

## Polychlorinated Biphenyls in Honey Bees

Roger A. Morse, <sup>1</sup> Thomas. W. Culliney, <sup>1</sup> Walter H. Gutenmann, <sup>2</sup> Cheryl B. Littman, <sup>2</sup> and Donald J. Lisk<sup>2</sup>

<sup>1</sup>Department of Entomology, <sup>2</sup>Toxic Chemicals Laboratory, New York State College of Agriculture and Life Sciences, Cornell University, Ithaca, New York, 14853–7401

Honey bees (Apis mellifera L.) may traverse a radius of several miles from their hives and contact innumerable surfaces during their collection of nectar, pollen, propolis and water (Seeley 1985). In the process, they may become contaminated with surface constituents which are indicative of the type of environmental pollution in their particular foraging area. Indeed, honey bees have been used as possible sentinels for radioactive (Gilbert and Lisk 1978; Morse et al. 1980) and heavy metal and toxic element contamination (Bromenshenk et al. 1985) over large areas. Honey has also been analyzed as a possible indicator of heavy metal pollution (Tong et al. 1975; Morse and Lisk 1980). Insecticides used in the vicinity of bee hives have been found in bees (Morse et al. 1963) and honey (Johansen et al. 1957).

Anderson and Wojtas (1986) recently reported finding appreciable concentrations of polychlorinated biphenyls (PCBs) in honey bees sampled throughout Connecticut. There could be multiple sources of such contamination since PCBs are ubiquitously present in the environment as a result of their use in electrical equipment, paper, plastics, adhesives, paints, waxes and many other products (Edwards 1971). Widespread environmental contamination can also result when PCB-containing waste oils are applied along unpaved roads or other areas for dust control. In the work reported here, an analytical survey was conducted on PCBs in honey bees, honey, propolis and related samples in several states to learn the extent of contamination and possible sources.

## MATERIALS AND METHODS

All samples were taken between April and September of 1985. Honey bees were collected from various locations in several states as indicated in Table 1. Those collected from within the hive would have been bees of all ages. Winter-killed bees would have been, for the most part, two to five months old at the time of death. Flying bees taken from in front of colonies would have been from two to six weeks of age. Live bees were killed by freezing. Samples of honey, pollen, propolis, wax and other insects were also collected. All samples, except honey, were freeze-dried, ground, mixed and subsampled for analysis. Five

Table 1. PCBs in honey bees sampled in 1985

Table 1. Tobs In noney bees sampled in 1905						
			PCBs			
	Date		ppm			
Location	sampled	Manner of collection (	Dry wt)			
Etna, NY	Aug 7	In-hive pupae	0.28			
Esopus, NY	Jun 2	In-hive bees from 2 colonies,a	0.24			
Fort Edward, NY	Apr 30	In-hive bees from 2 colonies <sup>D</sup>	0.76			
Fort Edward, NY	Apr 30	Flying bees from several colonies	1.40			
Fort Edward, NY	Apr 30	In-hive bees from 2 colonies <sup>C</sup>	0.76			
Fort Edward, NY	Apr 30	Flying bees from several colonies	0.46			
Ithaca, NY	Apr 24	In-hive bees from 1 colony	0.40			
Ithaca, NY	Apr 24	Winter-killed bees from several				
		colonies	0.55			
Ithaca, NY	Jul 12	In-hive bees	0.20			
Ithaca, NY	Jul 12	In-hive bees	0.23			
Kingston, NY	Jun 2	In-hive bees from 2 colonies	0.30			
Leroy, NY	Jul 12	In-hive bees from 2 colonies	0.22			
Saugerties, NY	May 3	In-hive bees from 3 colonies	0.22			
Lake Placid, FL	May 20	In-hive bees from 1 colony	0.24			
Gilford, NH	Apr 29	Flying bees from 4 colonies	1.00			
Middlebury, VT	Apr 29	Winter-killed bees from several				
·	_	colonies	1.30			
Middlebury, VT	Apr 29	Flying bees from several colonies	1.50			
Middlebury, VT	Apr 29	In-hive bees from 2 colonies	0.59			
Middlebury, VT	Sept 30	In-hive bees from 2 colonies	$nd^d$			
Little Pee Dee	_					
River, SC	May 25	In-hive bees from 2 colonies	0.16			
•	-					

<sup>&</sup>lt;sup>a</sup>Approximately 300 meters from the Hudson River.

