

# Tracking Recent DDT Contamination in a Northern New England Watershed

Amanda May (✉ [amanda.may1796@gmail.com](mailto: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:** August 11th, 2021

**DOI:** <https://doi.org/10.21203/rs.3.rs-373867/v2>

**License:**  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

---

# Abstract

Ecological research since 2005 into potential causes of declines in loon population at Squam Lake, New Hampshire, U.S.A., revealed multiple potential causes, but no particular source of contaminants. In 2017, tributary sediment analyses revealed specific sub-watersheds transporting contaminants to the lake (Vogel, 2019). For this study, from 2018 to 2020, we used an approach to this problem that allowed for rapid source area determination of DDT using soil and sediment analyses. We find modern presence of p,p' isomers of DDT and DDE within the Bennett Brook sub-watershed, arising from 60-year-old orchard applications and a former barn. Highest concentrations, 723 µg/kg p,p' DDT and 721 µg/kg p,p' DDE, occur near the barn's foundation rubble. DDT exceeds that of the daughter product, DDE, in some of the sub-watershed's soils, including but not limited to the barn site. In the soils where DDT>DDE, we infer delayed breakdown of DDT. DDT<DDE occurs in the streambed and lake deposits, as well as some soils. A Pb-210 dated sediment core, collected near the outlet of Bennet Brook, shows continuous accumulation of the daughter products, DDE and DDD, from 1951 to the present. Residuals are derived from multiple sources within the sub-watershed, including orchard soils, the barn site, and sediment accumulations in the stream. These DDT residues fall below mandatory soil remediation levels for the State of New Hampshire, but exceed some sediment quality guidelines for protection of aquatic life. Bioaccumulation of p,p' DDE is evident in crayfish that reside in Bennett Brook.

## 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 world (Rissato et al., 2006; Andrews et al., 2009; Hu et al., 2010; Yang et al., 2013; Bettinetti et al., 2016; Kang et al., 2016; Feingold and Benoit, 2018; Khuman et al., 2019; Das et al., 2020). 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; Leatherman, 1997; 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 the upper, aerobic layers of soils, DDE is the main residue, whereas in anoxic lake bottoms and wetlands, DDD is the main residue and the 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 isomer p,p' DDT degrades into p,p' DDD and/or p,p' DDE, and o,p' DDT degrades into o,p' DDD and/or o,p' DDE (Ricking and Schwarzbauer, 2012). 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; Leatherman, 1997). 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 (Johnson et al., 1988; Pham et al., 1993; Muir et al., 1995; Bailey et al., 2005; 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 geosystem and 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 contaminant; and 3) determine if DDT from the Bennett Brook watershed is entering the aquatic food chain.

## **1.1 Study area**

Squam Lake, New Hampshire (NH), U.S., located at 43.76°, -71.53° within the Merrimac River Watershed, is oligotrophic, and morphologically. Bennett Brook is a second order tributary to Squam Lake. Its 2.6 km<sup>2</sup> watershed comprises 2% of the 172 km<sup>2</sup> 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, 2019). Within this watershed, a 0.25 km<sup>2</sup> 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 moth (Glass and Fiori, 1955; Marshall, 1959). 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.

## Materials And Methods

### *2.1 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 new, clean, borosilicate glass jars. Outside the stream channel, a stainless-steel probe was used to collect the upper few centimeters of O and A soil horizons, 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.

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).

### *2.2 Lake core collection*

Lake deposits can preserve the chronological sequence of sediments (Last and Smol, 2001) and lake sediment cores, which collect a top to bottom column of sediment, can improve understanding of historical and current levels of DDT residues in lakes (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, provides insight for: 1) the duration of Bennett Brook sourcing DDT to the lake; 2) the historic and current levels the aquatic ecosystem has been and is exposed to; 3) the dominant DDT products in the lake, and; 4) triggers for mobilization from the Bennett Brook watershed to Squam Lake.

Ground penetrating radar (GPR), which creates images of subsurface deposits, can help identify locations with undisturbed, layered sediments. In February 2019, we collaborated with engineer Dr. Steven Arcone, Dartmouth, to identify suitable lake coring locations. Based on three, 130 m-long over-ice GPR transects, radiating lakeward from the mouth of Bennett Brook, we identified the edge of the littoral slope and, in March 2019, we collected three freeze cores, spaced 5 m apart, at 10-12 m water depth. Freeze cores preserve the very top, highly flocculent, layers of sediments usually disturbed and sometimes lost by traditional corers. This location, proximal to the outflow of Bennett Brook, should have sediments predominantly sourced from the Bennett Brook sub-watershed (Fig. 1). After removal of non-*in situ* sediments, we photographed and subsampled the frozen core at 1-cm intervals, using a band saw, and cleaned the subsamples with razor blades prior to thawing. Samples from SQ2019-2 (41 cm length) provided dried, homogenized material for  $^{210}\text{Pb}$ ,  $^{214}\text{Pb}$  and  $^{137}\text{Cs}$  analyses on a germanium gamma detector at Woods Hole Oceanographic Institution. By subtracting  $^{214}\text{Pb}$  from  $^{210}\text{Pb}$ , we calculate unsupported (excess)  $^{210}\text{Pb}$ , assumed to accumulate in the sediments at a constant rate from atmospheric sources. The relationship of decay versus accumulation rate provides an estimate of elapsed time. Samples from SQ2019-3 (56 cm length) provided material for DDT residue analysis.

