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Ecological Legacy of DDT Archived in Lake Sediments from Eastern Canada

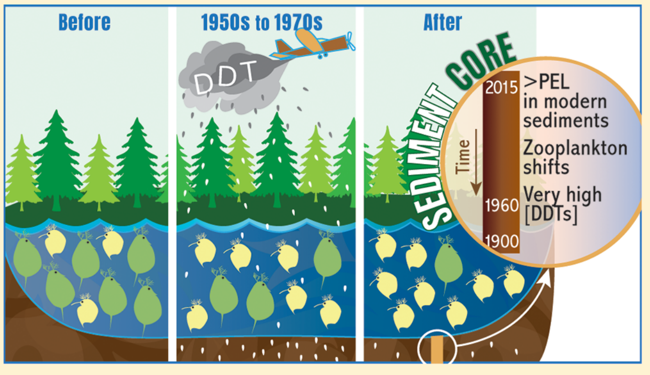
Joshua Kurek,*,† Paul W. MacKeigan,† Sarah Veinot,‡ Angella Mercer,‡ and Karen A. Kidd‡,§

†Department of Geography and Environment, Mount Allison University, 144 Main Street, Sackville, New Brunswick E4L 1A7, Canada

‡Canadian Rivers Institute and Department of Biological Sciences, University of New Brunswick, 100 Tucker Park Road, Saint John, New Brunswick E2L 4L5, Canada

§Department of Biology and School of Geography and Earth Sciences, McMaster University, 1280 Main Street West, Hamilton, Ontario L8S 4K1, Canada

Supporting Information



ABSTRACT: Historic forest management practices led to widespread aerial application of insecticides, such as dichlorodiphenyltrichloroethane (DDT), to North American conifer forests during ∼1950−1970. Lake basins thus may provide an important archive of inputs and aquatic responses to these organochlorines. We use dated sediment cores from five study lakes in multiple watersheds in New Brunswick (NB), Canada, to provide a regional paleo-ecotoxicological perspective on this potential legacy stressor in remote lake ecosystems. Peak sedimentary levels of *p,p*′- and *o,p*′-DDT (ΣDDT) and breakdown products ΣDDE (dichlorodiphenyldichloroethylene) and ΣDDD (dichlorodiphenyldichloroethane) generally occurred during the 1970s to 1980s. Sediments exceeded probable effect levels (PELs) by ∼450 times at the most impacted lake. Modern sediments in all study lakes still contained levels of DDT-related compounds that exceed PELs. For the first time, we show that aerial applications of DDT to eastern Canadian forests likely resulted in large shifts to primary consumers within several lake food webs, principally through lake-specific impacts on zooplankton community composition. Modern pelagic zooplankton communities are now much different compared to communities present before DDT use, suggesting that a regional organochlorine legacy may exist in the modern food webs of many remote NB lakes.

■ INTRODUCTION

Severe outbreaks of spruce budworm (*Choristoneura fumiferana*) occur every 30−50 years in the conifer forests of eastern Canada.[1,2] Economic costs to the forest industry and government are substantial. Estimates for the Province of New Brunswick (NB), Canada, are at tens to hundreds of millions of dollars annually during outbreaks.[3] Beginning in 1952, forest stakeholders in NB consisting of federal and provincial agencies and the forest industry coordinated a massive aerial spray program of pesticides to mitigate spruce budworm outbreaks and reduce economic losses. From 1952 to 1968, between 0.2 and 5.2 million acres of NB forests were treated annually, sometimes twice annually, with either dichlorodiphenyltrichloroethane (DDT: 1952−1968), phosphamidon (beginning in 1963), fenithrothion (beginning in 1967), or combinations thereof.[4,5] DDT, a highly persistent organochlorine,[6,7] was the preferred pesticide for aerial application in the 1950s and 1960s. Between 1952 and 1968, at least 5.7 million kg of DDT were applied to NB forests, compared to 0.9 million kg of DDT in Québec, and even lesser amounts in other Canadian provinces and the northeastern U.S.[4,8,9] New Brunswick was therefore one of the most heavily sprayed forested regions of North America. At ∼1970, DDT use in the province generally ceased because of the growing awareness of its adverse impacts on fish and wildlife. Today, historic DDT applications are recognized as a possible cause of widespread declines in swifts and other insectivorous birds through alterations to invertebrate prey,[10] but its legacy impacts on North American lake ecosystems are largely unstudied.

Freshwaters become contaminated with organochlorines via atmospheric deposition and terrestrial runoff,[6,11,12] but direct applications to surface waters has also occurred. For example, to reduce nuisance insects, ∼16 000 kg of dichlorodiphenyldichloroethane (DDD as Rhothane) were applied to the Saint Lawrence River near Montréal, Canada just before and during the World Exposition in 1967.[13] The low water solubility, high

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partitioning to organic matter and lipids, and resistance to biodegradation result in the accumulation of DDT and its breakdown products in sediments[6,14] and also its biomagnification through food webs.[15] The sediment half-life of DDT-related organochlorines is generally >20 years but varies depending on site-specific conditions.[11,16] Thus, lake sediments are recognized as important sinks and archives of DDT and its breakdown products.[11,12,17,18]

