Atmospheric transport of persistent pollutants governs uptake by holarctic terrestrial biota. Environ. Sci. Technol. 24, 1599-1601

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on a per molecule basis. Clearly, in any future plans to utilize MTHF in significant quantities as an automotive fuel additive the considerable atmospheric reactivity of this compound should be taken into account.

It is of interest to note that the measured rate constant, k_1, at 298 K in the present work is within 20% of the reactivity predicted by Atkinson's structure–activity relationship (*22*).

Finally, the present results can be compared with our recent determinations of the rate constants for the reactions of OH with other cyclic ethers (*23*). The reactivity of 1,3-dioxane was increased by about 20% upon the addition of one α-CH_3 group. The present results show that the reactivity of tetrahydrofuran, which is already more than 50% more reactive than 1,3-dioxane, is increased by about 40% upon α-CH_3 substitution. Thus, the higher reactivity observed for the four- and five-member-ring cyclic ethers appears to cause increased enhancements in substituent effects as well.

Registry No. MTHF, 96-47-9; OH, 3352-57-6.

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Atmospheric Transport of Persistent Pollutants Governs Uptake by Holarctic Terrestrial Biota

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■ The atmospheric deposition of PCBs, DDT, and lindane, governed uptake in terrestrial biota in the Scandinavian penninsula. Mammalian herbivores and predators as well as predatory insects contained higher levels of pollutants at locations where the fallout load was high than at stations where atmospheric deposition was lower, and the two variables were significantly correlated.

Introduction

Atmospheric transport of chlorinated hydrocarbons like PCB, DDT, and toxaphene (chlorinated camphenes) distributes the pollutants on a global basis (*1–4*). These pollutants have been found in the atmosphere of industrial regions as well as in remote areas far from urban centers, such as the Arctic and the Antarctic (*2–4*), and in the atmosphere over the oceans (*5*, *6*).

Chlorinated pollutants in the atmosphere reach terrestrial environments as dry and wet deposition (*7*, *8*). The substances exist in air as a gas or associated with particles (*7*, *8*). Atmospheric removal, both wet and dry, is thought to occur mainly in association with particles. Scavenging by rain droplets is determined by Henry's law constant, resulting in a higher deposition at low temperatures than at high (*7–9*). Recently, a hypothesis has been forwarded that pesticides used in warm midlatitudal regions are transported in their gaseous state to temperate climatic regions, where they contribute to airborne fallout (*9*). Additionally, thereoretical models propose that pollutants in their gaseous state in the atmosphere equilibrate with water of lakes and oceans, resulting in the contamination of the water bodies (*10*, *11*). However, no direct evidence has yet been provided that persistent pollutants originating from the atmosphere are taken up by terrestrial biota. The objective of this study was to examine if a relationship existed between deposition of pollutants from the atmosphere and uptake in terrestrial animals.

Sampling and Analytical Methods

In 1984/1985 a study regarding the atmospheric fallout of the polychlorinated biphenyls, DDT, DDE, and lindane (γ-hexachlorocyclohexane) was performed between 55° and 68° N on the Scandinavian penninsula (*9*). During the vegetation season several animal species were sampled, at the same 14 sampling locations. The species studied included mammalian herbivores (the voles, *Microtus agrestis*, at the stations below the Arctic Circle, and *Clethrionomys rufocanus* at stations above it), a mammalian predator (shrew, *Sorex araneus*), and an insect predator (dragonfly, *Aeschna sp.*). The mean atmospheric deposition during four sampling periods during the year was calcualted and presumed to affect uptake by the animals.