## 2.3 Crayfish collection

Crayfish reside and feed in sediments and are an important part of an aquatic food chain that includes fish, loons, heron, mink, otter, 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 streams and lake sediments (Dimond et al., 1968). Since crayfish reside in an area-bound region, their contaminant load represents conditions at the collection site and makes them a useful pollution indicator species (Schilderman et al., 1977).

Northern crayfish (*Faxonius virilis*) collections, obtained using beef liver lures at three locations in 2019, come from 1) the mouth of Bennett Brook; 2) a channel connecting Squam Lake to Little Squam Lake; and 3) Mirror Lake in Woodstock, NH (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. Crayfish sample processing follows a methodological variation of Tsygankov and Boyarova (2015), with Soxhlet extraction, rotary evaporation, purification with concentrated sulfuric acid, and 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 (Table 1).

## ***2.4 Analytical method and quantification***

Soil, 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 °C for 0.5 minutes and heated to 270°C at a rate of 6 °C/min, then held at 270°C for 10 minutes.

Samples were quantified using an external standard calibration with a minimum of four standards 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).

## ***2.5 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 is probably caused by 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, 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 going to Alpha Analytical, Westborough, MA, U.S.A., a commercial environmental testing laboratory, and half to 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, 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.

Elevated p,p' DDE concentrations occur in a NH RTE 113 gully 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 sample B53 was analyzed at Alpha Analytical, reporting 58% p,p' DDE. This compares well to our lab's results of 57% p,p' DDT, on the other split of this sample.

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  $336.5 \pm 264.3$  µg/kg and  $270.1 \pm 305.7$  µg/kg, respectively. ΣDDT levels are 232.1 to 1527.0 µg/kg and average  $637.5 \pm 604.4$  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.

**Table 2:** Summary data for Bennett Brook DDT isomer analyses

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 ( $1.5 \pm 2.1$ )	ND - 37.9 ( $13.2 \pm 10.2$ )	ND
Bennett Brook watershed soils (n = 25)	ND - 723.2 ( $58.2 \pm 155.4$ )	ND - 721.1 ( $46.5 \pm 147.0$ )	ND

n number of samples; ND No Detection

## **3.2 Lake sediments**

Radiometric dating of the freeze core lake sediments by  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  produced mixed results. The  $^{137}\text{Cs}$  signal rises from a pre-1950's zero background level to a plateau that combines the two, expected 1964 and 1989 (Chernobyl) peaks. Smearing of these two event peaks is common in anoxic sediments, due to mobilization of cesium in reducing conditions. The  $^{210}\text{Pb}$  results are more conclusive, showing a clear extinction tail in excess  $^{210}\text{Pb}$  activity. From the  $^{210}\text{Pb}$  dating results we create a sediment depth-age model for lake core SQ2019-2 and apply this age model to core SQ2019-3, collected just 3 m away. Both cores have two, identical marker horizons.

Squam Lake sediment core samples contain only p,p' DDE and p,p' DDD (Fig. 3). Residues appear in the lake sediments soon after DDT came into use. At 16 cm core depth (A.D. 1951), we find p,p' DDD, and soon afterwards, at 15 cm core depth (A.D. 1957), we find p,p' DDE. Below these depths, DDT residues are not detected. Above 16 cm, concentrations range from 7.7 – 42.3  $\mu\text{g}/\text{kg}$  p,p' DDE and 10.8 – 101.0  $\mu\text{g}/\text{kg}$  p,p' DDD, with p,p' DDD concentrations consistently above those for p,p' DDE. After 1957, concentrations of these residues increase until A.D. 1982, after which p,p' DDD levels decrease but p,p' DDE levels continue to increase. Overall,  $\Sigma\text{DDT}$  levels decrease after 1982 (Fig. 3). The DDT residue levels in Bennett Brook and Squam Lake sediments are of comparable magnitude to those found in other locales (Table 3).