Given the fate, persistence, and toxicity of DDT, exposures of benthic invertebrates and the resting stages of zooplankton to elevated DDT levels within sediments may alter species abundances and community composition in lake ecosystems.[6,19−21] Indeed, the widespread application of millions of kg of DDT to NB forests[4,8,9] may represent an unrecognized legacy stressor to many lake ecosystems in this aerially-sprayed region. To investigate potential impacts of aerial-sprayed organochlorines during historic spruce budworm outbreaks, we used dated sediment cores from five strategically-selected headwater lakes in multiple watersheds of north-central NB. Our goal was to compare temporal trends in sedimentary DDT-related organochlorines with the assemblage structure of subfossil zooplankton. Crustacean zooplankton such as Cladocera, a commonly used bioindicator, are an important link between primary production and secondary consumers.[22,23] Acute toxicity data generated under laboratory conditions demonstrate that several Cladoceran families are more sensitive to DDT, compared to most other invertebrate families.[24] For example, Bosminidae ranked as the fourth most sensitive taxon out of 84 families examined, in terms of their mode-specific sensitivity and recovery potential to organochlorine exposure. We anticipated that historic peak DDT inputs via aerial spraying are reflected within NB lake sediments and hypothesized that its elevated use during the 1950s to 1970 altered the assemblage structure of pelagic cladocerans. Most paleolimnological studies of contaminants focus on loadings through time and aim to identify sources and recent trajectories,[12,14] whereas our study provides an additional ecological context to DDT as a legacy stressor by examining responses of key invertebrates within aquatic food webs. Overall, our findings aid in understanding the environmental legacy of persistent pollutants and suggest that organochlorines applied during the mid-20th century, in arguably one of North America's largest aerial spray programs, have had long-term ecological consequences across presumably many of NB's ∼2500 lakes. Additionally, chronic stress from DDT inputs to lake ecosystems may also contribute to the long-term trajectory of zooplankton within the pelagic zone that, over recent decades, have likely experienced longer growing seasons, warmer surface water temperatures, and more stable thermal stratification due to climate change.

■ MATERIALS AND METHODS

Study Lakes. Five remote lakes within the Atlantic Maritime Ecozone from north-central NB were chosen for study (Figure S1 of the Supporting Information, SI). All lakes are headwater systems with no major inflowing streams. Watersheds are mainly forested with limited access by gravel roads. Coniferous tree species dominate, such as balsam fir and white and black spruce, while lesser coverage of deciduous species such as poplar, birch, and maple exists. Active forest management and harvesting operations are currently present and presumably historic logging has also occurred throughout each watershed. Mean summer and winter temperatures are 16.8 and −10.9 °C, respectively, and annual precipitation is ∼1010 mm.

We used historic maps of spruce budworm defoliation and pesticide treatments to select lake watersheds that likely experienced aerial spraying during the mid-20th century.[25,26] Small lakes of moderate depths (<70 ha; < 15 m depth) from four different watersheds were selected, with each lake being dimictic, circumneutral (pH of 7.1−7.5), and oligotrophic (total phosphorus of 4−10 μg L^{-1}), and with watersheds that are ∼10 to 40 times the lake's surface area (Table S1). All lakes currently have Brook Trout (*Salvelinus fontinalis*) populations in addition to various minnow species. Upsalquitch contains a remnant population of Arctic Char (*Salvelinus alpinus*) and Sinclair has Yellow Perch (*Perca flavescens*). Three study lakes (California, Goodwin, and Middle Peaked Mountain) are managed for their Brook Trout fishery and angler access is regulated. There is no record of fish stocking by provincial authorities at Upsalquitch, California, Sinclair, and Goodwin lakes, whereas 2000 juvenile Brook Trout were stocked at Middle Peaked Mountain Lake in 2000 (DeBouver, NB Energy and Resource Development, Pers. comm.).

Sediment Collection and Dating. Duplicate sediment cores were collected at each study lake with a 7.6 cm diameter gravity corer[27] between May 31 and June 9, 2016. We located the central, deep basin at each lake using bathymetry maps and on-site sonar soundings. Cores were sectioned immediately onshore at 0.5 cm resolution throughout using a vertical extruder. Instruments were cleaned with lake water between each section. Sediment intervals were placed into prelabeled Whirl-Pak bags and stored in an ice-pack filled cooler before refrigeration at ∼5 °C in the laboratory and freeze-drying of select intervals. One core was archived, and no analyses were completed on that core.

Sediment dates were determined using an Ortec High Purity Germanium Gamma Spectrometer (Oak Ridge, TN, U.S.A.). Certified reference materials were obtained from the International Atomic Energy Association (Vienna, Austria) and used for efficiency corrections. Decays of ^{210}Pb, ^{137}Cs, and ^{214}Bi were measured from 12 or 13 sediment intervals from each core following standard radioisotopic techniques at the University of Ottawa. ^{210}Pb dates were determined with the constant rate of supply model.[28] To assign estimated dates to each sediment interval in a core, linear interpolations were fitted between ^{210}Pb-dated intervals (Figure S2).

Organochlorine Analysis. Following dating results, 12−15 sediment intervals from each core were selected to assess legacy DDT congeners from aerial spraying. More specifically, we focused on DDT and its comparatively toxic breakdown products, dichlorodiphenyldichloroethylene (DDE) and DDD.[6,14] We used ∼2 g of freeze-dried sediment from each preselected sediment interval. In 37 of 65 intervals, adjacent 0.5 cm intervals were combined to obtain adequate masses for DDT analyses.

