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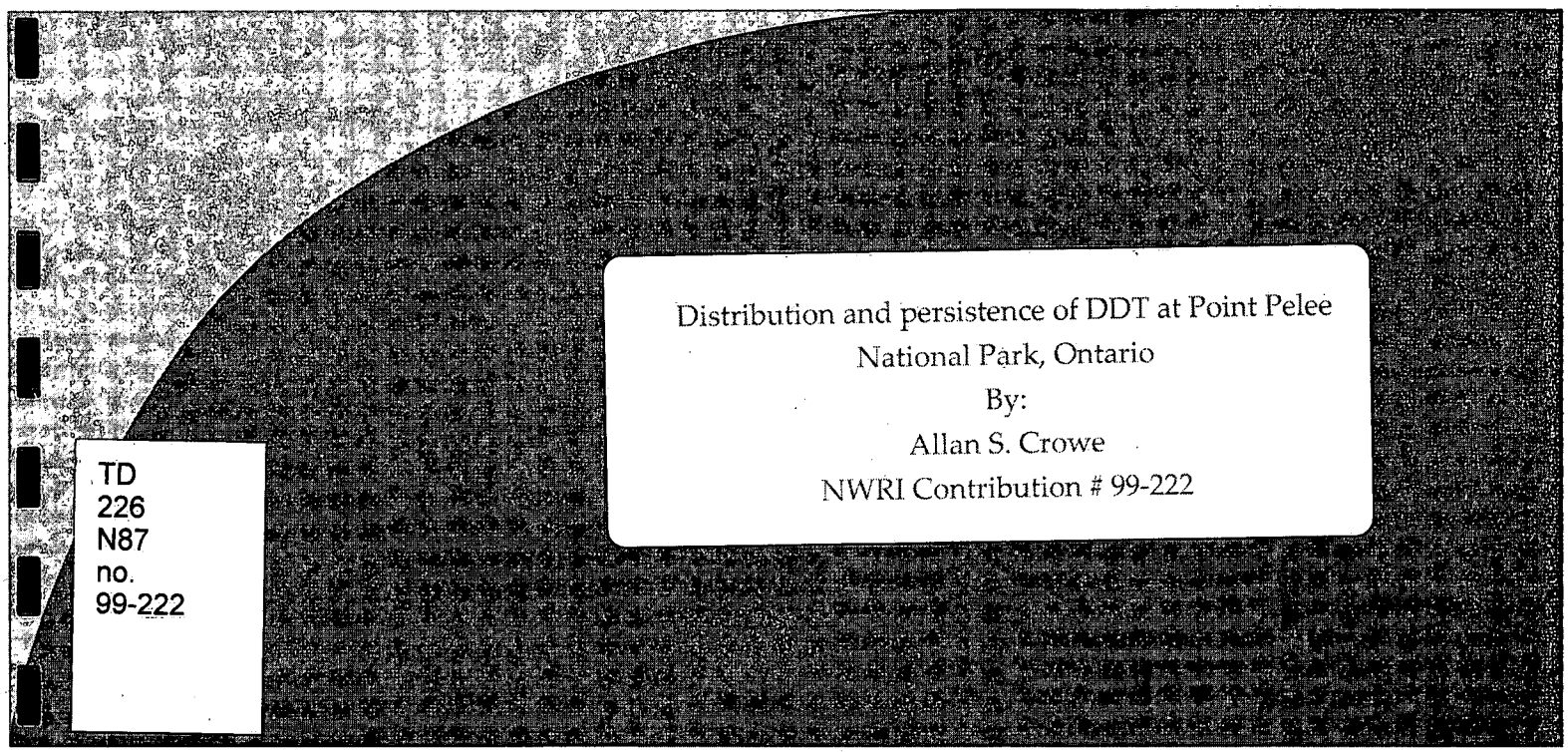

Distribution and persistence of DDT at Point Pelee National Park, Ontario

By:

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NWRI Contribution # 99-222

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MANAGEMENT PERSPECTIVE

Title: Distribution and Persistence of DDT at Point Pelee National Park, Ontario.

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EC Priority/Issue:

EC Business Line: Clean Environment
Outcome: Protection from domestic and global sources of pollution
Results: The environmental and human health threats posed by toxic substances and other substances of concern are prevented or reduced.

Current status:

In April 1998, high concentrations of DDT were reported in the soil at the camp ground at Point Pelee National Park. Because of the potential health risks to the campground visitors and staff, as well as the extensive media coverage, Parks Canada made an emergency request for the assistance of the National Water Research Institute of Environment Canada. NWRI was required to (1) confirm the previously reported high concentrations of DDT, (2) determine the extent of the area contaminated, and (3) check other areas and the groundwater for possible contamination. Following the confirmation of the high levels of DDT, as well as determining that high levels are found at Camp Henry and the Maintenance Compound, Park's Canada closed both of these areas to visitors and staff. Negligible concentrations of DDT were detected in the Park's groundwater.

