Persistence of Polychlorinated Biphenyls and 1,1-Dichloro-2,2-bis(*p*-chlorophenyl)ethylene (*p,p'*-DDE) with Age in Lake Trout after 8 Years

Patricia C. Wszolek and Donald J. Lisk*

Department of Food Science, Pesticide Residue Laboratory, Cornell University, Ithaca, N.Y. 14853

Timothy Wachs

Department of Chemistry, Cornell University, Ithaca, N.Y. 14853

William D. Youngs

Department of Natural Resources, Cornell University, Ithaca, N.Y. 14853

■ Lake trout, ranging in age from 6 to 12 years, were netted in Cayuga Lake in Central New York in 1978 and analyzed for polychlorinated biphenyls (PCBs) and 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (*p,p'*-DDE). Fresh weight concentrations in flesh of the 12-year old fish were about 13 ppm of PCBs and 3–4 ppm of *p,p'*-DDE. The data indicated that, whereas *p,p'*-DDE had decreased considerably, PCB concentrations remained about the same as those in a similar series of aged lake trout sampled from Cayuga Lake in 1970. The PCBs present in the fish most closely resembled Aroclor 1254 but appeared to contain a higher proportion of more highly chlorinated isomers.

In 1970, lake trout, 1 to 12 years old, were netted in Cayuga Lake in Central New York and analyzed for residues of *p,p'*-DDE (DDE) (*1*) and polychlorinated biphenyls (PCBs) (*2*). Residues found increased progressively with age reaching 11.7 ppm of DDE and an average of 15.7 ppm of PCBs (measured as Aroclor 1254) in 12-year old fish. Whereas DDT usage has virtually ceased, PCBs are still used to a limited extent. In the work reported, Cayuga Lake trout of increasing age were again sampled during 1978, and DDE and PCBs were determined in their flesh and liver to study the persistence of these compounds in the fish.

Experimental

The lake trout were netted in October, 1978. Only fish ranging in age from 6 to 12 years were captured. The ages of the fish were known, since they are stocked annually as yearlings in Cayuga Lake and marked as to year class. The fish were immediately decapitated and eviscerated and the fins were removed, with the remaining edible portion and liver taken separately for analysis. The flesh and liver were subdivided using a meat grinder, mixed, subsampled, and freeze-dried. One-half gram of sample was extracted for 6 h with glass-distilled hexane in a micro-Soxhlet apparatus. The hexane extract was partitioned with acetonitrile, and the latter solution was extracted with hexane prior to isolation on a Florisil column (*3*). The 6% ethyl ether in hexane eluate was concentrated and characterized by gas chromatography, and for one of the 12-year old trout the eluate was characterized by combined gas chromatography–mass spectrometry.

A Tracor Model 220 gas chromatograph equipped with a ^{63}Ni electron-capture detector was used to obtain quantitative data. A glass column 4 mm i.d. × 2 m long, packed with 3% OV-17 on 100/120 mesh Gas-Chrom Q and operated isothermally at 185 °C, was used. Nitrogen (60 cm^3/min) was the carrier gas. The gas chromatograph–mass spectrometer used to obtain electron impact spectra was a Finnigan Model 3300 with a System Industries 150 data system. The column was glass, 2 mm i.d. × 1.7 m long, packed with 3% OV-17 on 100/120 mesh Gas-Chrom Q. The column oven was programmed from 180 to 275 °C at 8 °C/min. Helium (20 cm^3/min) was the carrier gas.

Results and Discussion

Table I lists the concentrations of DDE and PCBs found in the trout flesh and livers, as well as age, size, and sex data for the fish. The figures obtained for the freeze-dried samples have been converted to the fresh weight basis.

Mass spectral data confirmed the presence of DDE and various PCB isomers. In addition, these data showed that the gas chromatographic peak for DDE (retention time, 11.6 min) was free from any major interference from other extract components or PCBs. Furthermore, it also allowed for selection of an appropriate major PCB peak to use for quantitation by gas chromatography. This latter peak had a retention time of 16.7 min. The concentrations of PCBs in each sample were estimated as total Aroclor 1254, since the pattern of peaks obtained most closely resembled this mixture. However, the mass spectral data showed that the fish contained a higher proportion of hexachlorobiphenyls and a lower proportion of tetrachlorobiphenyls compared with the reference standard. There are several possible explanations for these data. Firstly, the hexachloro isomers may be more persistent in the environment. Secondly, the hexachloro isomers may be selectively absorbed by the trout or organisms lower in the food chain. Careful analysis for PCBs in Cayuga Lake water and in organisms lower than trout would be required to determine this. Finally, the tetrachloro PCB isomers may be selectively metabolized in the trout and possibly in lower aquatic organisms also. *p,p'*-DDD (DDD) was detected by both electron-capture detection and mass spectrometric analysis of a 12-year old trout. There was also mass spectral evidence for the presence of DDT in the 12-year old fish, but the peak eluted simultaneously with a major PCB peak thus prohibiting its quantitation. Nevertheless, DDD and DDT appeared to constitute only minor constituents of the fish.