Extraction and clean up were based on US EPA protocols 3545A, 3660B, and 3640A.[29−31] Samples were spiked with a surrogate containing 4-chloro-3-nitrobenzotrifluoride and tetrachloro-m-xylene (Accustandard, New Haven, CT, U.S.A.), activated copper was added,[30] and then extracted using an accelerated solvent extractor (Dionex ASE 300) with 50:50 dichloromethane (DCM)/hexane (Optima grade, Fisher Scientific, Ottawa, ON). Extracts were concentrated to 6 mL using a Büchi rotavapor (R-200) and nitrogen evaporator (N-EVAPTM112, Organomation Associates Inc.) and then run

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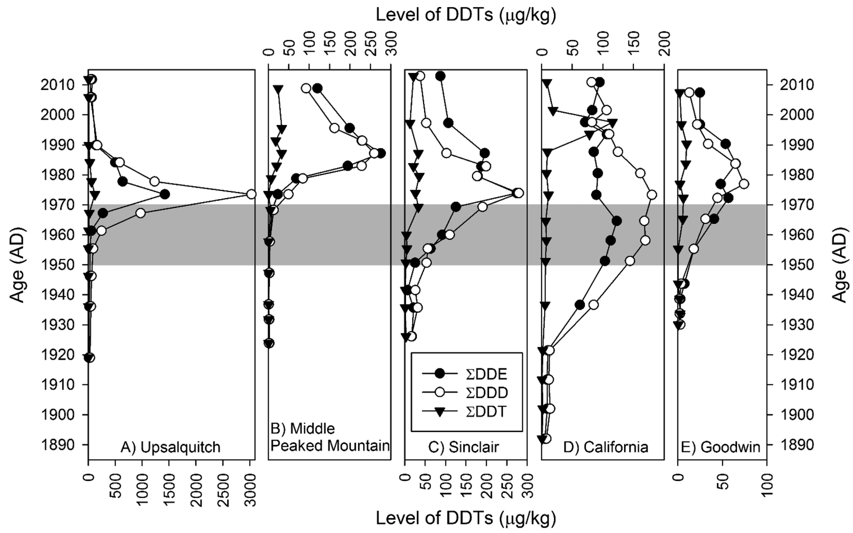

Figure 1. Sedimentary levels (μg/kg dw) of *o,p′*- and *p,p′*-DDT (ΣDDT), *o,p′*- and *p,p′*-DDE (ΣDDE), and *o,p′*- and *p,p′*-DDD (ΣDDD) in dated cores from remote, headwater lakes in north-central New Brunswick, Canada. Shaded area represents the known time period of DDT application in the region.

through a gel-permeation chromatography column using 50:50 DCM/hexane to remove interferences. Next, the sample was concentrated into 1 mL of hexane and eluted through a manually packed 1.2% deactivated Florisil column (HPLC grade water; Fisher Scientific). Three fractions were collected from the column using hexane to elute fraction A, 15:85 DCM/hexane to elute fraction B, and 50:50 DCM/hexane to elute fraction C.[32] Fractions were then each concentrated into 1 mL of isooctane and spiked with a known amount of pentachloronitrobenzene (AccuStandard, New Haven, CT, U.S.A.). Analysis of DDT congeners in the three fractions largely followed US EPA standard protocols 8082 and 8081.[33,34] Samples were run on a gas chromatography-electron capture detector (Agilent 6890 GC-ECD) and quantified using an internal standard calibration on a DB-5, 60 m, 0.25 mm, 0.25 μm Agilent J&W column. DDTs were confirmed on a second GC column with greater polarity (DB-XLB, 60m, 0.25 mm, 0.25 μm; Agilent J&W). Specifically, *p,p′*-DDT, *o,p′*-DDT, *p,p′*-DDE, *o,p′*-DDE, *p,p*'-DDD, and *o,p′*-DDD were measured. Herein, we report ΣDDT, ΣDDE, and ΣDDD as the sum of their two respective isomers, and total DDTs as the sum of all six congeners.

Each batch of samples included a method blank (MB), method spike (MS), certified reference material (CRM: NIST SRM 1941b Organics in Marine Sediments), and calibration checks for quality assurance. Surrogates and MS were reported as percent recoveries of the calculated target values and CRMs were reported as percent recoveries based on target values from the certificate of analysis. In addition, calibration check standards for both the target and surrogate compounds were run on every batch and were reported as percent recoveries based on the calculated target value. Method detection limits (MDLs) were determined by running eight low-level spike samples (5× higher than the expected MDL) through the entire process. The *t*-value ($n = 8$, 95%) was multiplied by the standard deviation of the eight runs to determine the MDL for each DDT congener. Reporting limit (RL) for a 2 g sample was based on the amount of the lowest calibration standard and determined to be 0.60 μg/kg dw for each congener. MDLs were ≤ the RL.