Next steps:

No further field work is planned. However, continued modelling will investigate the environmental factors contributing to the long-term persistence of DDT at Point Pelee National Park

ABSTRACT

The large scale use of the pesticide DDT occurred in Point Pelee National Park between 1948 and 1967 for mosquito control in recreational areas and pest control in the former apple orchards. By the late 1990's, it was expected that the DDT and its degradation products DDD and DDE would no longer exist at Point Pelee. However, during 1998 these compounds were detected in the shallow soil at several locations within the Park. Concentrations of DDT in the soil at ground surface were highest in areas formerly occupied by orchards, with a maximum concentration of 5 µg/g. Within the two main areas of concern to Parks Canada staff, the Camp Henry campground and Park's Maintenance Compound, concentrations of DDT at surface were typically less than 1 µg/g, with higher values occurring at a site which is suspect to have had a spill. The presence of DDT, DDE and DDD were restricted to the upper few cm of the soil profile where organic content is high. Computer simulations show that because of the highly adsorptive nature of DDT and its very low solubility, DDT would be retained in the organic-rich portion of the soil profile, and would not leach downward. In fact, DDT, DDE and DDD were not detected in the groundwater. The proportion of DDT to DDE and DDD is very high (50%-87%) in much of the areas sampled. It is estimated that the half-life of DDT here may be greater than 40 years. The long-term persistence of DDT is attributed to low biological activity and low moisture content in the upper soil profile.

INTRODUCTION

Point Pelee national Park was the first National Park created in Canada based on its biological value. However, even after the Park was established in 1918, a considerable amount of commercial and residential land use and activities continued. Apple orchards occupied a large proportion of the south and central area of the Park until the late 1960's. Numerous houses and summer cottages existed in the Park until the mid-1970's. Several campgrounds and trailer parks existed within the park until the 1960's and currently only one restricted-use campground remains. Accompanying these activities was the large scale use of the pesticide DDT between 1948 and 1967 for mosquito control in recreational areas and pest control in the apple orchards. DDT was applied within the Park primarily as a particulate spray over wide areas and also as "toss bombs" at specific sites or pools of water.

The US EPA declared DDT to be an environmental hazard because of its long residual life and its accumulation in food chains where it proved to be detrimental to certain forms of wildlife. The US EPA banned its use on January 1, 1973, and a similar ban soon followed in Canada. It was thought that DDT and its degradation products DDD and DDE would no longer exist at Point Pelee. However, during 1998, DDT was detected in the shallow soil within the Park by researchers from the University of Windsor undertaking a wildlife survey [R. Russell, pers. comm.]. Reported concentrations in soil exceeded the Ontario Ministry of Environment limits for DDT for Recreational/Parkland land use of 1.6 μg/g [MOE 1997]. The highest concentrations detected were located near the Camp Henry campground. This raised concerns about the potential health risk to Park employees and visitors.

OBJECTIVES

In April, 1998, Parks Canada requested the assistance of the National Water Research Institute of Environment Canada in assessing the extent of DDT contamination at two areas of concern, Camp Henry and the Park's Maintenance Compound. The objectives of the field sampling/analysis program were to:

1. verify the previous reported results (from University of Windsor);
2. determine the extent of the zones of high levels of DDT, both spatially and with depth;
3. determine if other areas of high levels of DDT exist in the soils within the campground and the Maintenance Compound;
4. check the Park's groundwater supply wells in the vicinity of Camp Henry for dissolved DDT.

A subsequent computer modelling study was undertaken to assess the environmental factors controlling the persistence, and distribution of DDT within the soil and groundwater.

FIELD AND LABORATORY METHODS

Sampling locations at Camp Henry and the Maintenance Compound were determined in consultation with a Park Warden. Shallow soil samples (5-10 cm below ground surface) were obtained using a chromed steel garden trowel. Samples were split and placed in two sterile 120 mL amber glass jars. Disposal latex gloves were worn during the sampling. After every sample was collected, the garden trowel was cleaned and rinsed with a 50/50 solution of acetone/hexane. Shallow cores (to 60 cm) where obtained by hand-pounding a sterile 5 cm diameter by 60 cm long Lexan™ core tube into the ground, and carefully extracting the core to prevent loss. Once extracted the core tube was sealed at both ends with plastic caps which were rinsed in the acetone/hexane solution. Deep cores (to 183 cm) were obtained by split spoon sampling from surface to depth, and using the NWRI trailer-mounted auger drilling rig. The split spoon was lined with a sterile 5 cm by 60 cm Lexan tube, which was capped upon retrieval. All equipment was cleaned with the acetone/hexane solution prior to the next sampling. All samples were maintained chilled and delivered to NWRI's NLET laboratory within 48 hours.

Soil and water samples were analysed at the National Water Research Institute's National Laboratory for Environmental Testing (NLET) laboratory for DDT and other related compounds, including DDE, DDD, PCB's, and organochlorine pesticides, as part of NLET's standard CB-OC-PCB analysis for soil and water.

FIELD STUDIES (1): CAMP HENRY

The primary concern was to assess the environments in which DDT may have come into contact with the campground's visitors. Therefore surficial soil samples were collected from 5 to 10 cm below ground surface, and samples were taken in the locations where people were most likely to come into contact with the soil. Sample locations focused on the two zones of previously reported high concentrations as well as other areas around the campground. A total of 36 samples were taken during the first field program. During a second field program undertaken a couple of weeks later, 27 surface samples and 11 cores to assess the depth of contamination were obtained over a regular 10 m grid spacing throughout the area occupied by the campground's buildings.

