analyzed in the study.

The presence of higher concentrations of p,p'-DDT than p,p'-DDE at the barn and other soil samples, but not in Bennett Brook sediments, suggests that p,p'-DDT is preserved while in the soils but degrades to p,p'-DDE once it enters Bennett Brook. This is consistent with studies that indicate longer persistence in soils than in mobilized sediments (Johnson et al., 1988; Pham et al., 1993).

Slower degradation is expected in the cold climates of New Hampshire, which has an average temperature of 6°C (Pham et al., 1993; Dimond and Owen, 1996; USGS, 2017). Flooding of soils, even of short duration, reduces the persistence of DDT by increasing anaerobic microbial activity that break down DDT into DDD by reductive dechlorination (Boul et al., 1994). The preponderance of DDE in the watershed's soils, therefore, is indicative of aerobic conditions. Also, the soils at the barn site are dominantly sandy-silt (53% sand, 41% silt, and 6% clay). Longer DDT half-lives are likely in these upland, sand-rich soils, because they drain water relatively rapidly, are less likely to be saturated for long periods and have low water-holding capacities (Crowe and Smith, 2007; USDA, 2019).

Lichtenstein (1971) shows that DDT is more persistent and stable in soils that received high doses of the insecticide. Also, Pereira et al. (1996) reports that a point source with high concentrations of DDT may resist degradation to a greater degree than a site with lower concentrations, or from nonpoint or diffuse sources. Degradation occurs more rapidly at some distance away from a point source, yielding higher DDE:DDT values further from the source, and vice versa at the point source (Pereira et al., 1996). This is because aerobic microbial activity is inhibited in the presence of high DDT levels. Also, because the insecticide eliminates soil-dwelling organisms, bioturbation and soil decomposition in these areas are minimized. Both effects result in longer persistence (Nash and Woolson, 1967; Pereira et al., 1996). At the barn site, soil microbial activity could be readily compared with locations out of the zone of contamination, providing more insight on this idea of persistence.

P,p'-DDT was not detected in the lake sediments, which may be due to rapid degradation of DDT to DDD by reductive dechlorination under anaerobic conditions (Wedemeyer, 1966; Miles and Harris, 1973; Johnson et al., 1988; Pham et al., 1993; Pereira et al., 1996). Supporting this, in this study we find DDD:DDE in the lake sediments are always greater than 1, indicating dominance of anaerobic conditions in the lake depositional environment (Zhang and Shan, 2014; Ma et al., 2016; Kurek et al., 2019). Other studies also report higher DDD than DDT and DDE in lake sediments, since anaerobic conditions are common in lake bottoms (Oliver et al., 1989; Muir et al., 1995; Bojakowska et al., 2012; Kurek et al., 2019).

4.4 Aquatic organisms

Crayfish reside and feed in sediments and are an important part of an aquatic food chain that includes large fish, loons, heron, minks, otters, and racoons as top predators. Crayfish accumulate DDT by direct ingestion of DDT-laden sediments or consuming prey with DDT in their fatty tissues (Schilderman et al., 1977). Prolonged contamination of crayfish arises as persistent DDT in soils mobilizes, through soil erosion and transport, into stream and lake sediments (Dimond et al., 1968). Since crayfish only travel up to a few hundred meters, their contaminant load represents conditions at the collection site and makes them a useful pollution indicator species (Schilderman et al., 1977). Therefore, p,p'-DDE detected in Bennett Brook-residing crayfish likely derives from sources in the Bennett Brook watershed. Crayfish collected in Bennett Brook have significantly higher concentrations of p,p'-DDE (mean = 5.03) than crayfish collected elsewhere in Squam Lake (mean = 0.83), distant from the brook based on a two sample t-test ($p = 0.042$). Therefore, crayfish results show that DDT residues sourcing from the Bennett Brook watershed have entered the aquatic food chain, at levels significantly higher than distant from the brook.