Zooplankton Subfossil Analysis. We examined subfossil remains of crustacean zooplankton (Cladocera) from sediments deposited during the period of peak DDT use in NB (~1950−1970), in addition to periods both before and after DDT use, to determine zooplankton community responses to aerial spraying. The bioindicator potential of pelagic Cladocera to chemical stressors is well recognized.[35−37] Pelagic cladocerans, such as Daphniidae and especially Bosminidae, are sensitive to DDT and other organochlorines.[24,38,39] Daphniids are also used worldwide as a model organism in toxicology[40] and can bioaccumulate DDT.[41,42] Even the resting stages of *Daphnia* sp., which are the products of sexual reproduction and often sink to the bottom of lakes and become incorporated in sediments, may accumulate organic contaminants from the aquatic environment.[20] Additionally, pelagic cladocerans are integral to lake food webs as both consumers and prey, and may bioaccumulate DDT more than organisms relying on benthic primary production from the littoral zone.[42]

Cladoceran subfossils were processed largely following standard methods.[43] Initially, 22 sediment intervals were selected from each study lake and included: 0−0.5 cm, 2−2.5 cm, 4−4.5 cm, and every consecutive interval between 6 and 15.5 cm. Several additional intervals were processed from all study lakes, except Upsalquitch, after sediment dating results were obtained. Briefly, 80 mL of 10% KOH was added to between ~1 and 3 g of wet sediment and then heated to ~70 °C for ~30 min. Sediments were then rinsed with deionized water on a 38-μm sieve and transferred to a 3 fluid dram vial with ~5 to 6 mL of deionized water. Several drops of 95% EtOH were added as a preservative. Next, a series of 100-μL aliquots of homogenized sample was pipetted onto coverslips. Coverslips were permanently mounted on slides using Entellan. Remains were identified with brightfield illumination at 200 or 400× magnification. Coverslips were scanned entirely and identifications were based on subfossil references from eastern North America.[44,45] All identifiable remains were tallied individually, with the most abundant remain used to determine the total number of individuals in each interval. Previous paleolimnological studies from low-nutrient lakes of northern NB showed that pelagic taxa such as

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Bosmina sp. and *Daphnia* sp. dominate the contemporary assemblage of most dimictic lakes.[46,47] Daphniids were grouped based on the presence of stout spines on the middle pectin of the postabdominal claw.[44] Our *Bosmina* sp. grouping refers to the sum of all *Bosmina* sp. and *Eubosmina* sp., as the pore location on the headshield can be obscured. Fragmented bosminid carapaces, which are not reliably distinguishable, were also often the most abundant remain.[44,48] Minimum total counts of 70−100 individual cladocerans were targeted for each interval to adequately characterize the assemblage.[48]

Cladoceran counts were first converted to relative abundances as a reliable ecological measure of an important group of primary consumers. Relative abundances of all taxa were then square root transformed to reduce the influence of dominant taxa when using an Euclidean-based ordination technique such as principal components analysis (PCA).[49] PCA and the resulting axis 1 sample scores were then used to summarize major assemblage variation from each study lake. Due to large differences in assemblage composition between lakes, lakes were grouped according to their average *D. longspina*-complex abundance throughout the record, with three lakes at >40% and two lakes at <10%. To examine temporal trends in the dominant pelagic taxa, relative abundances of *Daphnia* sp. and *Bosmina* sp. within each lake group were standardized using Z-scores to allow comparisons between groups of abundance data on a similar scale, including the magnitude of abundance shifts. Z-scores of *Daphnia* sp. (sum of *D. longispina* and *D. pulex* complexes) and *Bosmina* sp. were then compared within the lake groups across three time periods by use of a Kruskal−Wallis test. This is a rank-based, nonparametric method to evaluate the null hypothesis of no difference in group medians. The three time periods compared were defined by the known use of DDT within NB and related DDT sedimentary measures (Figure 1). The time periods were recognized as baseline (<1950), DDT increase (1950−1980), and recovery (>1980). PCA axis 1 sample scores of air temperature observations were also used to represent long-term climate change across seasons from the region. Direct observations of climate used in the PCA consisted of mean monthly air temperatures during the ice-free growing season (May through Oct) from the Edmundston climate station (ID: 810AL00), which is ~150 km west of the study lakes and represents a humid continental climate.

■ RESULTS AND DISCUSSION

Historic DDT Pollution from Aerial Spraying. Dated sediment records from all five headwater lakes reflected the widespread use of DDT in NB watersheds during the mid-20th century to manage spruce budworm outbreaks (Figure 1). Downcore trends of the *o,p′*- and *p,p′*- isomers were very similar, with the *p,p′*- isomers of DDT, DDE, and DDD observed at higher levels than the *o,p′*- isomers (Figure S3). Given the similar patterns, the two isomers for each of DDT, DDE, and DDD were combined for temporal trend assessments and comparisons among lakes. Peak organochlorine levels in the lake sediments during the mid-1970s were broadly consistent among Upsalquitch, Sinclair, and Goodwin lakes. This suggests a lag of at least ~5−10 years for the export of aerially applied organochlorines from the catchment to the headwater lake ecosystem for ultimate incorporation into the sediments. This lag is near the average error of the CRS-estimated sediment ages during this period in the record (Figure S2). In addition, these three lakes had the highest, moderate, and lowest sedimentary organochlorine levels during the period of maximum DDT. Only Upsalquitch Lake showed concurrent peaks of ΣDDT, ΣDDE, and ΣDDD in the same sediment interval, whereas the other four sites generally had peak sediment ΣDDE and ΣDDD at the same time, followed by sustained and higher ΣDDT in more recent decades. Maximum levels of DDT and its breakdown products at Middle Peaked Mountain Lake occurred about a decade later, during the mid-1980s, compared to the other lakes and suggest either later application to the catchment and/or delayed catchment export. In contrast to the other systems, at California Lake there was no clear, peak period of organochlorines. ΣDDE and ΣDDD remain elevated from the 1950s to the present and the highest ΣDDT level occurred surprisingly recently, in the 1990s, and suggests a recent application to the surrounding catchment. In addition, at our deepest lakes (Upsalquitch and California), there was more breakdown product ΣDDD than ΣDDE during the ~1950s to ~1990s, which may reflect their different physical-chemical environments (Table S1), such as constant anaerobic conditions.[12,14,17]