The elevated concentrations of DDT within Camp Henry noted by the University of Windsor study were confirmed. Concentrations of total DDT in surficial soil samples obtained from the wooded area (former orchard) north of the campground consistently exceeded the MOE (1997) guideline of 1.6 µg/g (Fig.1a). Within the campground, the concentrations of total DDT from surface samples exceeded MOE [1997] guidelines only near the campground buildings. Concentrations of total DDT from eight surficial samples in the campground's field range from 0.01 to 0.11 µg.g (not shown). It is suspected that the high concentrations observed near Building 880 are due to a

pesticide spill. Concentrations of total DDT from a depth of 60 cm were consistently well below the MOE [1997] guideline (Fig. 1b). The concentrations at depth are typical 2-3 orders of magnitude lower than concentrations of DDT at surface. Thus, it appears that DDT has not leached throughout the soil profile.

FIELD STUDIES (2): MAINTENANCE COMPOUND

The Park's Maintenance Compound was formerly the operational centre for the apple orchards and some of the original buildings are still used by Park staff. Thus, it is possible that DDT was handled and stored here. Soil samples were taken in the locations where Park's employees were most likely to come into contact with the potentially contaminated soil. Twenty surface samples were collected at a depth of approximately 5 cm below the ground surface, including the parking areas and roadways. In addition, 60-cm cores were also collected at each of these twenty sites. Soil samples were analysed from a depth of approximately 30-40 cm which corresponds to the base of the organic-rich soil horizon.

Concentration of total DDT from surficial soil samples are highest in the wooded areas (former orchards). However, only a couple of samples exceed the MOE [1997] guideline of 1.6 µg/g (Fig. 2a). Concentrations of total DDT at surface within the portion of the Maintenance Compound used by Park staff are less than the MOE guideline, and the maximum concentration observed is 0.65 µg/L. Very high concentrations of DDT were detected in surficial soil near the greenhouse and plant nursery (28.3 µg/g), and just beyond the fence of a storage area to the north (8.1 µg/g). These high concentrations are probably due to a past spillage or disposal of DDT. Concentrations of total DDT at a depth of ~30 cm were above detection limits only in the vicinity of former orchard-operations building (Fig. 2b). Concentrations of DDT near the maintenance building may be higher at 30 cm than surface due to the recent addition of fill.

FIELD STUDIES (3): GROUNDWATER

Twenty-litre samples of groundwater were obtained from seven well sites identified by Park's Canada where the groundwater is used as a source of drinking water. Samples were checked to ensure the drinking water does not exceed the Canadian Drinking Water Guidelines [CCREM, 1987] limit for DDT of 30 µg/L. These wells had been previous sampled and analysed for DDT in April 1995.

No significant levels of DDT, its metabolites, or other organochlorine pesticides were detected in the seven groundwater samples (Fig. 3). In fact, the maximum concentration of total DDT detected in the groundwater samples was 0.00011 µg/L, which is several orders of magnitude below the guideline. These wells had been previously sampled by Parks Canada and analysed for DDT at a commercial laboratory

in April 1995. At this time DDT, DDE and DDD were not detected. The detection of DDT in the present samples is due to larger volume of water being tested (20 L vs. 1 L) and improved analytical methods which lowered the detection limit.

MODELLING STUDIES

Numerical modelling studies, using the model LEACHM [Wagenet and Hutson, 1987] were undertaken to assess the environmental characteristics of the site and the pesticide which would lead to its distribution and persistence in the soil, and its absence from the shallow groundwater. This model simulates the major biological, physical, chemical, and environmental conditions that are involved in the mobility, attenuation, degradation, dissolution and volatilization of pesticides in the subsurface. It simulates the transport and fate of pesticides and water within a heterogeneous soil profile under transient meteorological conditions.

The simulations were run to 30 years. Temperature and precipitation were recorded at Point Pelee National Park and potential evaporation was estimated by LEACHM. The simulation was run for two years before the introduction of DDT at a depth of 5 cm in order to develop an accurate water balance within the soil profile. The DDT characteristics used are, solubility = 3.0×10^{-3} mg/L, organic carbon partition coefficient (Koc) = 2.4×10^{5} L/kg, molecular diffusion coefficient = 4.3×10^{-5} mm^2/d, vapour density = 3.9×10^{-3} mg/L. The water table was located at a depth of 1 m. Values of soil parameters used in the model are listed Table 1. Several simulations were run to assess various degradation rates for DDT in soil ($t_{1/2}$ = 5 - 40 years) and initial concentrations (10 - 1000 mg/m^2 active ingredient). There was assumed to be no plant uptake of DDT.

Table 1. Values for the soil parameters used in the simulations.

Depth (cm)	F.C.	W.P.	K_{sat}	%O.C.	%sand	%silt	%clay
0-5	0.180	0.080	750	0.60	89.0	10.0	1.0
5-25	0.125	0.055	1000	0.50	91.0	8.0	1.0
25-45	0.090	0.033	1700	0.30	94.5	5.0	0.5
45-100	0.090	0.033	1700	0.30	97.5	2.0	0.5

F.C.: field capacity, W.P.: wilting point, K_{sat}: saturated hydraulic conductivity (cm/d), %O.C.: % organic carbon

Simulations show that due to the high attenuation characteristics of DDT (high Koc) and the soil (high organic carbon), DDT is absorbed onto the organic matter in the soil at the surface and essentially remains there (Fig. 4a). After 25 years, the simulated downward movement of DDT is only a few centimeters. Due to the low rate of dissolution of DDT (low solubility), concentrations of DDT in the soil-water is very low and does not leach downward to the water table (Fig. 4b). It is unlikely that DDT would leach deeply into the soil in either pure or dissolved phases, or exist in groundwater above negligible concentrations.