The concentrations of PCBs and DDE in the flesh and livers have been plotted as a function of their ages in Figures 1 and 2. In each, a least-squares straight line has been constructed. Although the number of fish samples was small, there appeared to be a consistent decrease in the concentration of DDE in the flesh of the trout reported here as compared to those of comparable age samples in Cayuga Lake in 1970 (*1*). PCBs were found to be about the same in those sampled in 1978 as those of the same age netted in 1970 (*2*).

PCBs undoubtedly accumulate in fish from dietary sources, but absorption from their ambient water is also thought to be a major route of entry (*4*). Evidence has been presented for the disappearance of PCBs in water (*5*) and shellfish (*6*) coinciding with a reduction in their extent of use or release into the environment. Variations in the levels of persistent toxicants found in fish of the same age and location may be due in part to the wide range in aggressiveness found among in-

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Table I. Residues (Ppm, Fresh Weight) of PCBs and *p,p'*-DDE in Flesh and Livers of Cayuga Lake Trout Netted in 1978

age, years	sex	wt, kg	length, cm	PCBs in		*p,p'*-DDE in	
				flesh	liver	flesh	liver
6	M	2.4	65.3	4.4	2.5	1.3	1.0
6	M	3.5	69.9	4.1	4.2	0.9	1.0
6	F	2.4	66.3	4.8	1.2	1.0	0.3
7	M	2.6	66.5	4.3	2.6	1.3	0.6
7	M	3.3	68.6	6.1	4.9	1.8	1.0
7	F	3.3	69.3	5.2	1.6	1.4	0.6
8	M	3.0	66.3	5.7	1.9	1.2	0.5
8	M	2.9	69.9	7.4	4.1	1.9	0.8
8	M	2.7	70.1	7.4	5.5	2.1	1.1
9	M	2.9	68.6	8.6	10.2	2.1	2.3
9	M	3.0	70.9	7.5	4.9	1.6	0.8
9	M	4.0	77.2	11.7	6.3	2.0	1.2
10	M	3.5	68.8	9.3	3.7	2.3	1.0
10	M	3.1	70.6	9.8	7.0	3.2	1.5
10	F	3.1	72.9	11.6	7.1	2.3	1.2
12	M	4.0	79.5	13.5	12.0	3.7	2.6
12	M	4.1	77.2	12.8	10.8	3.3	2.2

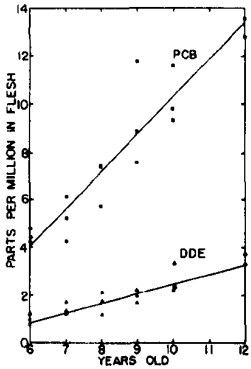

Figure 1. Concentrations of PCBs and DDE in the flesh of Cayuga Lake trout as a function of their age

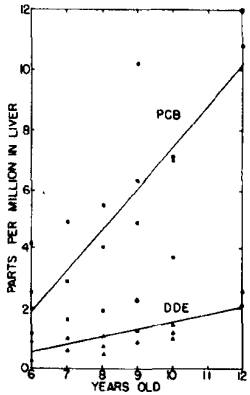

Figure 2. Concentrations of PCBs and DDE in the livers of Cayuga Lake trout as a function of their age

dividuals as regards foraging efficiency (*7*).

There is speculation that PCBs may be produced in part by natural processes, e.g., chlorine produced by the action of ozone on air-borne salt, which then reacts with aromatic organics deriving from automobile exhaust, coal burning, and other sources. PCBs have been detected in precipitation in the Lake Michigan basin (*8*). They have also been found in all sewage sludges sampled from 16 American cities (*9*), and sewage effluents typically flow into waterways including Cayuga Lake.

The excretion of PCBs by fish is a very slow process (*10, 11*). There is evidence that the persistence of PCB isomers in fish tissues is proportional to their degree of chlorination (*12*), but the opposite has also been noted (*13*). The efficiency of accumulation of tetrachlorobiphenyls by fish is also dependent on the position of chlorine substitution (*7*). The effects of PCBs on fish include production of blood anemia, hyperglycemia, liver enlargement and altered cholesterol metabolism (*14*), fish egg mortality (*15*), inhibition of ATPases (*16*), induction of hepatic mixed function oxidase activity (*17, 18*), glycogen depletion of hepatocytes, and white pulp depletion of the spleen (*19*).