Collectively, our NB headwater lakes record among the greatest regional contamination of DDT and its breakdown products within lakes in North America.[13,18,50−52] Maximum levels recorded are striking and range from ~139 μg/kg at Goodwin Lake to ~4500 μg/kg at Upsalquitch Lake for total DDTs (Figure 1), and historic levels in the latter exceeded probable effect levels (PELs)[6] by 18, 212, and 452 times for ΣDDT, ΣDDE, and ΣDDD, respectively. Only Clear Lake, California (U.S.A.) shows consistently higher sedimentary organochlorine values after DDD was added directly to the lake between the ~1940s and 1950s.[53] Maximum total DDTs at the other NB sites were also remarkable at ~297, 567, and ~580 μg/kg for California, Middle Peaked Mountain, and Sinclair lakes, respectively. These maxima were much higher than that observed (~120 μg/kg) in sediments dating to ~1980 from Britt Brook Lake in north-central NB, where surface water samples collected in late summer 1999 also had high levels of DDT congeners.[52]

To further place these NB values in perspective, 5 of 6 lakes within the Fraser River watershed (British Columbia, Canada) receiving aerial applications of DDT during the mid-20th century showed maximum ΣDDT of between 2 and 10 μg/kg.[50] Nicola Lake was the only exception at 323 μg/kg,[50] a value comparable to those found herein. Additionally, six of seven large lakes from Yukon Territory (Canada) with huge drainage areas (~30−35 000 km^2) showed maximum sedimentary ΣDDT levels of between ~0.5 and 21 μg/kg, with only Watson Lake at 2680 μg/kg ΣDDT during ~1952 being comparable to our NB study lakes.[51] Reservoirs in the central and southeastern United States had maximum levels of total DDTs in the ~1960s of between ~5 and 75 μg/kg and fluvial inputs from the varied watersheds exceeded potential atmospheric deposition pathways.[18] Recent sediment intervals from these reservoirs all record total DDTs < 10 μg/kg and thus indicate near complete chemical recovery from organochlorine pollution.

The most recent sediments at all NB sites exceed almost all PELs for ΣDDT and its breakdown products.[6] This is unexpected as >50 years have passed since DDT-based organochlorines were last sprayed on NB's conifer forests, and there were decreases from peak total DDT levels of between 97% (Upsalquitch) and 37% (California) in the lake

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sediment records. This lack of chemical recovery in our NB lakes differs considerably from other paleolimnological studies of DDT contamination in North America[13,18,50,51] and may be related to the unprecedented amounts applied in this province relative to most other North American regions. Between 1946 and 1962, the Fraser River watershed, British Columbia, had heavy aerial applications of DDT-based organochlorines;[4,50] however, total DDTs in modern sediments approached background values in all 6 study lakes and were well below PELs.[6,50] Similarly, contaminant levels in modern NB lake sediments far exceed even peak levels of Rhothane (ΣDDD; 50 μg/kg) observed from dated sediment records at Lake Saint-Pierre, ∼100 km downstream of Montréal, where this larvicide was applied directly to the river prior to the World Exposition in 1967.[13] Only Goodwin Lake located in the Northwest Miramichi River watershed, NB, shows ΣDDT less than the PEL in its two recent-most sediment intervals that date to post ∼1997; however, ΣDDE and ΣDDD from those intervals exceed the PEL values by 3.7 and 1.5 times, respectively. ΣDDE in most modern sediments at our study lakes are still on average 16 times above PEL and suggests there may be ongoing effects of this legacy contaminant on sediment-dwelling organisms.

Lake sediments from undisturbed depositional zones reflect the timing and magnitude of contaminant inputs given that postdepositional processes such as mixing and pore water diffusion are minimal.[14,17] Herein, only 10 out of 165 sedimentary measures of DDTs were below MDLs, all for ΣDDT in early intervals from Middle Peaked Mountain, California, and Goodwin lakes. Unexpectedly, even dated sediment intervals well before ∼1940, when DDTs were first used widely, showed measurable ΣDDT and its congeners. This is especially evident at California Lake and suggests that movement of DDTs within the sediments occurred at all sites following deposition from the water column. Differing inputs of dissolved organic matter may influence the pore water diffusion of DDTs.[17] Also, some bioturbation and other physical mixing processes may have occurred given our less well-resolved ^{137}Cs peaks in the mid-1960s (Figure S2). Nevertheless, these limitations common to paleolimnology do not discount the value of lake sediments for understanding chronic contaminant exposure and aquatic responses over ecologically-relevant time periods.[21,54,55]

Bioindicator Responses of Pelagic Cladocera. Planktonic, filter-feeding *Bosmina* sp. and *Daphnia* sp. dominated all assemblages in the NB lakes. Combined, these cladocerans comprised, on average, between ∼90 (Upsalquitch) and 75% (Sinclair) of all subfossils recovered at each lake, which is consistent with most dimictic, low-nutrient lakes in maritime Canada.[46,47,56] Several lakes show massive shifts in relative abundances over time (Figure 2) that may be linked to the period of DDT use, as these two pelagic taxa are vulnerable to organochlorine exposures at community to species levels.[24,35,39] Interestingly, 4 of 5 lakes (except Middle Peaked Mountain) showed greater relative abundances of the small-bodied *Bosmina* sp. relative to its larger-bodied pelagic competitor *Daphnia* sp. in recent decades compared to the baseline period (before ∼1950), after which DDT-based organochlorines were widely used for about two decades.

