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Mirex - A New Persistent Pesticide in Lake Ontario*

*By: Herman S. Forest  
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THE ROCHESTER COMMITTEE FOR SCIENTIFIC INFORMATION  
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Mirex - A New Persistent Pesticide in Lake Ontario\*  
by  
Herman Forest

*"What we must be concerned with is the chronic harm which may result from the total body burden of a multitude of these compounds, and the possibility that they may have a cumulative or synergistic (interacting) effect."*

*"While it is extremely unlikely that Mirex or other compounds are present in water to any significant degree, our study is being carried out to provide these communities with absolute assurance of the safety of their water supplies."*  
Dr. Robert P. Whalen, New York State Commissioner of Health, in news release of September 14, 1976 (1).

Summary

Unexpectedly high amounts of Mirex, a chlorinated hydrocarbon used as a pesticide and industrial chemical, have been found in Lake Ontario sediments, fish and herring gull eggs. Mirex was formerly manufactured by the Hooker Chemicals and Plastics Corp. of Niagara Falls under the trade name of Dechlorane. The plant, which discharged its wastes into the Niagara River, has been identified by State officials as one known source of the material in the lake sediments. However, the Mirex found at the eastern end of the lake may come from other sources, and the major discharges from the Hooker Corp. plant may have ended in 1968. That plant no longer manufactures Mirex at Niagara Falls but does buy it and grind it, and some is washed into the sewers. The material in the sewers gets into the lake because Niagara Falls does not yet have an adequate treatment plant.

\* RCSI thanks the Environmental Quality Research unit of the New York State Department of Environmental Conservation, Albany, and the Rochester Field Office of Region II, United States Environmental Protection Agency for their help in providing references, information and suggestions. Their aid was particularly appreciated at a time when there were few available sources, and access was difficult. As the Bulletin was being prepared, additional reports were released and public announcements began.

Canadian and New York officials advised against eating large amounts of several species of fish because of the hazard to human health. On September 14, 1976, actions by the Commissioners of Health and of Environmental Health prohibited the possession and consumption of fish species from Lake Ontario containing Mirex levels above federal standards.

The Hooker Corp. has been permitted to discharge a limited amount of all chlorinated hydrocarbons under the federal NPDES program since 1974. Toxic compounds of this class, such as Mirex, were not limited individually in the permit. The discovery of Mirex in sediments and fish demonstrates both the potential benefits and current weaknesses of the permit system. The main source of the chemical was easy to find, and permissible limits of discharge can easily be changed. However, setting limits by the best practical technology, as they are now set, was not sufficient to protect the environment and the public. Congress has delayed the next step, which would correct the problem, both by changing deadlines and by limiting funds for EPA personnel. Some useful corrective steps were taken recently by the Department of Environmental Conservation.

#### What is Mirex?

Mirex is the most widely known trade name for the chemical dodecachloro-pentacyclo-1,3,4 methano-2H-cyclobuta(cd)pentalene. It is a heavily chlorinated hydrocarbon. Mirex has been used as an insecticide; the same chemical with the name of Dechlorane has been offered as a flame retardant for rubber, paper, and plastic foam. It has been registered in nine southern states chiefly for the control of the fire ant. It is not licensed for use in Canada or in any state in the Great Lakes watershed. The acute toxicity (quick poisoning) is low for birds, mammals, and fish, but some insects and crustaceans such as crab and shrimp are highly susceptible (2). Mirex is not biologically degraded and persists longer in plants and animals than other insecticides (3). Residues were found in a wide variety of species in Mississippi estuaries in 1970 (4), after it was sprayed for fire ant control.

#### Source of Mirex in Lake Ontario

Mirex is not sprayed in the north, and airborne contamination has been ruled out as a significant source of contamination. It appears quite unlikely that only Lake Ontario would receive wind blown dust. Furthermore, a pattern of distribution in the sediments (see Figure 1) indicates a point source or sources, not a general distribution from the air. The pattern follows quite closely the known flow of Lake Ontario eastward, close to the southern (New York) shore, with the heaviest concentrations near the mouth of the Niagara River (below Buffalo); a secondary concentration in the Rochester embayment; and a third adjacent to Oswego.

Mirex (Dechlorane) may be used as a flame retardant, but RCSI has been unable to confirm any actual use. Alley (5) stated that two patents have been granted for this use, and apparently it has been advertised for sale.