PERSISTENCE OF DDT

The ratio of DDT to its metabolites, DDD and DDE, at Camp Henry indicates that DDT is the dominant compound in most samples (Fig. 5). In 22 of 37 samples, DDT comprises 50%-87% of the total concentration of DDT+DDD+DDE. The concentration of DDT is approximately 30% and 15% of the total concentration in another 12 and 3 samples, respectively. Concentrations of DDE are considerably greater than the respective DDD concentrations for each sample. There does not appear to be a definite correlation between concentration of total DDT in soil and percent DDT versus DDD+DDE. The only spatial pattern is that the proportion of DDT is lowest in the marsh sediments to the north.

Values of the half-life of DDT in soil reported in the literature range from 2 to 40 years. An uncertainty analysis was undertaken to provide insight into the half-life of DDT at Point Pelee. Eight simulations of the transport and persistence of DDT in typical soil at Point Pelee were run using the LEACHM model to determine the proportion of DDT remaining for half-lives of DDT in soil from 5 to 40 years (Fig. 6). Additional simulations, not shown, indicate that the proportion of DDT remaining is independent of the application rate for a given half-life. Assuming that the last major application of DDT would have occurred about 30 years ago, for 60% of the pesticide to remain as DDT after 30 years would require a half-life of DDT in soil of approximately 40 years (Fig. 6). It is more likely that the last major application was more than 30 years ago, and hence the half-life of DDT in the soil at Point Pelee is probably several years higher. The simulations also show that for approximately 30% of the DDT to remain as DDT after 30 years, the half-life in soil would be approximately 17 years (Fig. 6). In the marsh sediment where the concentration of DDT vs. DDE and DDD is lowest, the half-life in soil would be approximately 11 years for 15% to remain as DDT after 30 years (Fig. 6).

The variability in half life could reflect differing periods of application or varying soil conditions across the site. The long half-life (~40 years) in most of the former orchard at Point Pelee may exceed 40 years because of soil conditions. Here the soil is very sandy which would promote rapid draining and evaporation of soil moisture. Thus, with a limited moisture content, the microbiological activity that would promote degradation of DDT would be limited. The areas of the Park with more organic rich and wetter soil, such as the marsh sediments, would be more conducive to microbiological activity, and the half-life of DDT is much lower (~10 years).

SUMMARY

1. Analyses of shallow soil samples collected at Point Pelee National Park show the presence of DDT, and often in concentrations that exceed the Ontario Ministry of Environment limits for DDT in soil for Recreational/Parkland land of 1.6 µg/g.

2. Analyses of groundwater obtained from several wells show DDT is several orders of magnitude below the Canadian Drinking Water Guideline of 30 µg/L at all wells.

3. Concentrations of DDT decrease rapidly with depth, indicating that DDT is generally confined to the upper 20-40 cm of the soil. This corresponds to the organic-rich soil horizon.

4. DDT is not mobile in the soil horizon, either in its pure phase or dissolved phase;
   - properties of the soil (high organic carbon) and DDT (high Koc) lead to a strong attenuation of DDT to the organic matter at the surface of the soil.
   - the low solubility of DDT and the high hydraulic conductivity of the soil lead to negligible concentrations of dissolved DDT in the groundwater.

5. Localized areas of high concentrations of total DDT at Camp Henry and the Maintenance Compound are probably due to spills or disposal.

6. Computer simulations confirm that DDT is essentially not mobile in the soil, will remain at the soil surface, and will not leach to the water table.

7. The half-life of DDT in soil in most of the soil at Point Pelee probably exceeds 40 years. In marsh sediments, the half-life of DDT is probably <10 years.

REFERENCES

CCREM. 1987. Canadian Water Quality Guidelines. Canadian Council of Resource and Environment Ministers. Task Force on Water Quality Guidelines. Ottawa, Ont.

MOE. 1997. Guideline for use at Contaminated Sites in Ontario; Ontario Ministry of Environment publication PIBS 3161E01, revised February 1997.

Wagenet, R.J. and J.L. Hutson. 1987. LEACHM: Leaching Estimation And Chemistry Model, Volume 2. Water Resources Institute Continuum. Centre for Environmental Research, Cornell University, Ithaca, N.Y.