Smaller zooplankton, such as bosminids, are generally recognized as more tolerant to most contaminants[35,56] and their increases relative to larger-bodied planktonic competitors are hypothesized as an ecosystem-level response to chronic

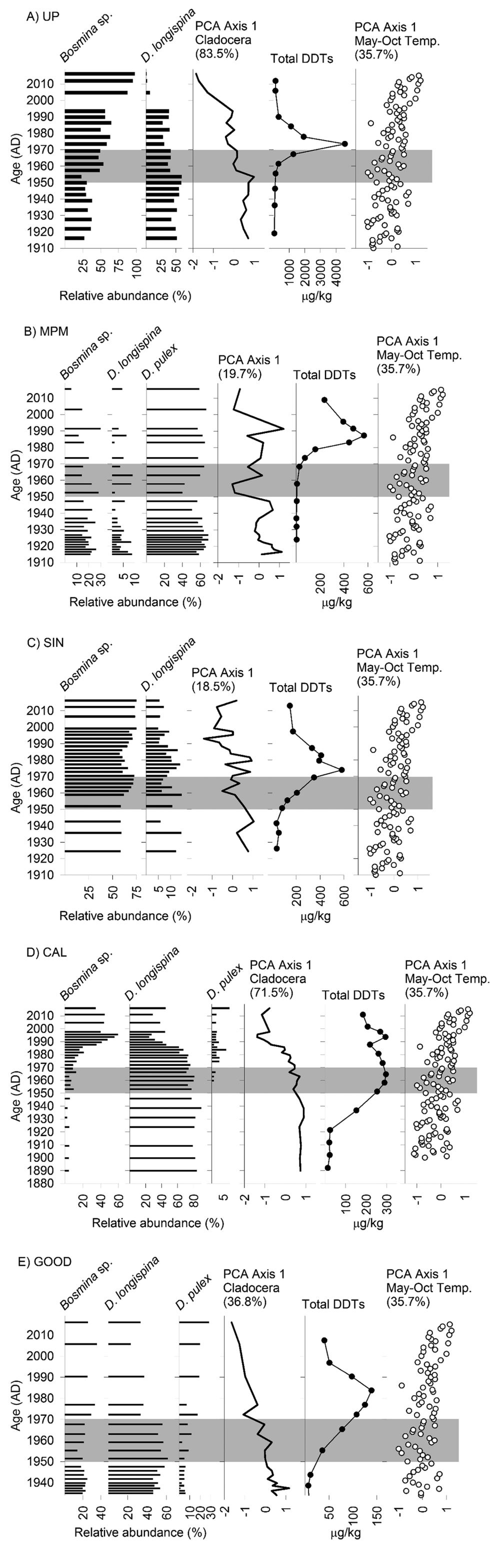

Figure 2. (A–E) Dominant pelagic Cladocera and PCA scores from all subfossil Cladocera observed in the dated cores from (A) Upsalquitch, (B) Middle Peaked Mountain, (C) Sinclair, (D) California, and (E) Goodwin lakes. Sedimentary levels of *o,p*′- and *p,p*′- isomers of DDT, DDD, and DDE were summed as total DDTs (μg/kg dw). Observed air temperatures during the ice-free growing season from the Edmundston station (ID: 810AL00) were summarized with PCA. Shaded area represents known time period of DDT application in the region.

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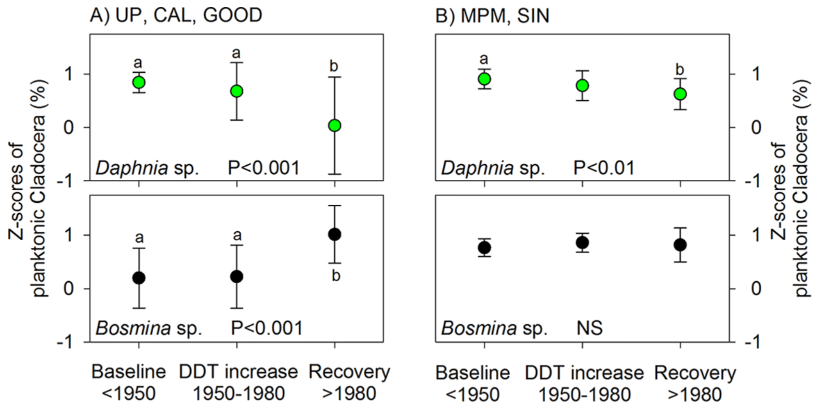

Figure 3. Standardized relative abundances (±1 SD) of *Daphnia* sp. and *Bosmina* sp. grouped by A) lakes with >40% *Daphnia longispina*-complex and B) lakes with <10% *Daphnia longispina*-complex. Time periods are based on known DDT application in the region and sedimentary DDT trends reported in Figure 1.

stressors.[57−59] Indeed, chronically-stressed aquatic environments are often associated with shifts in body size toward smaller zooplankton.[60,61] In a paleolimnological study of organochlorine pollution in shallow, productive ponds from Norfolk, England, both the absolute and relative abundances of *Bosmina longispina* increased coincident with sedimentary organochlorine levels during the mid-20th century.[62] Only Middle Peaked Mountain Lake, NB, which is compositionally different from the others in its ∼60% dominance of the *D. pulex*-complex, compared to the *D. longispina*-complex, throughout, did not exhibit a sustained *Bosmina* sp. increase toward modern times.