We hypothesized that DDE levels would increase with crayfish carapace length because larger, older crayfish accumulate residues over a longer interval than smaller, younger crayfish. Supporting this hypothesis, in fish, the accumulation of DDE is correlated with increasing age and fat content (Gutenmann et al., 1992; USDOI, 1998). Statistical analyses revealed no relationship between crayfish size and DDE levels in the crayfish we analyzed. However, the range of sizes we tested may not have represented enough a range to see this effect.

Crayfish usually have higher DDE than DDT, because the aerobic DDT-laden sediments they reside in have degraded to DDE, and DDT also breaks down in their bodies (Dimond et al., 1968; Boul, 1995). Prolonged crayfish contamination occurs through persistence of DDT residues in contributing soils, and residues in crayfish will accumulate as long as the watershed soils provide that input (Dimond et al., 1968). Results reveal that the Bennett Brook watershed continues to supply DDT-laden soils, and so we expect contamination in the crayfish and Squam Lake food chain for many more years. Even low levels in crayfish should not be overlooked, because of biomagnification (Dimond et al., 1968).

Most sediment samples analyzed from Bennett Brook and Squam Lake exceed sediment quality guidelines for the protection of aquatic life (CCME, 2001). For example, p,p'-DDD and p,p'-DDE concentrations in the upper 5 cm of the lake sediments are five and six times higher, respectively, than their PELs (Probable Effects Level), above which adverse biological effects are expected to occur frequently (CCME, 2001). Exceeding the PELs of DDT, DDE, and DDD at 4.77, 6.75, and 8.51 µg/kg, respectively, means that the levels are potentially harmful to Squam Lake's ecosystem.

Conclusions

Although DDT was available in the U.S. over a span of 27 years, it was only used on the Bennett Brook area orchards for a maximum of 15 years. Despite the short duration of use, and the 60 year interval since the last application, elevated ΣDDT is still detected in Bennett Brook watershed soils, sediments, and crayfish, and in Squam Lake sediments just offshore of the tributary inlet. In this study, we

demonstrate that DDT residues are still being transported from watershed soils to stream and lake sediments, and are bioavailable and present in Squam Lake's aquatic food chain.

Past and present sources of DDT to Bennett Brook and further, Squam Lake, include erodible orchard soils serving as a nonpoint source, the barn site, and perhaps other unidentified point sources. A preponderance of p,p'-DDT in most soil samples, and not in stream sediments, suggests that metabolite degradation occurs quickly once sediments reach Bennett Brook.

Although some studies point to reduced bioavailability with chemical aging of DDT (Sudharshan et al, 2012; Wang, 2019), evidence of bioaccumulation in crayfish from Bennett Brook suggests that, here, DDT poses an ongoing threat to aquatic life. The lake core data further demonstrate that Squam Lake's Bennett Cove has been exposed to DDT residues since 1951, although ΣDDT levels in the lake sediments have steadily decreased since 1982. Further research should be done to determine the geographic extent of high-DDT near the barn, the potential for mobilization of this soil within the watershed, and the extent of bioaccumulation and biomagnification within aquatic life local to Bennett Brook.

Declarations

Acknowledgements

This work was supported by multiple grants: Sigma Xi Student Research Grant, Plymouth State University (PSU) Student Research and Creativity Grant, PSU Faculty Research and Creativity Grant; and PSU Environmental Science and Policy program Student Travel and Research award. Special thanks for donated efforts by Steve Arcone, for the GPR analyses, Woods Hole Oceanographic Institute, for ^{210}Pb, ^{214}Pb, and ^{137}Cs analyses, the University of New Hampshire for allowing us to use their Microwave Accelerated Reaction System 5 (MARS 5), and the Loon Preservation Committee, for providing their unpublished crayfish data for this study.

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Figures

Figure 1

Study area in central New Hampshire, U.S. with sampling locations for crayfish, soils, stream sediments, and lake cores.

Figure 2

ΣDDT levels in sediment and soil samples within the Bennett Brook watershed. Only p,p'-DDT and p,p'-DDE were detected in the samples analyzed by PSU. The red dots, or the highest concentrations, are at the barn site. ND No Detection; BRL Below Reporting Limit; NH RTE 113 New Hampshire Route 113; * Two samples collected at location (too close to show on map).