grams of sample was Soxhlet extracted for 6 hours with 100 ml of hexane. Five grams of honey was diluted with 25 ml of distilled water and shaken out successively with four, 10 ml portions of hexane which were then combined. The hexane extract was then partitioned with acetonitrile and, after dilution with water, the acetonitrile solution was extracted with hexane. The latter hexane solution was chromatographed on Florisil® (US FDA 1971). Final determination was made by gas chromatography with a Tracor Model 222 instrument equipped with a Ni<sup>63</sup> electron capture detector. A glass column (180 cm long, 4 mm, id.) packed with 3% OV-17 on 100/120 mesh Gas Chrom Q. was used. Column, injector and detector temperatures were 190°C isothermal, 230°C and 300°C, respectively. PCBs were quantitated as Aroclor® 1254. The limit of detection of the method was 0.1 ppm.

 $<sup>^{\</sup>mathrm{b}}\mathrm{Located}$  adjacent to a PCB dump site and 300 meters from the Hudson River.

 $<sup>^{\</sup>text{C}}\textsc{Four}$  miles south of PCB dump site and 300 meters from the Hudson River.

dNot detectable, less than 0.1 ppm (dry weight).

## RESULTS AND DISCUSSION

The results of analysis of the honey bees for PCBs are listed in Table 1. The series of peaks in the gas chromatograms of the honey bees were an exact match in terms of retention time and relative peak height to those of the various PCB isomers in the Aroclor® 1254 standard. The possibility of inadvertent laboratory contamination from glassware or packaging materials in which the bees were transported was investigated but none was found. possible to positively relate the concentrations found to known, Two samples from Fort Edward, New York, nearby sources of PCBs. taken immediately adjacent to a PCB dumpsite and about 300 meters from the Hudson River and two others collected about 4 miles south of the dumpsite but equidistant from the river contained higher concentrations of PCBs than bees from most other sampling sites in New York state. Yet, bees collected in Middlebury, VT, contained levels and no nearby source of PCB contamination was comparable known of there. The water in the Hudson River in the vicinity of Fort Edward has been found to contain relatively high levels of PCBs (Brown et al. 1985). Bees obtain water by contacting the immediate water surface layer. An imperceptably thin organic layer may typically reside on the water surface consisting of the remains of aquatic organism decomposition and other debris. This organic layer could contain lipid-soluble PCBs which might therefore inadvertently contaminate bees.

PCBs have been reported in water and caddisfly larvae in the upper Hudson River (Bush et al. 1985) and in adult mayflies in the upper Mississippi River (Clements and Kawatski 1984). PCBs have also been found in various marine insects (Cheng and Bidleman 1977). PCB contamination of water may result from PCB-containing industrial waste effluents or sewage wastewater (Mumma et al. 1983, 1984) discharged into receiving waters or the sources could be aerial (Anonymous 1979). PCBs can be emitted from hazardous waste landfills (Lewis et al. 1985), municipal landfills and incinerators (Murphy et al. 1985). Accumulation of airborne PCBs in foliage in the vicinity of Fort Edward, NY (Buckley 1982) and chlorinated hydrocarbon insecticides in pine needles (Gaggi and Bacci 1985) has been reported but a decline in PCB concentration was found in vegetation in New York State between 1978 and 1980 (Buckley 1983). Considerable variation among plant species was found in the concentration of PCBs in foliage with aspen, goldenrod and sumac being higher than some others. Less than 1 percent Aroclor® 1242, one of the slightly more water-soluble groups of PCB isomers, was found to be taken up through the roots of goldenrod and corn plants (Buckley 1982). Bees forage on many plants growing near streams especially in spring. There does not appear to be any relation between the PCB content of the bees and their manner of collection (Table 1) which is related to their age as described earlier. Also, there does not appear to be a relation between the concentration of PCBs in bees and the time of year sampled. Interestingly, PCBs have been shown to increase the toxicity of organophosphorus insecticides to house flies (Fuhremann and Lichtenstein 1972).

Ten samples of honey were taken for analysis of PCBs. These included samples from apiaries in five locations in New York State and one in Vermont. Four samples were also obtained from grocery shelves in New York. No detection concentrations of PCBs (less than 0.1 ppm fresh weight) were found in any of the samples. Lipid-soluble compounds such as PCBs would not expectedly occur in honey except possibly as water-soluble metabolites. Honey might, of course, become contaminated during processing and packaging.