Two of our headwater lakes, Upsalquitch and California, demonstrated remarkable assemblage shifts in planktonic cladocerans from the baseline period prior to the 1950s when assemblages were relatively stable for the previous five decades (Figure 2). This suggests that mid-20th century stressors have led to new ecological states now apparent within the zooplankton communities, including the rise of small-bodied bosminids at both lakes and novel daphniid taxa at California Lake. Presumably, chronic stress favors smaller zooplankton given their faster reproductive rates and fewer molts required prior to reproduction when cladocerans are most sensitive to contaminants.[60,63] In particular, Upsalquitch Lake demonstrated a near loss of a keystone grazer, the *D. longispina*-complex, from on average ∼50% before ∼1950 to <5% after the mid-1990s. In modern sediments, *Bosmina* sp. comprised >95% of all Cladocera at Upsalquitch. This unprecedented shift in the intermediate trophic level at Upsalquitch Lake occurred in two distinct stages and is captured well by PCA axis 1 scores (Figure 2). The first stage began nearly coincident with widespread DDT application in NB. The second stage began after the ∼1990s, although our sample resolution in modern times was sparse and made it difficult to determine the exact timing of this recent *Bosmina* sp. increase. The rise of *Bosmina* sp. at California Lake from, on average,∼5% before ∼1950 to ∼45% after ∼1990, was of similar magnitude as the rise at Upsalquitch Lake. Notably, California Lake also showed the occurrence of the *D. pulex*-complex for the first time in the record coincident with widespread DDT application in NB at ∼1960. The long-term ecological consequences of such large-magnitude zooplankton shifts to lake food webs are currently unknown, but these zooplankton groups are integral to nutrient transfers among phytoplankton and secondary consumers.[23]

Historic daphniid species turnover and abundance declines through both size-selective predation and abiotic mechanisms can increase a lake's susceptibility to greater algal production.[47,64,65] In northwestern NB, Lac Unique has experienced decreased *Daphnia* sp. abundance by ∼10% and a concurrent bosminid rise at the expense of mostly generalist, littoral taxa since ∼1960, and since the late-2000s exhibits late-summer algal blooms that are presumably exacerbated by regional climate warming in spring and summer.[47] Reduced transfer of key nutrients across trophic levels, such as phosphorus and calcium,[66,67] may also result in poorer food quality to secondary consumers when declines in daphniids occur. Given substantial, long-term *Daphnia* sp. declines observed at Upsalquitch Lake and to a lesser extent at California Lake, especially since the ∼1990s, deterioration of each lake's food web and vulnerability to increased algal production are likely underway.

There were differences among lakes in the concurrence of the increased sedimentary DDTs associated with the aerial application of DDT to NB conifer forests and the responses of pelagic cladocerans, indicating that lake-specific responses to stressors exist (Figures 1 and 2). This is a common feature of ecological data that may be related to the species present and their traits (such as stressor tolerance) during the period prior to stressor exposure, and likely influences how each cladoceran community responds to initial and subsequent stressors.[68,69] While pelagic cladocerans from Upsalquitch and California lakes shifted in relative abundances beginning approximately coincident with the period of DDT use in NB, as captured by PCA axis 1 score trajectories, other study lakes showed no obvious (Middle Peaked Mountain Lake) or only minor (Sinclair and Goodwin lakes) assemblage responses to chronic DDT contamination reflected by the sediments. This exists despite substantial PEL exceedances for sedimentary DDT and its breakdown products at all study lakes. For example, PCA axis 1 scores at Middle Peaked Mountain (19.7%) and Sinclair (18.5%) lakes capture much less assemblage variation than at other lakes and also demonstrate no association in their trajectory with elevated total DDTs. Goodwin Lake PCA axis 1 scores capture moderate variation of 36.8% and seem to represent a longer-term ecological trajectory that began decades prior to peak total DDTs at ∼1980. However, pelagic taxa from Goodwin Lake do show directional changes after the 1960s coincident with greater sedimentary total DDTs. Increased *Bosmina* sp. and *D. pulex* complexes and decreased

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D. longispina-complex were apparent by ~1970, but the magnitude of assemblage response was much less than assemblages at Upsalquitch and California lakes.