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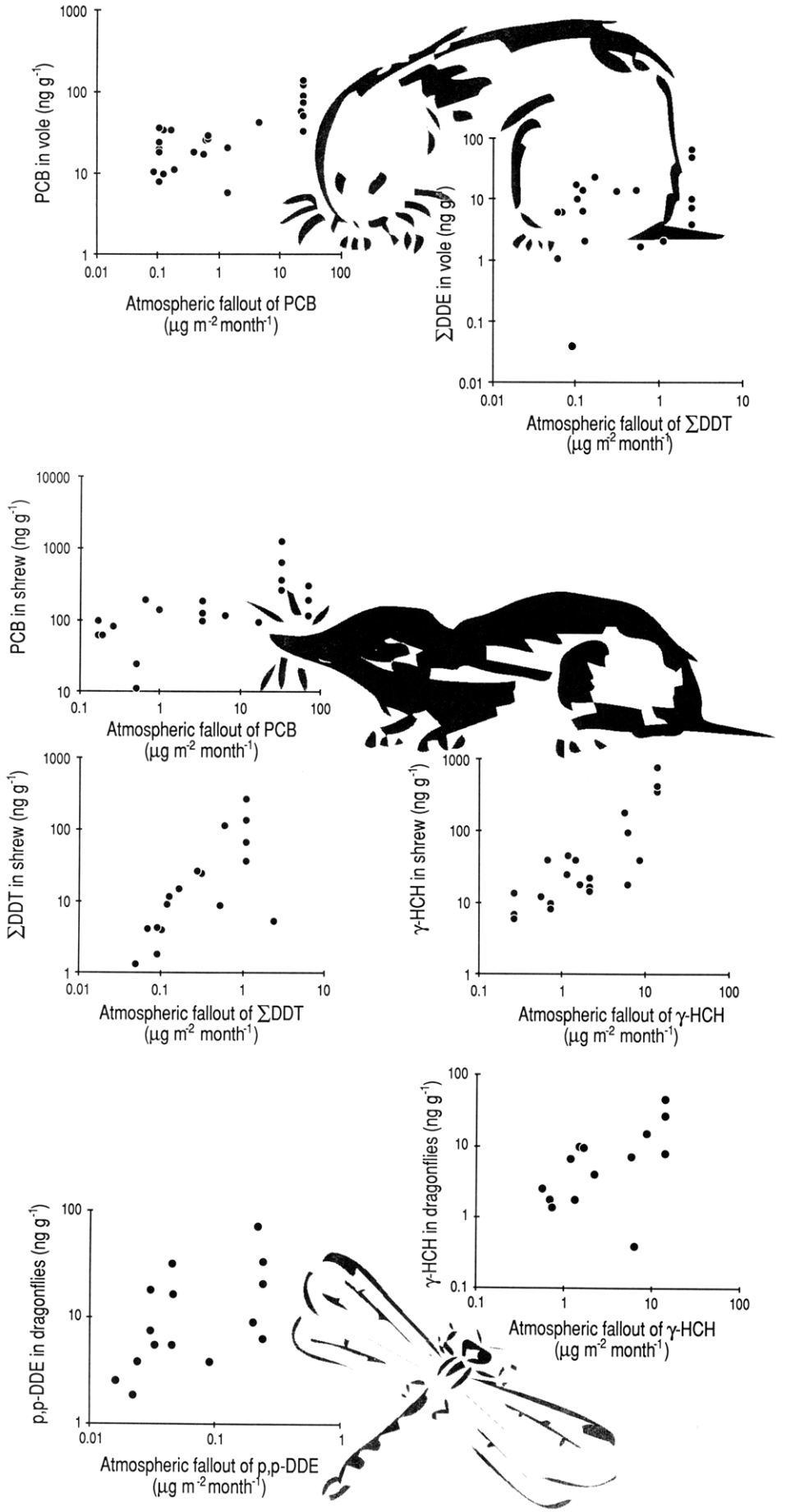

Figure 1. Correlations between atmospheric fallout of persistent pollutants and uptake in vole (A), shrew (B), and dragonflies (C). Samples were taken at 14 stations at the Scandinavian penninsula. Each point represent one animal (vole, shrew) or three to five animals pooled together (dragonflies).