**Table 3** Comparison of  $\Sigma\text{DDT}$  ( $\mu\text{g}/\text{kg}$ ) levels in sediments in recent studies

Location	$\Sigma$ DDT ( $\mu\text{g}/\text{kg}$ )	Reference
Squam Lake, New Hampshire	ND – 152.02	This study
Changhua County, Taiwan	0.03 - 2.63	Das et al., 2020
Hooghly River, India	0.46 - 41.2	Khuman et al., 2019
Pine River, Michigan	7.9 - 154.1	Harwood et al., 2019
Southern California	ND - 256	Kivenson et al., 2019
China	0.033 - 4140.07	Lv et al., 2019
Cape Cod, Massachusetts	ND - 119	Feingold and Benoit, 2018
Lake Como, Italy	50 - 63	Bettinetti et al., 2016
Lake Chaohu, China	0.31 - 25.41	Kang et al., 2016
Quanzhou Bay, China	0.21 – 7.83	Yang et al., 2013
North Bohai Sea, China	<LOD - 86.46	Hu et al., 2010
Northwest Mexico	0.21 - 55.0	Sánchez-Osorio, 2017

ND No Detection; LOD Limits of Detection

### 3.3 Crayfish

Crayfish results are shown in Table 3. 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  $\mu\text{g}/\text{kg}$  wet weight (ww) but neither p,p' DDT or p,p' DDD were detected. The p,p' DDE values in crayfish collected in 2019 at Squam Lake, distant from Bennett Brook, range from no detection to 0.8  $\mu\text{g}/\text{kg}$  ww. A 2013 crayfish study in Squam Lake found a p,p' DDE range of 0.29 – 1.1  $\mu\text{g}/\text{kg}$  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  $\mu\text{g}/\text{kg}$  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).

**Table 1** p,p' DDE ( $\mu\text{g}/\text{kg}$  wet weight) concentrations in crayfish collected in Bennett Brook and in Squam Lake.

Location	Sample ID	Year collected	Carapace Length (mm)	p,p' DDE ( $\mu\text{g}/\text{kg}$ wet weight)
<b>Bennett Brook</b>	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
<b>Squam Lake</b>	BC7-3	2019	38	0.8
	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)

## 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), which explains the presence of DDT residues throughout the orchard area. The orchard lands are located updrainage and on both sides of Bennet Brook. This means that, as the soils erode and are transported within the drainage, all of the orchard's soils might be nonpoint sources to Bennett Brook and, eventually, to Squam Lake. Furthermore, DDT contamination is largely constrained to the historical 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 historical orchard operation, and failure to remove stored DDT prior to destruction of the barn. 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 (to 6 cm depth), suggesting residues may be concentrated in the A horizon, below the O horizon. 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 (Muir et al., 1995; Kurek et al., 2019). We hypothesized that watershed erosion events would produce spikes of  $\Sigma$ DDT 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, although we clearly see debris horizons in the cores from those events. Higher resolution core subsampling, for instance at 0.25 cm intervals, may provide more information on impacts from individual storms.

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) find 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 structures, and perhaps another unidentified point source in the upper orchard.

High levels in the barn site samples (max = 1,527.0  $\mu\text{g}/\text{kg}$   $\Sigma$ DDT), but not in samples downgradient of the barn (max = 34.8  $\mu\text{g}/\text{kg}$   $\Sigma$ DDT) 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; U.S. Geological Survey, 2016). Flooding, 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 (53% sand, 41% silt, and 6% clay). Longer DDT half-lives are likely in sandy soils, because they drain water rapidly and have low water-holding capacities (Crowe and Smith, 2007; National Cooperative Soil Survey, 2019).

Lichtenstein (1971) shows that DDT is more persistent and stable in soils that are applied with 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.

Although p,p' DDT was not detected in the lake sediments, this is not surprising given the rapid degradation rate 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, 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). 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; Kurek et al., 2019).

## ***4.4 Aquatic organisms***

Since crayfish only travel up to a few hundred meters, crayfish collected in Bennett Brook represent those that live in or just outside the brook (Byron and Wilson, 2001; Craddock 2009). 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 than crayfish collected elsewhere in Squam Lake, distant from the brook. 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.

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 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

DDT usage in the U.S. spans about 27 years, but it was only used on the Bennett Brook area orchards for a maximum of 15 years. Although it has been almost 60 years since the last application, elevated ΣDDT is still detected in the Bennett Brook watershed soils, sediments, and crayfish and in Squam Lake sediments. In this study, we demonstrate that DDT residues are transported from watershed soils to stream and lake sediments and into the aquatic food chain. This watershed systems approach aids in understanding the extent of the contamination.

The orchard is a source of DDT to Bennett Brook and Squam Lake. Past and present sources include erodible orchard soils serving as a nonpoint source, the barn site, at culverts, behind beaver structures, and perhaps other unidentified point sources. A preponderance of p,p' DDT in most soil samples but not in sediment samples, suggests degradation once transported into Bennett Brook and Squam Lake. Based on lake core results, Squam Lake's food chain has been exposed to DDT residues at potentially harmful levels to the ecosystem since 1951. ΣDDT levels in the lake sediments have a decreasing trend from 1982 to the present. 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. Further research should be done to determine the constraints and mobilization potential of DDT contamination at the barn

site, and to understand if Squam Lake's aquatic life is experiencing adverse effects from the contaminant.

