PCB Congeners and Chlorinated Pesticides in Pine Needles Collected in Peregrine Falcon Breeding Territories in northern New England, U.S.A.

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Introduction

Vegetation has recently been viewed as an important, dynamic, and active environmental compartment that influences the atmospheric transport, global turnover, and cycling of many semi-volatile organic pollutants [1]. Pine needles have been demonstrated as a fixed-site, regenerative, annual monitoring matrix for the evaluation of local and regional distribution of lipophillic air pollutants [2,3]. As part of a viability study of Peregrine falcon (*Falco peregrinus*) populations in northern New England (USA), atmospheric deposition of chlorinated pesticides and polychlorinated biphenyl (PCB) congeners was evaluated in this region using pine needles as passive diffusive samplers. Environmental contamination by persistent organochlorine compounds (OC), especially DDE, caused the extirpation of the entire US peregrine population in the late 1950s - 1960s [4,5]. Due to toxic health effects, the United States banned DDTs in the early 1970s and consequently the residue levels declined in aquatic and terrestrial animals. However, some recent studies [6-8] showed presence *p,p'*-DDT in variety of matrices in different parts of the U.S. which indicated a more recent input of DDT. Northern New England, U.S.A. is one of the major breeding territories for Peregrine falcons (*Falco peregrinus*), information on recent atmospheric input of organochlorine compounds is essential to protect the peregrine populations. The objective of this study was to determine the concentrations of persistent and toxic organochlorine contaminants including PCB congeners and chlorinated pesticides (DDT compounds, Hexachlorobenzene, Lindane and Chlordane compounds) in surface resins of white pine (*Pinus strobus*) tree needles within Peregrine Falcon breeding territories in northern New England (New York, Vermont, New Hampshire and Maine) (Fig. 1).

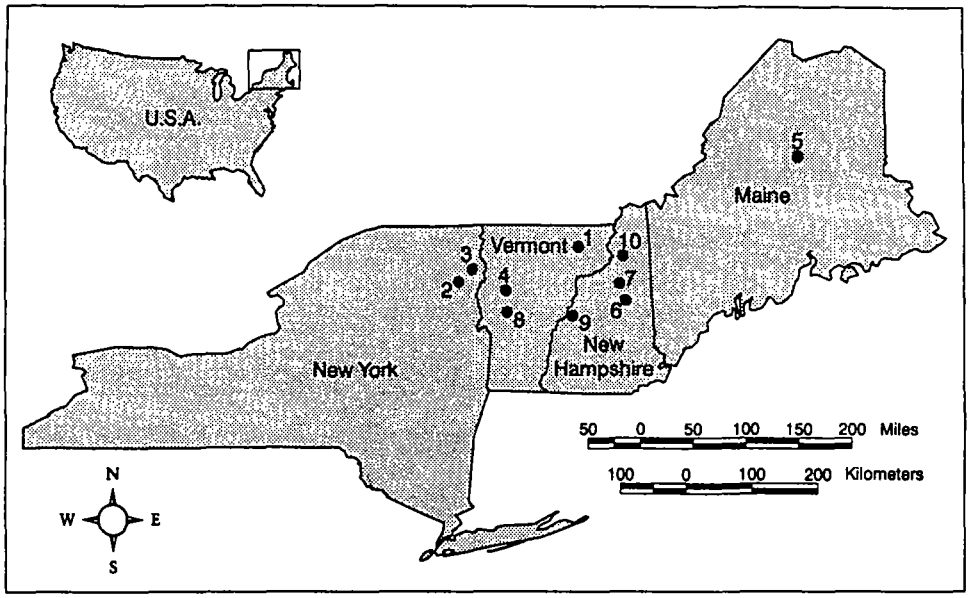

Fig. 1. Map showing pine needle sampling locations (•).

1) Mt. Pisgah, VT, 2) Hurricane Mtn. NY, 3) PM, NY, 4) Deer Leap, VT, 5) Mt. Katahdin, ME, 6) Square Ledge, NH, 7) Crawford Notch, NH, 8) Mt. Horrid, VT, 9) Holts Ledge, NH, 10) Devils Slide, NH.

Material and Methods

Details of sampling locations and samples are presented in Figure 1 and Table 1. Second year class (one year old) live needles were plucked from white pine trees. Needles from more than one tree were mixed up and approximately 20 g needle were wrapped in pre-cleaned aluminum foil and stored at -20 °C until analysis. The pine needles were cut in to small pieces (<3 cm). About 10 - 20 g of the needles was used for Soxhlet extraction. Analytical procedures including clean-up and quantitations of the analytes were similar to the one described elsewhere [9]. Shimadzu Model 17-A gas chromatograph and Shimadzu Model AOC-17 Model Autoinjector was used for the analysis. DB-5 and DB-17 capillary columns (30 m x 0.25 mm diameter and 0.25μ film thickness) were used for separation of the analytes. Helium (1.5 mL/ min.) and nitrogen (28 mL/min.) were used as carrier and make-up gases, respectively. The NIST-SRM 2262 (PCB congeners) and SRM 2261 (chlorinated pesticides) calibration standards were used for generating response factors and analyte quantitations. Co-eluting PCB congeners are PCB-66/95, PCB-138/163/164, PCB-187/182/159, PCB-170/190 and PCB-105/132. Therefore, the concentrations of these congeners are summed.