In terms of overall assemblage structure, Middle Peaked Mountain and Sinclair lakes showed low abundances of *D. longispina*-complex at typically <10%, whereas Upsalquitch, California, and Goodwin lakes typically had much higher abundances. When comparing three distinct periods that represent conditions prior to (baseline; < 1950), during (DDT increase; 1950−1980), and following (recovery; > 1980) DDT use within lake groups defined by high or low *D. longispina*-complex abundances, significant differences ($P < 0.001$) in both medians of *Daphnia* sp. and *Bosmina* sp. were only observed during the recovery period of lakes with high abundances of *D. longispina*-complex (Figure 3). Within the high-abundance lake group, standardized median values of pelagic zooplankton taxa were not significantly different between baseline and DDT increase periods (Figure 3A). At lakes with low abundances of *D. longispina*-complex, only significant differences ($P < 0.01$) in *Daphnia* sp. were observed between the baseline and recovery periods (Figure 3B). These findings are somewhat surprising given the high amounts of DDT applied to NB forests during the mid-20th century which resulted in exceptional levels of DDTs within all our dated sediment records (Figure 1). This apparent lag in assemblage response may be the result of lake-specific processes and the ecological inertia present as key pelagic taxa shift in relative abundances following exposure to a novel stressor. After ~1980 when sediments reflected less total DDTs, daphniids were fewer and small-bodied *Bosmina* sp. increased markedly, which is consistent with many lakes in NB, including low-nutrient, reference systems and those experiencing late-summer algal blooms.[46,47] In the lake group with low abundances of *D. longispina*-complex (Middle Peaked Mountain and Sinclair), *Daphnia* sp. abundances were significantly different ($P < 0.01$) between times prior to DDT use and those of the recovery period after ~1980 (Figure 3). Collectively, these data suggest that, despite each lake receiving substantial organochlorine inputs, zooplankton community responses since ~1950 were to some extent dependent on lake-specific processes, such as food web interactions or climate change and its influence on thermal and mixing processes within the pelagic zone. Unfortunately, no historic measures of fish populations or aquatic food web structure exist at our remote study lakes. This limitation makes it challenging to account for potential shifts in predation regime or predation intensity that may have co-occurred with environmental changes. Predation dynamics affect lake trophic structure and are often recognized as important in structuring zooplankton composition and body size within the pelagic zone,[22,64,70] although the relative roles of abiotic factors and predation are difficult to reconcile.[71] Nonetheless, cladoceran responses to future stressors in these low-nutrient, remote lakes may be assumed to follow ecological trajectories that are lake specific. This observation points to the difficulty in estimating recovery targets for lake ecosystems based on chemical or biological measures alone.

Implications to Modern Food Webs. A paleolimnological approach to understand the chronic effects of mid-20th century organochlorines used in north-central NB provides a valuable perspective on aquatic ecosystem impacts to legacy chemical stressors and recoveries through long-term geochemical and ecological measures. Chemical recovery from peak DDT inputs is underway in eastern North America. In the Great Lakes region most DDT exists in the atmospheric vapor phase and its reductions since the 1970s are mirrored by fish tissues.[73] Yet, modern sediments at all NB study lakes surprisingly still showed DDT and congener values above PEL,[6] which suggests a much different exposure route than through mostly atmospheric inputs.[73] This likely means that aquatic organisms in these NB lakes are still exposed to appreciable amounts of sedimentary DDT and may contain high levels of DDT within their tissues. Indeed, surface water samples collected in 1999 from two small, headwater lakes in north-central NB show elevated levels of DDT at 125 and 8600 pg/L.[52] North-central NB lake sediments may now be acting as a source of organochlorines to nearby environments rather than as an organochlorine sink as they once functioned during the mid-20th century. This likely has implications for the movement of DDT and its breakdown products in modern aquatic and terrestrial food webs near many NB lakes, given the high and widespread applications of DDT in NB during ~1950 to 1970. A recent food web study demonstrates that this mechanism is possible. For example, direct trophic transfer of pharmaceuticals present in surface water from emerging adult aquatic insects to predators in the adjacent riparian zone is recognized.[72] Because organochlorines such as DDT and its breakdown products are persistent in the environment and bioaccumulate readily, we believe that the the potential for direct transfer of DDT from the aquatic to terrestrial ecosystem exists given the DDT legacy in NB. Further ecotoxicological research is required to address this modern threat that our paleolimnological investigation has uncovered.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b01396.

> Table S1. Select physical characteristics and surface water chemistry for north-central New Brunswick, Canada, study lakes; all water chemistry measurements were obtained during the summer stratification period; Figure S1. Map of five study lakes in north-central New Brunswick, Canada, and their respective major watersheds; Figure S2. Radioisotopic activities of ^{210}Pb (filled circles, ± 1 SD) and ^{137}Cs (±1 SD) for the five lake sediment cores in this study, insets show age-depth models developed using the midpoint of core depth intervals, their CRS-inferred age, and linear interpolation; and Figure S3. Stratigraphies of *o,p′*- and *p,p′*-isomers for DDT, DDE, and DDD (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jkurek@mta.ca

ORCID

Joshua Kurek: 0000-0003-4590-4823

Karen A. Kidd: 0000-0002-5619-1358

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Notes

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ABBREVIATIONS USED

AD	*anno Domini*
CAL	California
CRM	certified reference material
CRS	constant rate of supply
DCM	dichloromethane
DDD	dichlorodiphenyldichloroethane
DDE	dichlorodiphenyldichloroethylene
DDT	dichlorodiphenyltrichloroethane
EtOH	ethyl alcohol
GC-ECD	gas chromatography-electron capture detector
GOOD	Goodwin
HPLC	high performance liquid chromatography
KOH	potassium hydroxide
PCA	principal components analysis
PEL	probable effect level
MB	method blank
MPM	Middle Peaked Mountain
MS	method spike
MDL	method detection limit
NB	New Brunswick
NS	not significant
RL	reporting limit
SIN	Sinclair
UP	Upsalquitch
U.S.A.	United States of America
US EPA	United States Environmental Protection Agency

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