## Declarations

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  $^{210}\text{Pb}$ ,  $^{214}\text{Pb}$ , and  $^{137}\text{Cs}$  analyses, the University of New Hampshire for their Microwave Accelerated Reaction System 5 (MARS 5), and the Loon Preservation Committee, for unpublished crayfish data.

## References

- Ames PL (1966) DDT Residues in the Eggs of the Osprey in the North-Eastern United States and Their Relation to Nesting Success. *Journal of applied Ecology* 3:87–97
- Andrews JT, Belt ST, Olafsdottir S, Massé G, Vare LL (2009) Sea ice and marine climate variability for NW Iceland/Denmark Strait over the last 2000 cal. yr BP. *Holocene* 19:775–784
- Agency for Toxic Substances & Disease Registry (ATSDR) (2002) Public health statement for DDT, DDE, and DDD. Agency for Toxic Substances & Disease Registry, Atlanta, Georgia
- Bailey, P., D. Waite, L. Quinnell-Abbott, and B. D. Ripley. 2005. Residues of DDT and other selected organochlorine pesticides in soils from Saskatchewan, Canada (1999). *Canadian Journal of Soil Science* 85:265–271.
- Bettinetti R, Quadroni S, Boggio E, Galassi S (2016) Recent DDT and PCB contamination in the sediment and biota of the Como Bay (Lake Como, Italy). *Science of the Total Environment* 542:404–410
- Boul HL (1995) DDT residues in the environment - A review with a New Zealand perspective. *New Zealand Journal of Agricultural Research* 38:257–277
- Boul HL, Garnham ML, Hucker D, Baird D, Aislabie J (1994) Influence of agricultural practices on the levels of DDT and its residues in soil. *Environmental Science and Technology* 28:1397–1402
- Byron CJ, Wilson KA (2001) Rusty crayfish (*Orconectes rusticus*) movement within and between habitats in Trout Lake, Vilas County, Wisconsin. *Journal of the North American Benthological Society* 20(4):606–614
- Canadian Council of Ministers of the Environment (CCME) (2001) Canadian sediment quality guidelines for the protection of aquatic life. Canadian Council of Ministers of the Environment, Winnipeg, MB, Canada

Craddock CL (2009) Should I stay or should I go? The influence of habitat quality on movement patterns in Northern crayfish (*Orconectes virilis*). Dissertation, University of Arizona.

Crowe AS, Smith JE (2007) Distribution and persistence of DDT in soil at a sand dune-marsh environment: Point Pelee, Ontario, Canada. Canadian Journal of Soil Science 87:315–327

Das S, Aria A, Cheng J, Souissi S, Hwang J, Ko F (2020) Occurrence and distribution of anthropogenic persistent organic pollutants in coastal sediments and mud shrimps from the wetland of central Taiwan. PloS one 15:1–17

Dimond JB, Kadunce RE, Getchell AS, Blease JA (1968) Persistence of DDT in crayfish in a natural environment. Ecology 49:759–762

Dimond JB, Owen RB (1996) Long-term residue of DDT compounds in forest soils in Maine. Environmental Pollution 92:227–230

Food and Agriculture Organization (FAO) (2016) Submission and evaluation of pesticide residues data for the estimation of maximum residues in food and feed. 3rd edn. Food and Agriculture Organization of the United Nations, Rome, Italy

Feingold BJ, Benoit G (2018) A novel method to infer historical DDT use on Cape Cod, Massachusetts (USA), based on ΣDDT degradation and 210Pb dating in lake sediment cores. Journal of Paleolimnology 60:461–472

Gao J, Zhou H, Pan G, Wang J, Chen B (2013) Factors influencing the persistence of organochlorine pesticides in surface soil from the region around the Hongze Lake, China. Science of the Total Environment 443:7–13

Glass EH, B Fiori (1955) Codling moth resistance to DDT in New York. Journal of Economic Entomology 48:598–599

Gutenmann WH, Ebel JG, Kuntz HT, Yourstone KS, Lisk DJ (1992) Residues of p,p'-DDE and mercury in lake trout as a function of age. Archives of Environmental Contamination and Toxicology 22:452–455

Harwood, A. D., G. E. Sutherland, M. M. Woller-Skar, M. J. Lydy, and M. C. Borrello. 2019. Evaluating toxicity risk in sediments after remediation at a Superfund megasite using a Triad approach. Environmental Monitoring and Assessment 191.