In an attempt to determine the source or sources of PCBs in honey bees, samples of pollen, propolis and wax collected from various sites mainly in New York State were analyzed for PCBs and the results are shown in Table 2. Pollen and propolis are collected by

Table 2. PCBs in pollen and propolis

			PCBs
	Date	Sampling	ppm
Sample <sup>a</sup>	sampled	location	(dry wt)
Pollen	Aug 14	Dryden, NY (Site 1)	0.14
Propolis	Aug 14	Dryden, NY (Site 1)	0.11
Pollen	Sept 4	Dryden, NY (Site 2)	0.10
Propolis	Sept 4	Dryden, NY (Site 2)	0.10
Pollen	Sept 4	Etna, NY (Site 1)	0.17
Propolis	Sept 4	Etna, NY (Site 1)	0.20
Pollen	Sept 4	Etna, NY (Site 2)	0.13
Propolis	Sept 4	Etna, NY (Site 2)	0.17
Pollen	Sept 4	Etna, NY (Site 3)	nd <sup>b</sup>
Propolis	Sept 4	Etna, NY (Site 3)	0.42
Wax (light)	Sept 4	Etna, NY (Site 3)	0.74
Wax (dark)	Sept 4	Etna, NY (Site 3)	0.63
Pollen	Sept 3	Lansing, NY	0.20
Propolis	Sept 3	Lansing, NY	0.20
Propolis (from bottom			
boards)	Sept 18	Leroy, NY (Site 1)	0.62
Propolis (from bottom			
boards)	Sept 18	Leroy, NY (Site 1)	0.16
Propolis (from supers)	Sept 18	Leroy, NY (Site 1)	nd
Propolis (from supers)	Sept 18	Leroy, NY (Site 1)	nd
Propolis (from supers)	Sept 18	Leroy, NY (Site 2)	nd
Propolis (from supers)	Sept 18	Leroy, NY (Site 2)	nd
Propolis (from supers)	Sept 18	Brazil	nd

<sup>&</sup>lt;sup>a</sup>Samples were composites from 5 hives except when noted otherwise; pollen, propolis, etc. were from the same bee hives in the designated sampling location.

bees and many of these samples contained detectable concentrations of PCBs. Propolis is the name given the tree gums and resins that bees collect to waterproof and varnish the hive interior. Bees will collect drying paint, road tar, window putty and similar materials in areas where natural propolis is scarce.

<sup>&</sup>lt;sup>b</sup>Not detectable, less than 0.1 ppm (dry weight).

It was of interest to learn if insects other than honey bees were also contaminated with PCBs. A number of other insect species were collected and the results of their analysis are listed in Table 3. Interestingly, the wasps which are predator insects, showed the highest PCB levels perhaps because they acquire it during consumption of PCB-containing prey insects. Future studies are underway to determine the extent to which toxicants in insects may be deposited in tissues of insect-consuming avian species.

Table 3. PCBs in other insects

Table 3. Tobs in cener inseces			PCBs
	Date	Sampling	ppm
Insect	sampled_	location	(dry wt)
Crickets ( <u>Gryllus</u> <u>assimilis</u> )	July 26	Oswego, NY	0.47
Deerflies (Chrysops vittatus			
2/3 and C. macquarti $1/3$ )	Aug 14	Lansing, NY	0.43
Gypsy Moth larvae (Lymantria			
<u>dispar</u> )	July 16	Ithaca, NY	0.18
Horse flies ( <u>Tabanus</u>			
<u>quinquevittatus)</u>	July 26-28	Lansing, NY	nd <sup>a</sup>
Horse flies ( <u>Tabanus</u> <u>sulcifrons</u> )	July 26-28	Lansing, NY	0.31
Squash bugs ( <u>Anasa tristis</u> )	Sept 22	Ithaca, NY	0.17
Wasps ( <u>Vespula</u> sp.)	July 17	•	2.60
Wasps ( <u>Vespula</u> sp.)	July 23	Ithaca, NY	
Wasps ( <u>Vespula</u> brood)	July 17	Ithaca, NY	0.50
Yellow jackets ( <u>Dolichovespula</u>			
<u>maculata</u> )	Sept 18	Ithaca, NY	nd
Yellow jackets ( <u>Vespula</u>			
<u>germanica</u> )	Sept 20	Ithaca, NY	0.22
Yellow jackets brood			
( <u>Dolichovespula</u> <u>maculata</u> )	Sept 18	Ithaca, NY	0.18

aNot detectable; less than 0.1 ppm.

