Tracking Recent DDT Contamination in a Northern New England Watershed: A Geosciences Approach

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Abstract

The p,p' isomers of DDT, DDE, and DDD were analyzed in soils, sediments, and crayfish in the Squam Lake watershed in central New Hampshire (NH), U.S.A. Bennett Brook sources elevated levels of DDT residues to Squam Lake through sediment transport, likely due to legacy contamination from applications to an apple orchard surrounding the stream in the mid 1900s. Results reveal a point source located at a barn used during the orchard operation, which was burned down around 1967, with up to 723 µg/kg p,p' DDT and 721 µg/kg p,p' DDE in the soils. Higher DDT than DDE in soil samples, but not in sediment samples, suggests persistence of the contaminant in watershed soils, and faster degradation once mobilized into Bennett Brook and Squam Lake. DDT residues in the lake sediments from 1951 to the present, reveal DDT has consistently been entering Squam Lake since usage began in the U.S. There are likely multiple sources that have contributed to the constant supply, including the orchard soils treated with DDT serving as a nonpoint source, the barn site, and DDT-laden soils vulnerable to erosion, including stream banks and logged or steeply sloped land. Detections of residues in the stream and lake sediments exceed certain sediment quality guidelines for the protection of aquatic life. Higher p,p' DDE levels in crayfish collected in the mouth of Bennett Brook versus crayfish collected in Squam Lake, distant from Bennett Brook, suggests that residues sourcing from this sub-watershed are entering the aquatic food chain at levels higher than other parts of the lake.

Introduction

DDT was banned in the United States (U.S.) in 1972, due to its adverse impacts on ecosystems and persistence in the environment (USEPA 1975). Despite the ban of DDT 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, followed by 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 2019).

Sediment transport is the leading mechanism for dispersal and also is 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 is 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 from a watershed and geosystems perspective, including transportation pathways of DDT residues from soils to aquatic sediments to aquatic life via an array of processes. System-wide effects of DDT in watersheds develop as geologic weathering and erosion processes interact to mobilize DDT-laden sediments. Chemical interactions of DDT with environmental parameters determine persistence and the dominant breakdown products. Hydrologic processes determine rates and forms of DDT-laden sediment transport, in runoff and stream load, and sediment deposition in flood plains, ponded areas, deltas and, eventually, lake basins or other sediment traps. Biological processes determine both the bioavailability and bioaccumulation of DDT residues, while biomagnification determines the toxicity impacts in the aquatic food chain. So, although DDT has ultimate impacts on ecosystems, the pathways for introduction to the ecosystem begin with geosystem and sedimentary processes. This holistic 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 biomagnification is distinguishable on a sub-watershed scale.

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 with 30 named islands and 16 basins, and a maximum depth of 30 meters (Figure 1). Prevailing winds and currents transport surface waters northeast to southwest, through a channel into Little Squam Lake, with outflows to the Squam River and, eventually, the Pemigewasset and Merrimac rivers. Bennett Brook is a second order tributary to Squam Lake. Its 2.6 km² watershed comprises 2% of the 172 km² Squam Lake watershed. Mean annual precipitation, snowfall, and temperature are 109 cm, 218 cm, and 6 °C, respectively (USGS 2016). The dominant soil is Rumney fine sandy loam, which is 71% sand, 22% silt, and 7% clay. The entire Squam Lake area was heavily glaciated until about 13,000 years ago. Poorly sorted glacial drift forms the parent material of most of the soils,

overlying early Devonian Winnepesaukee Tonalite of the Squam Lake basin and the Kinsman Granodiorite and metasedimentary rocks of the surrounding highlands in the Squam Range (Lyons et al. 1997).

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 km² 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 site. The barn was destroyed in a controlled burn around 1967 and, based on site observations today, the area was likely bulldozed afterwards, disrupting the foundation.

Methods

Soil and sediment collection

Historic data on land uses and watershed characteristics guided strategic selection of sampling locations to determine DDT source area(s) (Figure 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 digester (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).

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.