Acknowledgements

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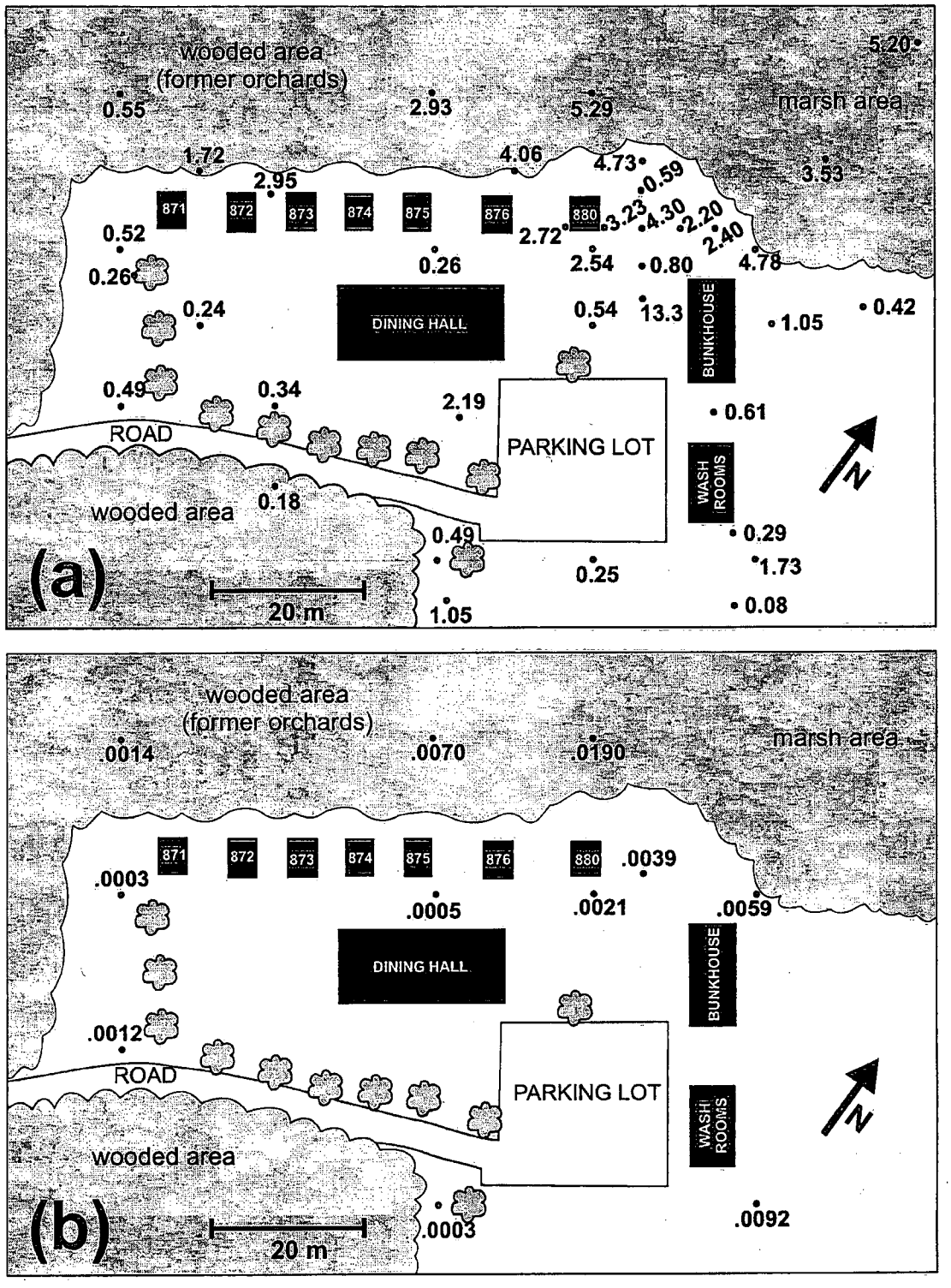

Fig. 1. Total DDT (μg/g) at Camp Henry: (a) at ground surface, (b) at a depth of 60 cm.