Hitch RK, Day HR (1992) Unusual persistence of DDT in some Western USA soils. Bulletin of Environmental Contamination and Toxicology 48:259–264

Hu W, Wang T, Khim JS, Luo W, Jiao W, Lu Y, Naile JE, Chen C, Zhang X, Giesy JP (2010) HCH and DDT in sediments from marine and adjacent riverine areas of North Bohai Sea, China. Archives of Environmental Contamination and Toxicology 59:71–79

- Johnson A, Norton D, Yake B (1988) Persistence of DDT in the Yakima River drainage, Washington. *Archives of Environmental Contamination and Toxicology* 17:289–297
- Kang L, He Q, He W, Kong X, Liu W, Wu W, Li Y, Lan X, Xu F (2016) Current status and historical variations of DDT-related contaminants in the sediments of Lake Chaohu in China and their influencing factors. *Environmental Pollution* 219:883–896
- Kaste JM, Heimsath AM, Bostick BC (2007) Short-term soil mixing quantified with fallout radionuclides. *Geology* 35:243–246
- Khuman SN, Bharat G, Chakraborty P (2019) Spatial distribution and sources of pesticidal persistent organic pollutants in the Hooghly riverine sediment. *Environmental Science and Pollution Research* 27(4):4137-4147
- Kivenson, V., K. L. Lemkau, O. Pizarro, D. R. Yoerger, C. Kaiser, R. K. Nelson, C. Carmichael, B. G. Paul, C. M. Reddy, and D. L. Valentine. 2019. Ocean Dumping of Containerized DDT Waste Was a Sloppy Process. *Environmental Science and Technology* 53:2971–2980.
- Kurek J, MacKeigan PW, Veinot S, Mercer A, Kidd KA (2019) Ecological legacy of DDT archived in lake sediments from eastern Canada. *Environmental Science & Technology* 53:7316–7325
- Last WM, Smol JP (2001) An introduction to basin analysis, coring, and chronological techniques used in paleolimnology. In: Last WM, Smol JP (eds) *Tracking environmental change using lake sediments: Basin analysis, coring, and chronological techniques*. Springer Netherlands, Dordrecht, pp 1–5
- Leatherman M (1997) Environmental effects: DDT. University of Delaware.  
<http://www1.udel.edu/chem/C465/senior/fall97/insecticide/environ.html>. Accessed March 6 2021
- Lichtenstein EP, Fuhrmann TW, Schulz KR (1971) Persistence and vertical distribution of DDT, lindane, and aldrin residues, 10 and 15 years after a single soil application. *Journal of Agricultural and Food Chemistry* 19:718–721
- Loon Preservation Committee. 2013. Investigation of contaminants in crayfish from the Squam Lakes, New Hampshire watershed. Unpublished data.
- Lv, M., X. Luan, X. Guo, C. Liao, D. Guo, J. Miao, X. Wu, R. Zhou, D. Liu, D. Wang, Y. Zhao, and L. Chen. 2019. A national-scale characterization of organochlorine pesticides (OCPs) in intertidal sediment of China: Occurrence, fate and influential factors. *Environmental Pollution* 257:1–9.
- Ma J, Pan L, Yang X, Liu X, Tao S, Zhao L, Qin X, Sun Z, Hou H, Zhou Y (2016) DDT, DDD, and DDE in soil of Xiangfen County, China: Residues, sources, spatial distribution, and health risks. *Chemosphere* 163:578–583

Marshall J (1959) Resistance to DDT in the codling moth in British Columbia. Entomological Society of British Columbia 56:59–63

Miles JRW, Harris CR (1973) Pesticides in water: organochlorine insecticide residues in streams draining agricultural, urban-agricultural, and resort areas of Ontario, Canada - 1971. Pesticides Monitoring Journal 6:363–368

May A (2020) DDT Contamination in Squam Lake, NH: A Watershed Approach. Master's thesis, Plymouth State University

Muir DCG, Grift NP, Lockhart WL, Wilkinson P, Billeck BN, Brunskill GJ (1995) Spatial trends and historical profiles of organochlorine pesticides in Arctic lake sediments. Science of the Total Environment 160–161:447–457

Munn MD, SJ Gruber (1997) The relationship between land use and organochlorine compounds in streambed sediment and fish in the central Columbia plateau, Washington and Idaho, USA. Environmental Toxicology 16:1877–1887

Nash RG, Woolson EA (1967) Persistence of Chlorinated Hydrocarbon Insecticides in Soils. Science 157:924–927

National Cooperative Soil Survey. National Cooperative Soil Characterization Database.  
<https://websoilsurvey.sc.egov.usda.gov/App/WebSoilSurvey.aspx>. Accessed September 16 2019

Nearing MA (2001) Potential changes in rainfall erosivity in the U.S. with climate change during the 21st century. Journal of Soil and Water Conservation 56:229–232

Nygård T (1983) Nordic society oikos pesticide residues and shell thinning in eggs of peregrines in Norway. Ornis Scandinavia 14:161–166