Freeze cores preserve the very top, highly flocculent, layers of sediments usually disturbed and sometimes lost by traditional corers. Freeze cores were collected from Squam Lake, proximal to the outflow of Bennett Brook, to obtain sediments sourced from the Bennett Brook sub-watershed (Figure 1). In conjunction with ground penetrating radar (GPR), which creates images of subsurface deposits, suitable coring locations beyond the littoral slope zone with undisturbed, layered sediments were identified. Using data from three, 130 m-long GPR transects, radiating away from the mouth of Bennett Brook and established over the ice surface in 2019, three side-by-side freeze cores were collected. All were taken from the ice surface in February and March of 2019, from 10-12 meters water depth. Frozen cores were subsampled using a band saw, with cuts at 1-cm intervals, and each sample surface was scraped with a clean razor blade before thawing. Samples from SQ2019-2 (41 cm length, 43.774750, -71.548517) were dried, homogenized and analyzed for ²¹⁰Pb, ²¹⁴Pb and ¹³⁷Cs on a germanium gamma detector at Woods Hole Oceanographic Institution. Unsupported (excess) ²¹⁰Pb was calculated by subtracting ²¹⁴Pb from ²¹⁰Pb. Samples from SQ2019-3 (56 cm length, 43.774867, -71.548450) analyzed for DDT residues.

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 stems from DDT persistence in soils and subsequent inputs to stream and lake sediments with soil erosion and mobilization (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*) were collected using beef liver lures at three locations in 2019: 1) the mouth of Bennett Brook (43.77698167, -71.54922819); 2) a channel connecting Squam Lake to Little Squam Lake (43.73230127, -71.58728496); and 3) Mirror Lake, Woodstock, NH (43.94283783, -71.69436269) (Figure 1). Mirror Lake is a 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). The crayfish samples were processed following a variant of the Tsygankov and Boyarova (2015) methodology. Samples were extracted via Soxhlet extraction, rotary evaporated, purified with concentrated sulfuric acid, and dried through a column with sodium sulfate. Next, samples were rotary evaporated and reconstituted, then cleaned with florisil (1 g, 6 mL). All samples were single crayfish, except one composite sample of three small crayfish (Table 3).

Analytic 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 were 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, to 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).

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 with Alpha Analytical, a commercial environmental testing laboratory, and our lab resulted in 57% of p,p' DDT and 58% of p,p' DDE of the Alpha Analytical results.

Results

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 (Figure 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 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 (Figure 2). These high-value samples are from a location just 2 meters east and downgradient of the bulldozed barn foundation (the barn site). One half of B53 was analyzed at Alpha Analytical, a commercial environmental testing laboratory, whose results support our findings. 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 ± 264.3 µg/kg and 270.1 ± 305.7 µg/kg, respectively. ΣDDT levels (FAO 2016) are 232.1 to 1527.0 µg/kg and average 637.5 ± 604.4 µg/kg. The barn site 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.

Lake sediments

Radiometric dating of the lake sediments with ^{137}Cs and ^{210}Pb produced mixed results. The ^{137}Cs signal rose from a typical pre-1950's zero background to an atypical plateau instead of peaking in 1964 and declining until a low Chernobyl peak in 1989. Smearing of the two peaks is not uncommon in anoxic sediments, because cesium is mobilized in reducing conditions. The ^{210}Pb results are more conclusive, showing a clear extinction tail in excess ^{210}Pb activity. From these ^{210}Pb dating results, we developed a sediment depth-age model for lake core SQ2019-2 that we also apply to SQ2019-3 based on the less-than-3 meter distance between the SQ2019-2 and SQ2019-3 core sites, and the identical sediment depths of two marker horizons in both cores.

Squam Lake core sediment samples contain only p,p' DDE and p,p' DDD (Figure 3). Residues appear in the lake sediments soon after DDT came into use in the U.S. At 16 cm core depth (A.D. 1951), we find p,p' DDD, and at 15 cm core depth (A.D. 1957), we find p,p' DDE. Below these depths, residues are not detected. 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. The p,p' DDD concentrations are consistently higher than p,p' DDE. After initial appearance, concentrations of both residues increase until A.D. 1982, after which p,p' DDD concentrations decrease, p,p' DDE concentrations continue to increase and, overall, ΣDDT levels decrease to the present (Figure 3). The DDT residue levels in Bennett Brook and Squam Lake sediments are comparable to those in recent studies for other locales (Table 1).

Crayfish

Crayfish results are shown in Table 3. Crayfish from Mirror Lake, the reference site, 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). Neither p,p' DDT or p,p' DDD were detected in the crayfish. Crayfish collected in Squam Lake, distant from Bennett Brook have p,p' DDE values from no detection to 1.7 µg/kg ww, which is comparable to other crayfish collected and analyzed in 2013 from Squam Lake with p,p' DDE levels of 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

Sources of DDT

DDT residues in Bennett Brook sediments are likely from multiple sources. DDT applied to an area can remain in soil for years, which explains the presence of DDT residues throughout the orchard area. Thus, it is probable that the orchard, as a whole, serves as a nonpoint source of DDT to Bennett Brook and, eventually, to Squam Lake. Furthermore, DDT contamination is largely constrained to the orchard operation, since 90% of samples collected outside the orchard resulted in no detection of residues. Therefore, DDT residues detected in Bennett Brook are likely sourced from legacy contamination from past DDT use on the orchard (Gao et al. 2013).