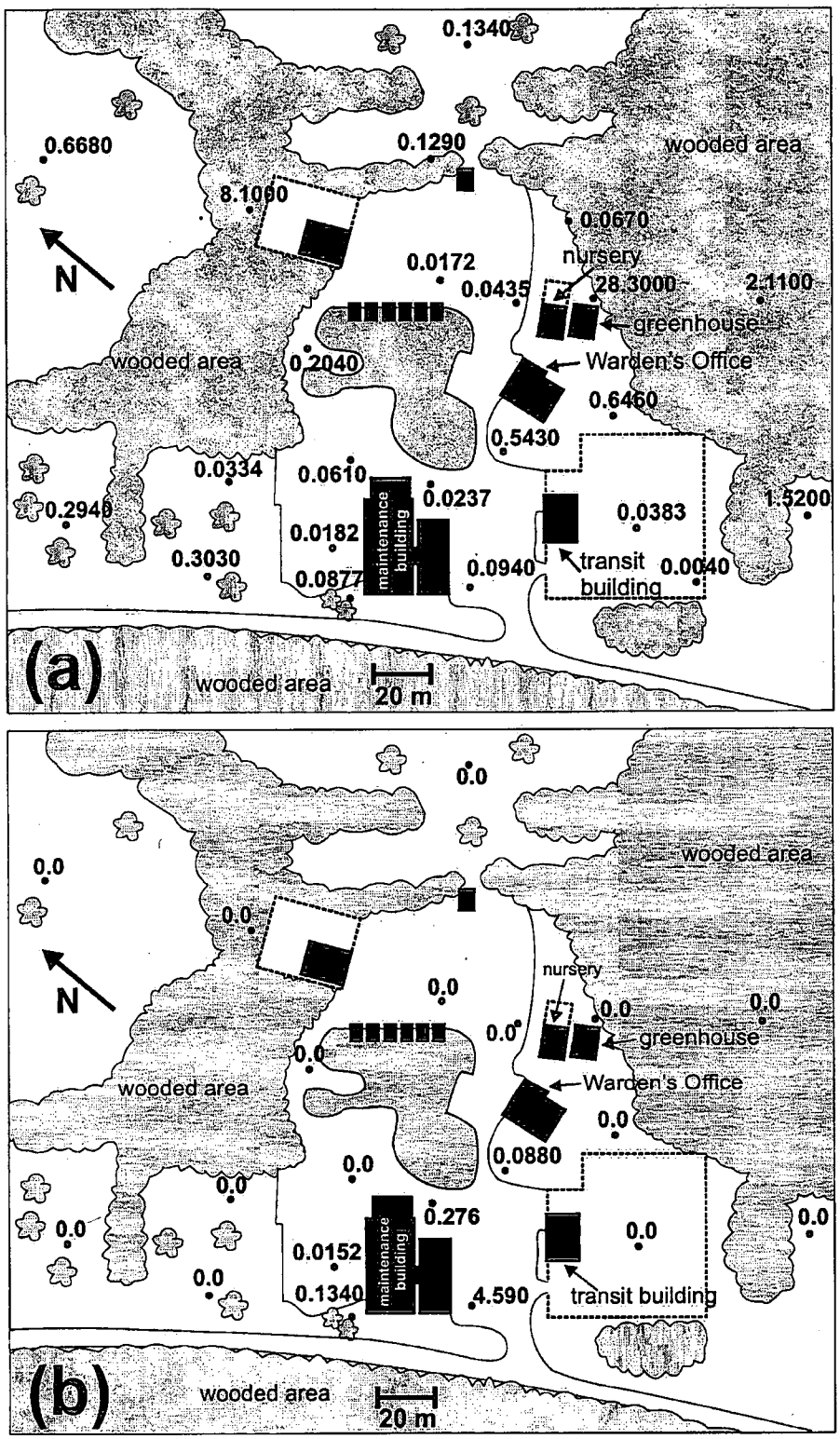

Fig. 2. Total DDT (μg/g) the Maintenance Compound: (a) at ground surface, (b) at a depth of 30 cm.

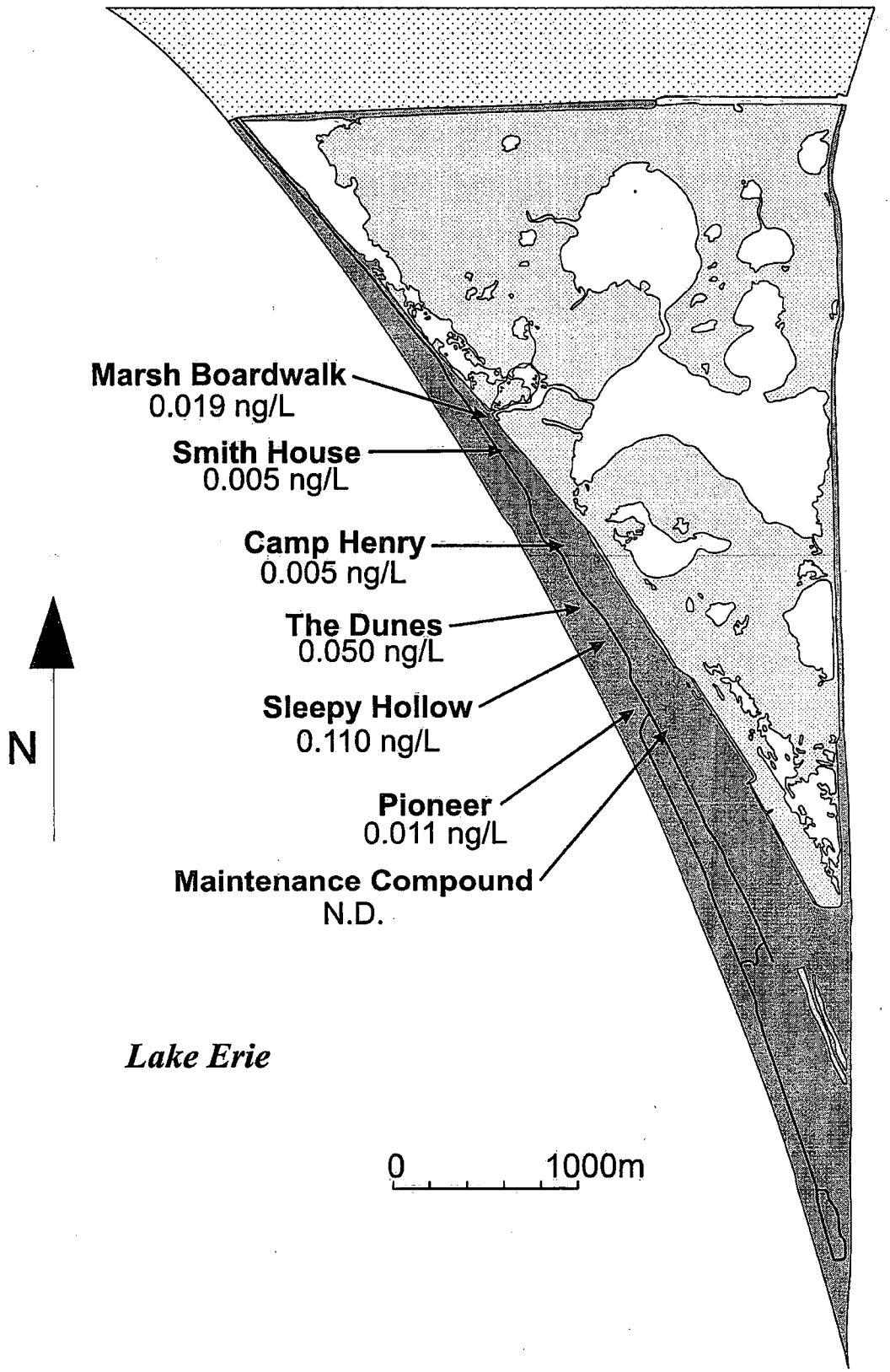

Fig. 3. Dissolved DDT in Groundwater (concentrations in ng/L).