Results and Discussion

Total PCBs (sum of PCB congeners quantitated) and 6 pesticides concentrations in the pine needles from various sampling locations are presented in Table 2. In general, several of the lower chlorinated PCB congeners and pesticides including HCB, 4,4'-DDE and lindane were

detected in more than 70% of the samples. Among the several samples, pine needles from Hurricane Mountain, New York (#2) showed the greatest concentrations (23.62 ng g^{-1} d wt.)

Table 1. Pine needle sample site details.

Site #	Date	Latitude	Longitude	Aspect	Elevn. (m)	Trees (#)
1	9/17/'96	44 43 00	72 01 50	north	390	3
2	9/6/'96	44 14 00	73 39 45	southeast	500	3
3	9/5/1996	44 24 30	73 30 00	northeast	270	2
4	9/12/'96	44 07 45	73 02 30	south	280	3
5	9/25/96	45 53 45	68 58 00	west	655	3
6	10/2/'96	43 59 15	71 21 00	north	378	3
7	10/1/'96	44 13 15	71 24 30	west	585	1
8	9/12/'96	43 50 30	72 59 30	northwest	469	3
9	9/17/'96	43 46 40	72 06 30	east	305	3
10	9/23/'96	44 36 00	71 25 00	southwest	335	3

of total (sum of the PCB congeners measured) PCBs, followed by those from Crawford Notch, New Hampshire (#7), which contained 18.23 ng g^{-1} dry wt. of total PCBs. Total PCB concentrations in other locations were comparatively smaller. Sample from Mount Horrid, Vermont (#8) recorded 8.0 ng g^{-1} dry wt. of PCBs, which may be due to the influence of downwind from the New York (#2). PCB concentration was below the detection limit for sites 1 (Mt. Pisgah, VT), 9 (Holts Ledge, NH) and 10 (Devils Slide, NH). Among the PCB congeners quantitated, PCB-28 (2,4,4'-T_3CB), PCB-44 (2,2',3,5'-T_4CB), PCB-101 (2,2',4,5,5'-P_5CB) and PCB-153 (2,2',4,4',5,5'-H_6CB) were found detectable concentrations in several samples. Among the PCB congeners detected in pine needles, the concentrations of lower chlorinated PCB congeners (di-, tri- and tetrachlorobiphenyls) showed relatively higher concentrations than penta-, hexa-, hepta, and octachlorobiphenyls and their percent contribution on the average was >50%. Lower chlorinated PCBs have higher vapor pressure [10,11] and are therefore easily transportable. Higher chlorinated PCBs have comparatively lower vapor pressure and higher particle affinity. Many non-detects of higher chlorinated PCBs in the pine needles correspond to their physico-chemical properties.

Among the chlorinated pesticides, hexachlorobenzene (HCB) showed a tendency for uniform distribution. HCB concentration was ranged from 1.04 to 2.65 ng/G d. wt. except at site # 1 where HCB was near the detection limit. 4,4'-DDE concentrations ranged from 0.2 to 5.80 ng/G d. wt. In contrast to PCB concentrations, Site #9 (Holts Ledge, NH) recorded highest concentrations of 4,4'-DDE, alpha-chlordane and lindane. 4,4'-DDT was below the detection limit (0.1 ng g^{-1} d wt.) in all of the samples analyzed. Further studies using larger sample size and analyses of other environmental and biological samples from this region are needed to elucidate presence or absence of current input of DDT in this region. Gamma-HCH (Lindane) was detectable in almost all sample analyzed. Considering the biomonitoring studies using pine needles and other plants in Asia, Europe and Japan [12,], organochlorine concentrations

Table 2. Total PCB and chlorinated pesticide concentrations (ng g^{-1} dry weight) in pine needles (*Pinus strobus*) collected from several locations in the New England, U.S.A.

Compound	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10
tPCBs	<1.0	23.62	5.17	4.11	2.71	2.12	18.23	8.00	<1.0	<1.0
HCB	0.23	1.5	2.65	1.69	1.81	1.04	2.82	1.36	2.71	1.91
Lindane	1.64	1.41	0.50	1.22	0.53	0.39	1.61	0.52	1.05	1.00
alpha-CHL	0.61	<0.1	<0.1	<0.1	0.17	<0.1	0.79	<0.1	4.81	0.76
trans-Nona	<0.1	<0.1	0.21	<0.1	0.14	0.10	<0.1	0.17	1.07	0.16
4,4'-DDE	0.35	1.00	0.80	1.29	0.50	0.20	1.38	0.79	5.80	0.54
4,4'-DDT	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

recorded in the present study were in the medium or lower range. Present study on pine needle organochlorine concentrations will contribute to the overall data-base on organochlorine contaminants and Peregrine Falcon populations and associated end-point evaluation. Further, present data may also be useful in studies leading to the examination of filter effects of forests as a function of physical-chemical properties of organic pollutants.

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