Oliver BG, Charlton MN, Durham RW (1989) Distribution, redistribution, and geochronology of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in Lake Ontario sediments. Environmental Science & Technology 23:200–208

Olsson M, Bignert A, Eckhäll J, Jonsson P (2000) Comparison of temporal trends (1940s–1990s) of DDT and PCB in Baltic sediment and biota in relation to eutrophication. Royal Swedish Academy of Sciences 29:195–201

Pereira WE, Hostettler FD, Rapp JB (1996) Distributions and fate of chlorinated pesticides, biomarkers and polycyclic aromatic hydrocarbons in sediments along a contamination gradient from a point-source in San Francisco Bay, California. Marine Environmental Research 41:299–314

Pham T, Lure K, Lemieux C (1993) The occurrence, distribution and sources of DDT in the St. Lawrence River, Quebec (Canada). Chemosphere 26:1595–1606

Quensen JFI, Mueller SA, Jain MK, Tiedje JM (1998) Reductive dechlorination of DDE to DDMU in marine sediment microorganisms. *Science* 280:722–724

Ricking M, Schwarzbauer J (2012) DDT isomers and metabolites in the environment: An overview. *Environmental Chemistry Letters* 10:317–323

Rissato SR, Galhiane MS, Ximenes VF, de Andrade RMB, Talamoni JLB, Libânia M, de Almeida MV, Apon BM, Cavalari AA (2006) Organochlorine pesticides and polychlorinated biphenyls in soil and water samples in the Northeastern part of São Paulo State, Brazil. *Chemosphere* 65:1949–1958

Sánchez-Osorio JL, Macías-Zamora JV, Ramírez-Álvarez N, Bidleman TF (2017) Organochlorine pesticides in residential soils and sediments within two main agricultural areas of northwest Mexico: Concentrations, enantiomer compositions and potential sources. *Chemosphere* 173:275–287

Santschi PH, Presley BJ, Wade TL, Garcia-Romero B, Baskaran M (2001) Historical contamination of PAHs, PCBs, DDTs, and heavy metals in Mississippi River Delta, Galveston Bay and Tampa Bay sediment cores. *Marine Environmental Research* 52:51–79

Schilderman PAEL, Moonen EJC, Mass LM, Welle I, Kleinjans JCS (1977) Use of crayfish in biomonitoring studies of environmental pollution of the river Meuse. *Ecotoxicology and Environmental Safety* 44:241–252

Tang XY, Zhang XB, Guan Z, Long Y, Tang Q, Lü YJ (2014) Historical sediment record of  $^{137}\text{Cs}$ ,  $\delta\text{-HCH}$ , and  $\delta\text{13C}$  reflects the impact of land use on soil erosion. *Journal of Mountain Science* 11:866–874

Tsygankov VY, Boyarova MD (2015) Sample preparation method for the determination of organochlorine pesticides in aquatic organisms by gas chromatography. *Achievements in the Life Sciences* 9:65–68

United States Department of the Interior (USDOI) (1998) Guidelines for interpretation of the biological effects of selected constituents in biota, water, and sediment. United States Environmental Protection, Washington, D.C.

United States Environmental Protection Agency (USEPA) (1975) DDT: A review of scientific and economic aspects of the decision to ban its use as a pesticide. United States Environmental Protection, Washington, D.C.

United States Environmental Protection Agency (USEPA) (2017) DDT - A brief history and status. United States Environmental Protection Agency, Washington, D.C.

Vogel H (2010) The Squam Lake loon initiative: Progress report September 2010.

<https://www.nuttallclub.org/wp-content/uploads/2017/01/Squam-Lake-Loon-Initiative.pdf>. Accessed March 6 2021

Vogel H (2019) The Squam Lake loon initiative: Progress report November 2019. <https://loon.org/wp-content/uploads/2020/01/2019-November-SLLI-report.pdf>. Accessed March 6 2021