According to Alley, the usual formulations for fire resistant polymers contain 5%-30% Dechlorane. Residues of industrial uses of this fire retardant may have entered the lake with waste water: Alley estimated that such releases could amount to more than the Mirex sprayed to control fire ants. RCSI does not know whether any factory in the Oswego Canal watershed has a permit for discharging Dechlorane, and it is still possible that this was one of the sources of Mirex found in Lake Ontario.

The one verified point source of Mirex is at Niagara Falls. New York State Department of Environmental Conservation (DEC) Commissioner Peter Berle was reported on September 2 to have identified Hooker Chemical and Plastics Company as the major source of industrial pollution. The Hooker Co. and Allied Chemical Co. hold patents for the manufacture. Mirex is the name originally patented by Allied. Hooker has a large plant in Niagara Falls that formerly manufactured Mirex which was marketed under the name of Dechlorane. Hooker Chemical Co. has a permit from the federal government (NPDES Permit Number 74-584) to release 115kg of all chlorinated hydrocarbons a day into the Niagara River. The permit became effective 9/30/74, and permitted release of hydrocarbons for 2 years. In all, the company discharges 27 million gallons of waste water into the river from its four outlets each day. The river is classified "A special". "A" means drinkable, "special" is a dispensation for the chemical company. It is well to remember that the "A" classification is a goal, not a fact. The amount of insecticide permitted to enter an "A" river was on the basis of the "Best Practicable Technology" for cleaning the waste water at the Hooker plant.

Hooker Corp. plant manufactured Mirex until 1968. This was, presumably, the period when the largest amount has been discharged with wastewater. From 1968 on, Mirex was only ground to powder and packaged at the Hooker Plant: it is shipped into the plant, in bulk, from Nease Chemical Co. (State College, Pa.). This is a clean operation when compared to manufacturing. Grinding is a dry process, but the equipment and room are washed down afterwards. The entire building drains through a sewer into the Niagara Falls sewage treatment plant, which handles 90 million gallons of liquid a day. Into this volume, the Hooker plant released an estimated 1.4 pounds (0.6kg) of Mirex on days when the material was processed. This release was estimated by the U.S. Environmental Protection Agency (EPA)(6). If Mirex was the only organochlorine compound in the plant's wastewater, then the amount released was about  $\frac{1}{2}\%$  (0.5%) of the amount allowed in the 1974 permit. This is not good evidence, but it indicates that the Hooker plant has been releasing only small amounts of Mirex since 1968, long before the releases became limited by the NPDES permit.

#### Niagara Falls Sewage Treatment Plant

Treatment at Niagara Falls Sewage Plant is primary, consisting of bar screening, settling and chlorination. Niagara Falls is third in priority in a list of 316 for available grant money for 1976-77 (7). They plan an increase in treatment level. In the meantime the river is polluted with a variety of industrial and municipal wastes. Some of them enter the food web and accumulate in fish. It is probable that the fish and gulls tested

are showing a delayed effect of bioaccumulation. The first organisms to be contaminated probably picked up the chemical when the Hooker plant was actually manufacturing a considerable amount of Mirex, rather than recently from the wash-water. In the future, when the Town of Niagara Falls applies for a discharge permit for its new sewage treatment plant, it will have to regulate all chemical industrial wastes before the wastes come into the Niagara Falls sewage system.

#### Mirex in Lake Ontario Fish

The Ontario Ministry of the Environment analyzed approximately 1000 fish from various locations in the Great Lakes, but only fish from Lake Ontario were found to contain measurable Mirex residues. The locations in Lake Ontario and smaller inland Ontario waters were listed in the news release of July 16, 1976 by the Ministry (2). Twelve locations included at least one species which averaged 0.1 ppm or more in Mirex content.

<u>Location</u>	<u>Fish</u>
Frenchman's Bay	white perch, brown bullhead
Duffin's Creek	white & yellow perches, brown bullhead
Etobicoke Creek	northern pike
Rouge River	brown bullhead
Ganaraska River	coho salmon
Traverse Shoal	smelt
Port Dalhousie	smelt, coho, brown trout
Hamilton Harbor	alewife
Humber River	smelt
Port Hope	smelt
Wilmot Creek	smelt

The highest averages for individual species were 0.25 ppm (white perch and yellow perch from Duffin's Creek) and 0.24 ppm (coho salmon from Ganaraska River), but the highest individual analyses were from specimens of brown bullhead (0.8 ppm; Rouge River) and white perch (0.5 ppm; Duffin's Creek).