## REFERENCES

Anderson JF, Wojtas MA (1986) Contamination of honey bees (<u>Hymenoptera</u>: <u>Apidae</u>) with pesticides and polychlorinated biphenyls. J Econ Entomol (In press)

Anonymous (1979) The invisible snowfall. Environ Sci Technol 13:1337-1339

Bromenshenk JJ, Carlson SR, Simpson JC, Thomas JM (1985) Pollution monitoring of Puget Sound with honey bees. Science 227:632-634

Brown MP, Werner MB, Sloan RJ, Simpson KW (1985) Polychlorinated biphenyls in the Hudson River. Environ Sci Technol 19:656-661

Buckley EH (1982) Accumulation of airborne polychlorinated biphenyls in foliage. Science 216:520-522

Buckley EH (1983) Decline of background PCB concentrations in vegetation in New York State. Northeastern Environ Sci 2:181-187.

Bush B, Simpson KW, Shane L, Koblintz RR (1985) PCB congener analysis of water and caddisfly larvae (Insecta:Trichoptera) in

- the Upper Hudson River by glass capillary chromatography. Bull Environ Contam Toxicol 34:96-105
- Cheng L, Bidleman TF (1977) Chlorinated hydrocarbons in marine insects. Estuar Coastal Mar Sci 5:289-291
- Clements JR, Kawatski JA (1984) Occurrence of polychlorinated biphenyls (PCB's) in adult mayflies (Hexagenia bilineata) of the upper Mississippi River. J Freshwater Ecol 2:611-614
- Edwards R (1971) The polychlorobiphenyls, their occurrence and significance: a review. Chem Ind 20 Nov:1340-1348
- Fuhremann TW, Lichtenstein EP (1972) Increase in the toxicity of organophosphorus insecticides to house flies due to polychlorinated biphenyl compounds. Toxicol Appl Pharmacol 22:628-640
- Gaggi C, Bacci E (1985) Accumulation of chlorinated hydrocarbon vapours in pine needles. Chemosphere 14:451-456
- Gilbert MD, Lisk DJ (1978) Honey as an environmental indicator of radionuclide contamination. Bull Environ Contam Toxicol 19:32-34
- Johansen CA, Coffey MD, Quist JA (1957) Effect of insecticide treatments to alfalfa on honey bees, including insecticidal residue and honey flavor analyses. J Econ Entomol 50:721-723
- Lewis RG, Martin BE, Sgontz DL, Howes JE, Jr. (1985) Measurement of fugitive atmospheric emissions of polychlorinated biphenyls from hazardous waste landfills. Environ Sci Technol 19:986-991
- Morse RA, Lisk DJ (1980) Elemental analysis of honeys from several nations. Amer Bee J 120:522-523
- Morse RA, St. John LE, Lisk DJ (1963) Residue analysis of sevin in bees and pollen. J Econ Entomol 56:415
- Morse RA, Van Campen DR, Gutenmann WH, Lisk DJ, Collison C (1980) Analysis of radioactivity in honeys produced near Three-Mile Island nuclear power plant. Nutr Rpts Int 22:319-321
- Mumma RO, Raupach DR, Waldman JP, Hotchkiss JH, Gutenmann WH, Bache CA, Lisk DJ (1983) Analytical survey of elements and other constituents in Central New York State sewage sludges. Arch Environ Contam Toxicol 12:581-587
- Mumma RO, Raupach DC, Waldman JP, Tong SSC, Jacobs ML, Babish JG, Hotchkiss JH, Wszolek PC, Gutenmann WH, Bache CA, Lisk DJ (1984) National survey of elements and other constituents in municipal sewage sludges. Arch Environ Contam Toxicol 13:75-83
- Murphy TJ, Formanski LJ, Brownawell B, Meyer JA (1985) Polychlori nated biphenyl emissions to the atmosphere in the Great Lakes region. Municipal landfills and incinerators. Environ Sci Technol 19:942-946
- Seeley TD (1985) Honeybee ecology. Princeton University Press: Princeton, NJ.
- Tong SSC, Morse RA, Bache CA, Lisk DJ (1975) Elemental analysis of honey as an indicator of pollution. Arch Environ Health 30:329-332
- US Food & Drug Administration (1971) Dept Health Educ & Welfare: Pesticide Analytical Manual, Vol 1, revised Sec 211.14a & 211.14d Washington, DC
- Received June 8, 1986; accepted August 23, 1986.