Others have found concentrations of DDT residues in fish proportional to their size (*20, 21*) and tissue lipid (*22*) or oil content (*23*). Absorption of DDT by fish is believed to be mainly from their diet (*24*). Residues of DDE were detected in a number of small fish species sampled in Cayuga Lake in 1962 (*21*). DDT is believed to be converted to DDD (*25, 26*) and DDE (*27*) in fish largely through the action of intestinal microflora (*28*). The slow conversion of DDT to DDE in water has also been shown (*29*). DDT has been found to decrease slowly but only over a matter of years in fish (*30*), crayfish (*31*), and aquatic ecosystems (*32*). The toxicity of DDT to fish is inversely proportional to their size (*33, 34*). DDT produces a variety of abnormal effects in the nervous system of exposed fish (*35, 36*) and may inhibit ATPase activity (*37*). DDT in-

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creases mortality in fish eggs (*38*) and sac fry (*39*).

In summary, this study indicates that PCBs and DDE residues in Cayuga Lake trout still remain at appreciable levels. This may be due to the very slow release and metabolism of such compounds and to possible continuing release of such compounds into the environment. It would be of interest to conduct careful histopathologic examination of such fish to discover possible lesions resulting from these residues.

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On the Nature of the Diurnal Variation of Sulfates at Rural Sites in the Eastern United States

George T. Wolff*, Paul R. Monson, and Martin A. Ferman

Environmental Science Department, General Motors Research Laboratories, Warren, Mich. 48090

Recent legislation designed to prevent the deterioration of visibility necessitates that visibility reducing aerosols be characterized in rural as well as urban areas. Measurements of optical properties of aerosols at rural sites in the Eastern United States have implicated sulfates as the principal visibility reducing aerosol (*1*). Consequently, it is important that information on the concentrations and formation mechanisms of rural sulfates be collected. During the Aerosol Characterization Experiment (2) in the Los Angeles Basin, a considerable amount of data was collected on the diurnal pattern of sulfate concentrations. This data shows that most areas of the Basin generally experience an afternoon sulfate maximum and a nighttime minimum. This corresponds to the photochemical activity cycle as demonstrated by diurnal ozone patterns and this correspondence has been used as evidence for the existence of a photochemical sulfate formation mechanism in Southern California (*2*).

Unlike the locally created sulfate problem in Los Angeles, a regionwide, summertime sulfate problem (*3, 4*), associated with synoptic scale meteorology (*5, 6*), has been reported to exist in the northeast quadrant of the United States. Based on the simultaneous occurrence of ozone and sulfate episodes (*3, 5*) and the observations that sulfates are highest during the summer months (*3, 4, 6, 7*), a photochemical formation mechanism has also been postulated for the Northeastern United States (*6*). Unfortunately, diurnal sulfate data have not been available to use in these previous analyses.

During the summer of 1976, General Motors Research (GMR) Laboratories' mobile Atmospheric Research Laboratory (ARL) collected 4-h sulfate samples for a period of 29 days at two rural sites in the eastern part of the United States. This paper discusses the results of these measurements.

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■ During the summer of 1976, the General Motors Research Laboratories' mobile atmospheric research laboratory collected 4-h sulfate samples for 29 days at two rural sites in the Eastern United States. In addition, simultaneous measurements of other pollutant parameters including O_3, SO_2, and b_{scat}, and meteorological parameters including temperature, relative humidity, wind speed and direction, ultraviolet intensity, and inversion height were obtained. The results indicate that the sulfate levels are governed by meteorology rather than local sulfur sources. Two types of distinct diurnal patterns were observed. In the first type, a peak was observed in mid-afternoon at about the time of the O_3 maximum. Data presented in the text, however, indicate that photochemistry by itself cannot account for the sulfate peak. Afternoon vertical mixing of sulfates transported above the nocturnal inversion layer appears to play a significant role. The second type of diurnal pattern, a nocturnal sulfate peak, occurred on calm nights when surface transport was not occurring and it was most pronounced on clear nights when ground fog developed. The data suggest that the O_3–SO_2–olefin reaction mechanism is significant on nonfoggy nights and the O_3–SO_2–fog droplet mechanism is important on foggy nights.