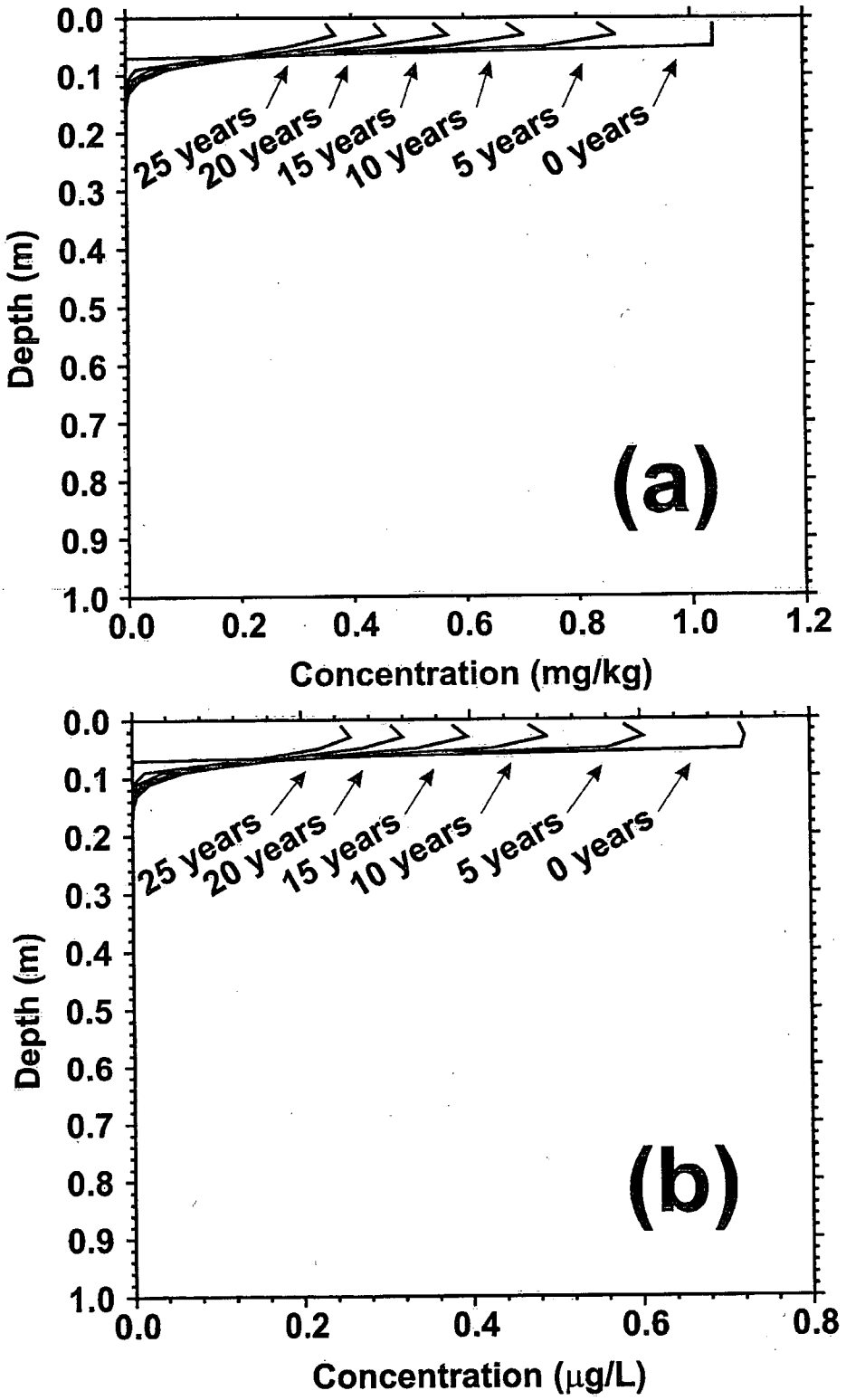

Fig. 4. Simulated amount of DDT (a) sorbed to soil and (b) dissolved in soil water, for a half-life of DDT in soil of 20 years.