Based on the high levels detected at the barn site, DDT may have been stored there during the orchard operation, resulting in a point source of the contaminant. Of the barn site samples, B42 has the highest levels of residues (1,527.0 µg/kg ΣDDT) and was the deepest sample collected in the soil horizon (0 – 6 cm), 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.

Roadside gullies along NH RTE 113 in the study area carry runoff, including any DDT-laden sediments, directly into Bennett Brook. We find p,p' DDE in the gully samples along the stretch of NH RTE 113 that is immediately downgradient of the upper orchard area and upgradient from the barn site. 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. 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 the soils 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 of additional point sources contributing to p,p' DDE in the gullies.

Transportation potential

The main peak in p,p' DDD and p,p' DDE concentrations in the lake core sediments in 1982, ten years after the U.S. ban, indicates retention of DDT-laden particles in the watershed soils or Bennett Brook, creating a lag in delivery of residues to Squam Lake (Muir et al. 1995, Kurek et al. 2019).

We hypothesized that watershed erosion events would produce spikes of ΣDDT in the lake sediments, as floods and other disturbances mobilize stream sediments into Squam Lake. However, the extreme events of the Mother's Day Storm in 2006 or Hurricane Irene in 2011, and the beaver ponds breach in the lower reaches of Bennett Brook in 2002, all fail to leave a distinct DDT signature in the lake core. Higher resolution subsampling, for instance at 0.25 cm intervals, may provide more information on impacts from individual storms. Nonetheless, since unstable soils are eroded and mobilized during events such as these, it is reasonable to assume that extreme events have and will continue to trigger mobilization of the contaminant. The destruction of the barn in a controlled burn in about 1967 destabilized soils on the barn floor and also, potentially, stored DDT, allowing them to mobilize from the barn and into Bennett Brook. Bulldozing around the barn's foundation, which occurred sometime after the building was burned, likely increased the mobilization and flux of DDT.

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 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.

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 (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).

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. However, fish and piscivorous birds, such as loons, kingfishers, and bald eagles, are not confined to as small a range as crayfish. They can easily travel and ingest prey with differing contaminant levels, depending on their location in the lake. Any such predator, whose range includes Bennett Brook, could experience higher DDT bioaccumulation.

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, USDOJ 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 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.

Conclusion

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 (Figure 4). This watershed systems approach aids in understanding the extent of the contamination.

The orchard is a significant 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.

Climate change models for New England predict an increase in the frequency of intense storms, and therefore an increase in runoff and soil erosion that might expose and release additional, relatively undegraded DDT (Nearing 2001). This study calls attention to possible ongoing threats of persistent chemicals like DDT, despite bans in use decades ago.

Declarations

Funding: Sigma Xi, Plymouth State University, Woods Hole Oceanographic Institute

Conflicts of interest/Competing interests: Not applicable

Availability of data and material: Available data: May A (2020) DDT contamination in Squam Lake, NH: A Watershed Approach. Thesis, Plymouth State University. (Also available at https://www.researchgate.net/publication/350442076_Amanda_May_Master%27s_Thesis_DDT_Contamination_in_Squam_Lake_NH_A_Watershed_Approach)

Available material: A duplicate frozen core is available for additional work by contacting Dr. Lisa Doner (ladoner@plymouth.edu) at Plymouth State University (17 High St, Plymouth, NH 03264).

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Consent for publication: Yes

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Tables

Table 1 Comparison of ΣDDT ($\mu\text{g/kg}$) levels in sediments in recent studies

Location	ΣDDT ($\mu\text{g/kg}$)	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 - 257	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

Table 2: Summary data for Bennett Brook DDT isomer analyses

Sample Type	p,p' DDT	p,p' DDE	p,p' DDD
	Range (average $\pm$ standard deviation) $\mu\text{g/kg}$		
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

Table 3 p,p' DDE ($\mu\text{g/kg}$ wet weight) concentrations in crayfish collected in Bennett Brook and in Squam Lake

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

ND No Detection. * denotes average carapace length (composite sample of three crayfish)

Figures

Figure 1

Study area located in central New Hampshire, U.S. and sampling locations for crayfish, soils, sediments, and lake cores Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

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 Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Figure 3

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

Figure 4

Conceptual diagram of transportation pathways of DDT residues from the Bennett Brook watershed to Squam Lake