Experimental Procedures

Particulate matter was collected on 47-mm diameter 1-μm-pore fluoropore filters mounted in Nuclepore open-faced aerosol membrane holders. Samples were collected with a GMR-designed sequential filter sampler, which consisted of six filter ports connected to a Gast Model-0522 vacuum pump through six solenoid valves. The solenoid valves were actuated by a control timer, which started the sampler and stepped through each of the six filters in succession at a preset time interval of 4 h. A flow rate of 0.045 m^3/min ± 4% was maintained through the filters. Because there was no rain shield over the units, samples were collected only on days that had no precipitation.

Following sample collection, the filters were stored in plastic dishes and returned to GMR, where they were analyzed for soluble sulfates by the barium chloranilate (BCA) method. In a previous study (*8*), the experimental error of this procedure was determined to be ±0.5 μg/m^3 at a concentration of 10 μg/m^3.

A detailed description of the measurements made by the ARL has been previously reported (*9, 10*). Pollutant measurements that will be discussed in this report include ozone (McMillan 1000-2 chemiluminescent monitor), b_{scat} (MRI-1550 nephelometer), and sulfur dioxide (Meloy-SA160 flame photometric monitor). Although the flame photometric technique responds to all S atoms, it is assumed that SO_2 is the predominant gaseous species. Our tests have shown that there is no response to particulate sulfate at concentrations up to 15 μg/m^3. The reason for this is presumably due to particulate losses in the SO_2 sampling train. Interferences at sulfate concentrations above 15 μg/m^3 have not been examined.

Site Descriptions

The two rural sites, McKee, Ky., and Keysville, Va., were chosen for their remoteness, lack of local anthropogenic pollutant sources, and availability of electrical power and other necessary services. The McKee site was located in the hills of central Kentucky, at an elevation of 410 m msl. The ARL was parked in an open field in Jackson County, about 10 km south of McKee on County Road 290. Keysville is situated in the south-central part of Virginia, in an area of gently rolling farmland and hardwood forests. The elevation of the Keysville site was 180 m msl.

Results

The mean diurnal patterns for sulfates, ozone, and b_{scat} at both sites are shown in Figures 1a and 1b. Although the mean amplitude of the variation of the sulfate patterns is relatively small (2.9 μg/m^3 at McKee and 2.5 μg/m^3 at Keysville) compared to the amplitude of the variations of ozone, a diurnal variation is apparent at McKee. The diurnal variation in b_{scat} closely follows the sulfate variation at McKee (r = 0.92). At

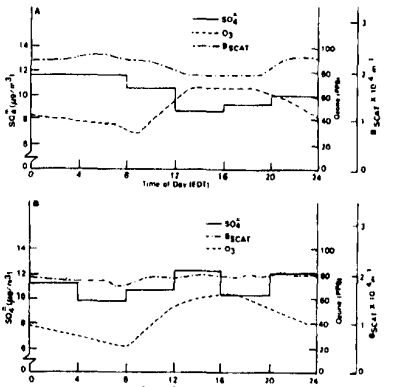

Figure 1. (A) Mean diurnal variation in SO_4^{2-}, O_3, and b_{scat} at McKee, Ky., during July and August 1976. (B) Mean diurnal variation in SO_4^{2-}, O_3, and b_{scat} at Keysville, Va., during June and July 1976

Keysville, both the b_{scat} and sulfate show a more uniform diurnal profile and both parameters tend to fluctuate together (r = 0.66).

At Keysville, the sulfate maximum is reached in the afternoon during the 1200–1600-h samples. In addition, a second peak between 2000 and 0400 h is observed during the nighttime. At McKee, the nighttime peak is observed, but not the afternoon peak. In fact, the sulfate minimum is observed in the afternoon.

Upon examination of the diurnal sulfate patterns for individual days, a tremendous variation was observed. This is evident from Table I, which shows the frequency of occurrence of the maxima and minima for the 25 days where samples for complete diurnal cycles were obtained. On 4 other days which are not included in Table I, incomplete diurnal cycles were obtained. Of the 29 total days, 25 showed evidence of a nocturnal (2000–0800) sulfate peak, 16 showed evidence of an afternoon (1200–2000) peak (8 occurrences at each site), and four showed relatively constant diurnal profiles. This latter group was comprised of days with very low sulfate (less than 5 μg/m^3) that followed the passage of a cold front. Diurnal data for various parameters on the days with the most pronounced afternoon sulfate peak are presented in Figure 2a. On these days, the afternoon peak was at least 25% higher than the nighttime peak. The data in Figure 2a are from 5 days, 2 at McKee and 3 at Keysville

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