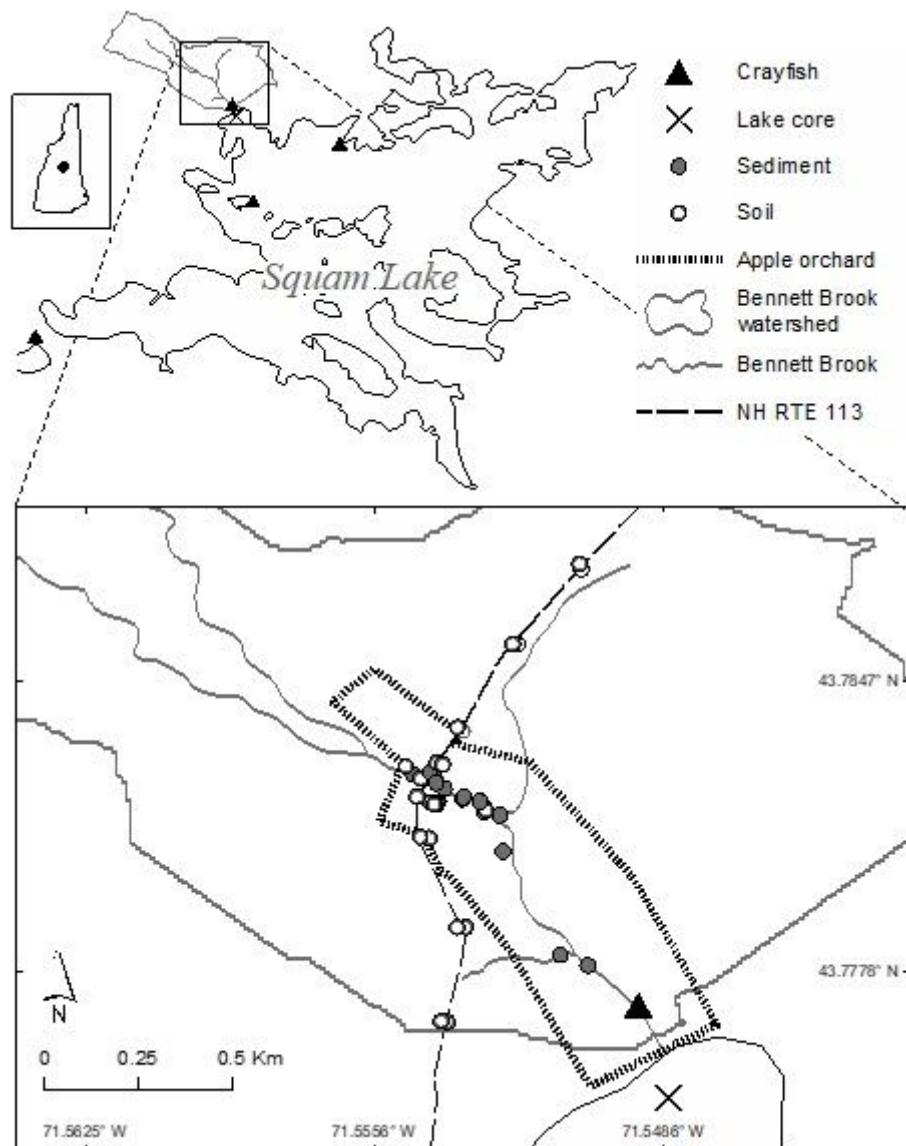
Wedemeyer G (1966) Dechlorination of DDT by *Aerobacter aerogenes*. *Science* 152:647

Wohl E (2015) Legacy effects on sediments in river corridors. *Earth-Science Reviews* 147:30–53

Yang D, Qi S, Zhang J, Wu C, Xing X (2013) Organochlorine pesticides in soil, water and sediment along the Jinjiang River mainstream to Quanzhou Bay, southeast China. *Ecotoxicology and Environmental Safety* 89:59–65