Chlorinated hydrocarbons in airborne fallout were sampled with a nylon net (mesh size 200 μm) impregnated with a silicone oil. The samplers were located 2.5 m above the ground, in a area free of buildings and trees. The method was identical with that used by Södergren (*12*, *13*). The lipophilic pollutants as well as airborne particles are collected and retained in the lipophilic oil. Lipophilic pollutants present in rainwater are extracted by the oil as the water percolates through the net. The screens thus sample chlorinated residues resulting from both dry and wet deposition, but may only be regarded as semiquantitative samplers, a problem that has been reviewed by Södergren (*13*), Bidleman and Christensen (*7*), and Eisenreich et al. (*14*). Measured values of atmospheric fallout depend on the sampling method employed. Chlorinated hydrocarbons from the fallout nets were extracted with hexane in a Soxhlet apparatus according to Södergren (*12*, *13*). The extracts were cleaned with fuming H_2SO_4 and evaporated to 0.5 mL before the compounds were analyzed by capillary gas chromatography/ECD.

Voles and shrews were cut into small pieces and subsamples of 5–10 g were taken. Three to five dragonflies were pooled together in order to obtain enough sample for an analysis. The tissues were homogenized in acetone/hexane (1:1) and the persistent pollutants were extracted and cleaned with concentrated sulfuric acid according to Larsson and Lindegren (*15*).

PCBs, lindane, *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, and *o,p'*-DDT (∑DDT) in the samples were analyzed by capillary gas chromatography/ECD (*16*). The column conditions were optimized for PCBs and 28 major peaks of Clophen A 60 were recognized. The PCB congeners were identified on the basis of the work of Ballschmiter and Zell (*17*) and Duinker and Hillebrand (*18*).

Results and Discussion

Uptake of persistent pollutants by the mammalian herbivores was governed by the atmospheric deposition as shown by a positive correlation between the two variables (Figure 1). This was the case for PCBs (Spearman rank correlation, $r_s = 0.64$, $0.005 > p > 0.0005$, one-tailed) and ∑DDT (*p,p'*-DDT and metabolites, $r_s = 0.63$, $0.005 > p > 0.0005$). Lindane could not be detected in the vole due to unknown interferences. Similar correlations were recorded for the shrew: for indane ($r_s = 0.79$, $0.005 > p > 0.0005$), for PCBs ($r_s = 0.72$, $0.005 > p > 0.0005$), and for ∑DDT ($r_s = 0.76$, $0.005 > p > 0.0005$). For the dragonfly, positive correlations between uptake and fallout were recorded for lindane ($r_s = 0.63$, $0.025 > p > 0.01$) and DDE (a major metabolite of *p,p'*-DDT, $r_s = 0.64$, $0.025 > p > 0.01$), while PCBs were not detected.

Presumably, herbivores take up the pollutants by feeding on internally or surface-contaminated vegetation (*19*, *20*). An increase in atmospheric deposition leads to an increase in plant uptake and, consequently, to elevated levels in herbivores. This in turn leads to an increase in pollutant intake by predators feeding on the herbivores. However, some of the pollutants transferred from prey to predators are metabolized. Thus, the predatory shrew contained a larger proportion of recalcitrant, highly chlorinated PCBs (*21*) than did the herbivorous vole, which contained a higher proportion of the more easily metabolized low-chlorinated PCBs. Similarly, Muir et al. (*22*) found that several tri-, tetra-, and pentachlorobiphenyls were detected in arctic cod muscle but were not detected in seal blubber or polar bear fat. The authors concluded that PCB congeners lacking adjacent unsubstituted carbons (higher chlorinated biphenyls) were metabolized at a lower rates and, consequently, were more persistent. The most frequent congeners in shrew were PCB 138, PCB 153, PCB 170, and PCB 180, which were consistent with the results of Muir et al. (*22*) for predators.

In a field study, Forsyth and Peterle (*23*) found that after spraying a field with [^{36}Cl]DDT there were positive correlations between the stomach content of DDT in vole (*Microtus pennsylvaticus*) and concentrations of DDT in various organs. No such correlations were, however, found for predators (shrew).

The results from our study show that persistent pollutants deposited from the atmosphere are reflected by uptake in terrestrial animals. Animals in locations subjected to high atmospheric exposure of pollutants reflect the contamination situation despite their trophic level position. An ecosystem subjected to high inflow of chlorinated hydrocarbons from the air will contain animals with high pollutant load.

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