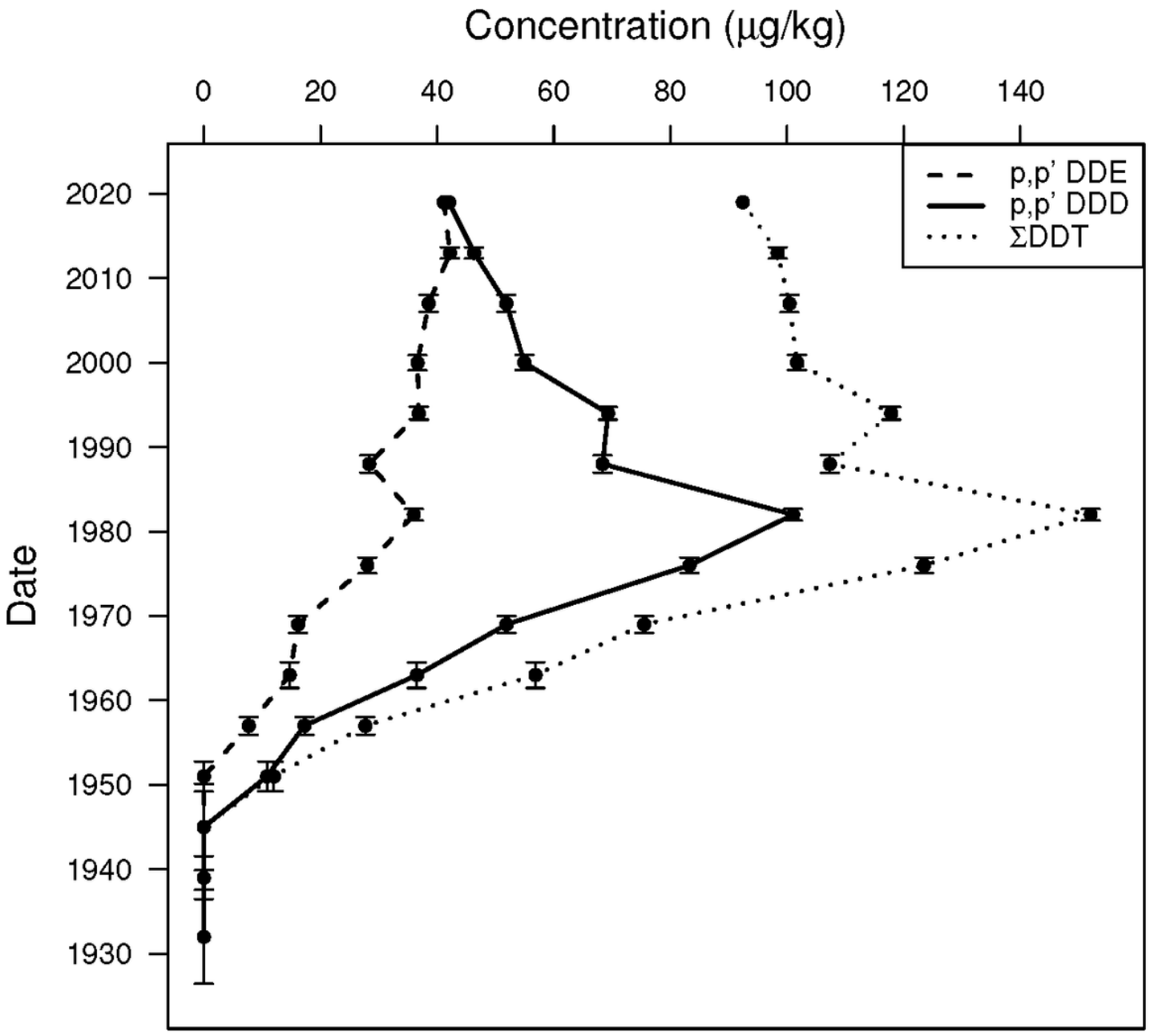

Figure 3

p,p’-DDE, p,p’-DDD, and ΣDDT concentrations from the lake core SQ2019-3. The vertical bars represent the 210Pb error. P,p’-DDT was not detected in the core.

Supplementary Files

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