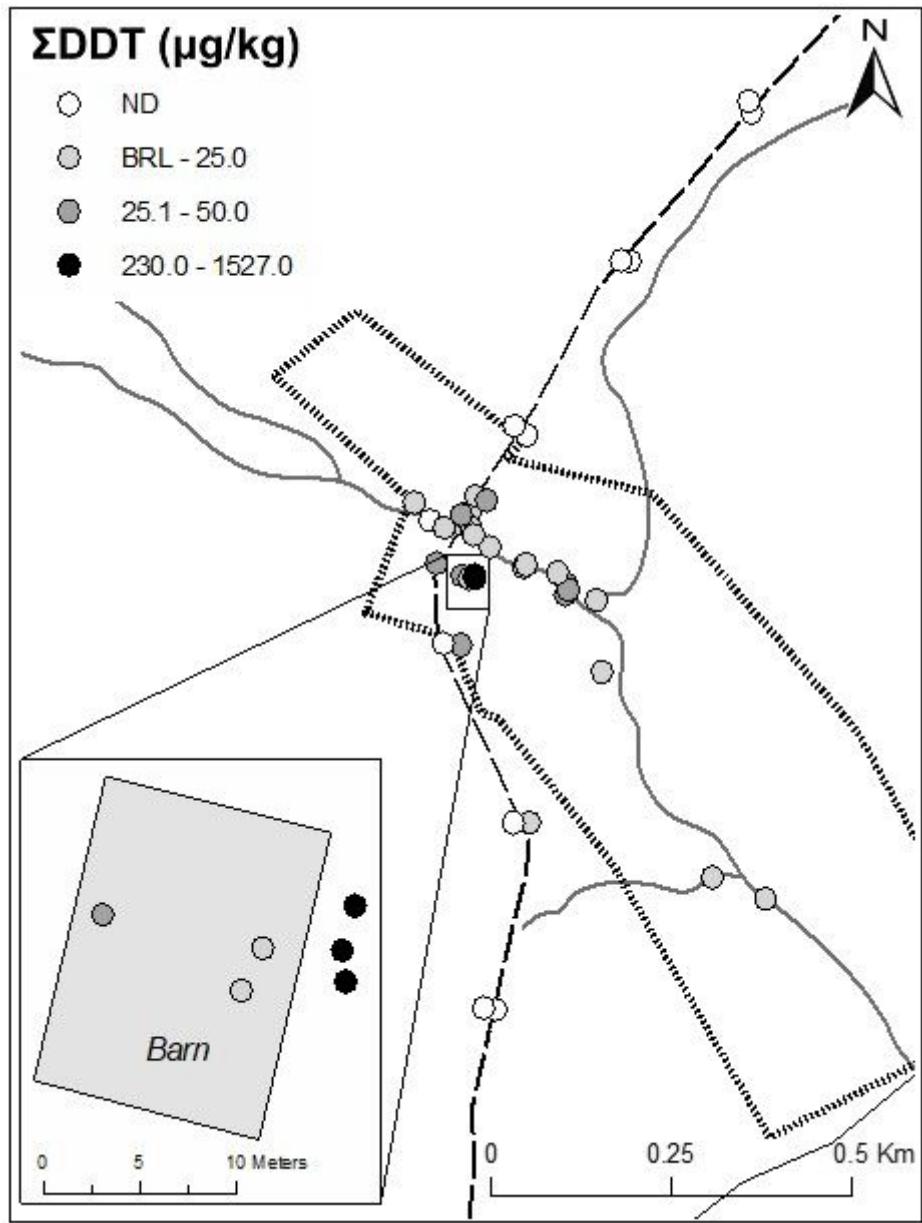
Zhang H, Shan B (2014) Historical distribution of DDT residues in pond sediments in an intensive agricultural watershed in the Yangtze-Huaihe region, China. *Journal of Soils and Sediments* 14:980–990

## Figures



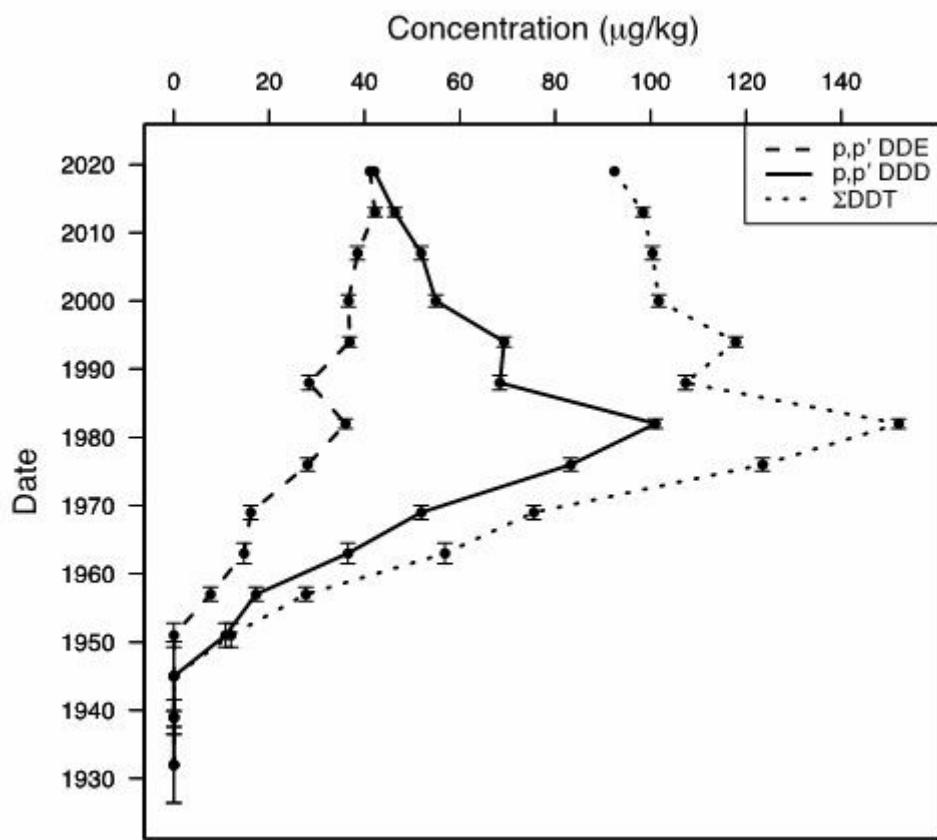
**Figure 1**

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



**Figure 2**

$\Sigma\text{DDT}$  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



**Figure 3**

p,p' DDE, p,p' DDD, and  $\Sigma\text{DDT}$  concentrations from the lake core SQ2019-3. The vertical bars represent the  $^{210}\text{Pb}$  error