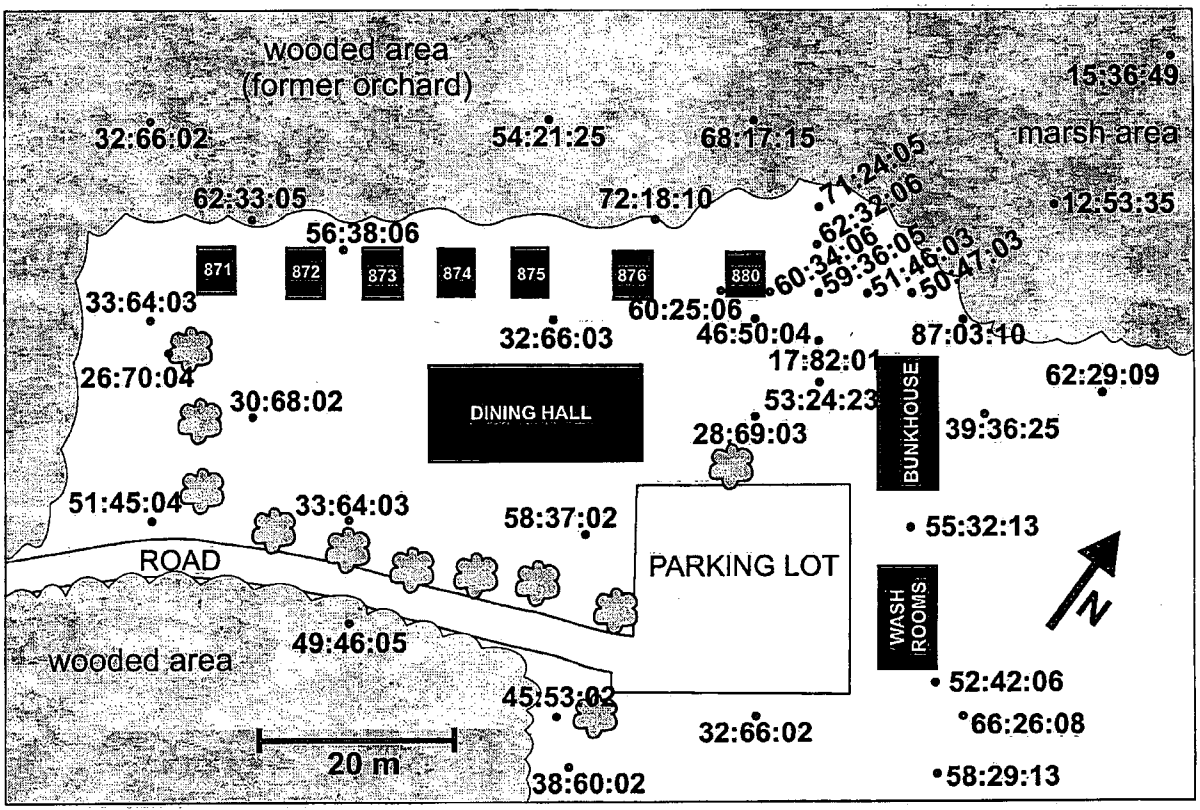

Fig. 5. Ratio of DDT:DDE:DDD at the surface at Camp Henry.

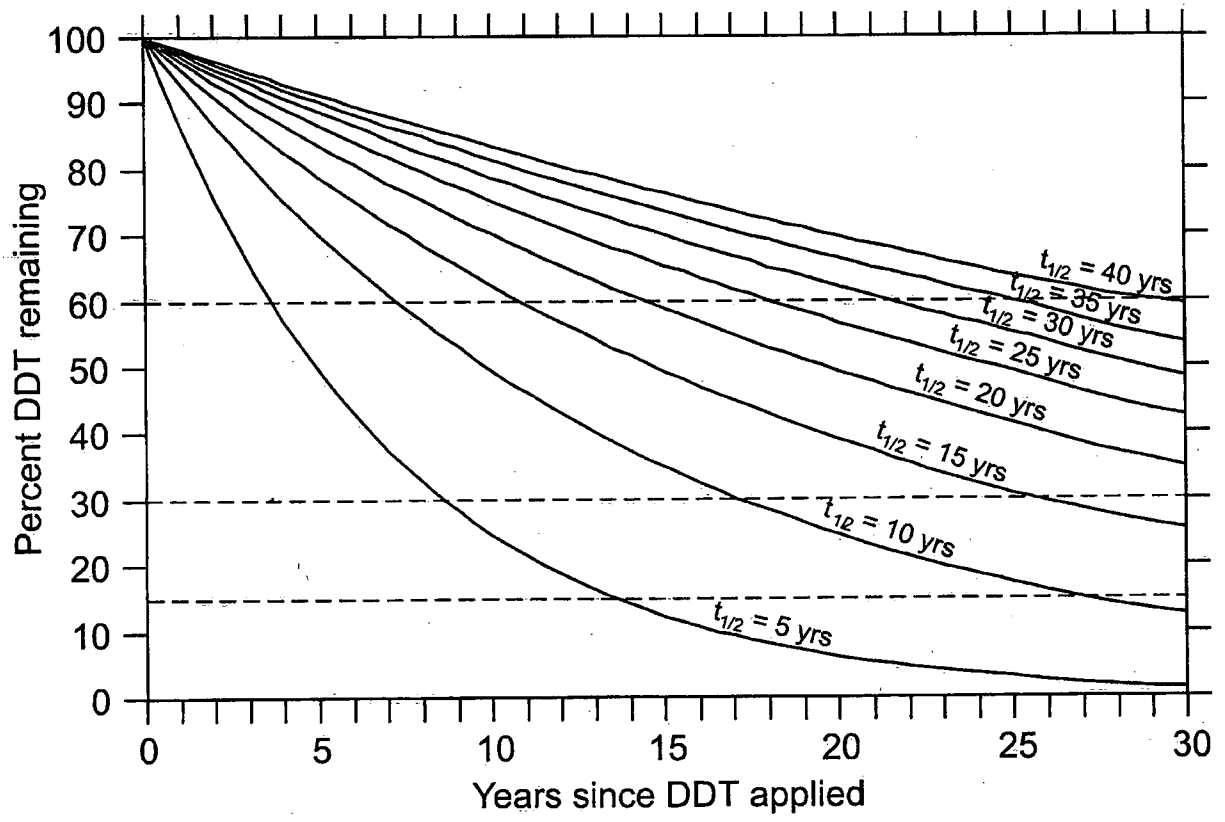

Fig. 6. Simulated percent DDT remaining in soil at Point Pelee according to various $t_{1/2}$ of DDT in soil.

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