In addition, 18 fish (10 species) mostly from the eastern Lake Ontario region of New York, were examined by the Buffalo District Laboratory, Bureau of Foods of the Federal FDA. These had been caught by the NYS DEC in August and September, 1975. In a report of February 2, 1976 (8), the Buffalo Laboratory found levels of Mirex exceeding 0.1 ppm in four fish:

smallmouth bass	Chaumont Bay	0.19 ppm
white perch	Chaumont Bay	0.12 ppm
coho salmon	Salmon River outlet, Pulaski, New York	0.35 ppm
lake trout	source unknown	0.53 ppm

### Mirex in Herring Gulls

In 1975 a Canadian study (9) found that the Herring Gulls in Lake Ontario were producing only 1/15th as many young as the gulls of the best Great Lakes colony. There were both hatching failures and changes in the behavior of adult birds. Analysis of two eggs showed high levels of Mirex (4.18 ppm compared with 0.09 ppm in Lake Erie). However, other toxicants were also present in quantity: DDT, dieldrin, heptachlor epoxide, hexachlorobenzene, polychlorinated biphenyls, and mercury.

### Why Mirex Was Not Recognized Earlier in Lake Ontario

Although gas chromatographic methods permit detection of chlorinated hydrocarbons at low levels, distinguishing between various man-made varieties has been difficult. In 1966 it was finally recognized that an isomer of polychlorinated biphenyls (PCBs) was not being separated from DDT, and in 1974 a compound previously assumed to be a PCB was recognized as Mirex (10). Reliable methods are now used by the Canadian Division of Inland Waters to monitor for its presence in fish. The United States had monitored for Mirex in the South where it is applied for insect control, and is now monitoring in the North as well, with the cooperation of New York State.

### Is Mirex Dangerous in New York?

The toxicity of Mirex has been established in controlled experiments. In environmental situations it is never alone, but mixed with other chemicals which may be more toxic and present in greater amounts. Consequently its exact hazard is difficult to judge. In May, 1976, the US FDA proposed a level of 0.1 ppm (one tenth part per million or 100 parts per billion) as unacceptable in fish used for food. No Canadian level has been announced, but the Ontario Ministry of the Environment (2) advised against frequent eating of the fish which it listed (above, this bulletin) as containing more than 0.1 ppm of Mirex. Also, Dr. Theodore Hullar, Deputy Commissioner of the NYS DEC suggested that no more than six ounces of Lake Ontario fish should be eaten per week (11). In the Rochester area there are no commercial fisheries, but the total New York catch is 320,000 lbs. annually and the Canadian total is about seven times higher (8). There are no data to indicate where the commercial catch is marketed, nor the amount of sports fishing catch which is eaten. However, since fishing for coho salmon has become popular, the limitations on intake are particularly applicable to sports fishermen.

### Ban on Eating Contaminated Fish

The most recent official action has been a prohibition against possession (and consequently the opportunity to eat) of several species of fish from the Lake Ontario watershed: coho and chinook salmon, brown bullheads, catfish, lake trout, smallmouth bass, and the alewife-herring group. In addition pregnant women were warned not to eat white perch and white bass, and all others were cautioned to eat these fish no oftener than weekly. This action was taken by three government agencies. First, the federal Food and Drug

Administration decided that 0.1 ppm is the permissible limit for Mirex in meat and fish. Next, the New York State Commissioner of Health issued official guidelines listing the seven kinds of fish which exceeded the FDA standard and banning their consumption. Finally, the DEC issued an emergency regulation which prohibited possession of these fish and required that those caught should be returned immediately to the water (12). The DEC, through its Conservation Officers, generally enforces regulations on the taking and possession of fish and game.

#### Was the National Pollutant Discharge Elimination System at Fault?

The Federal Water Pollution Control Act, passed in 1972, called for the enormous job of registering and controlling every point source of polluting discharges (13). Hooker Corporation received its National Pollutant Discharge Elimination System (NPDES) permit in 1974. The current damage to fishing, however, may well be caused by pollutants discharged before the end of 1968. If this turns out to be true, then the NPDES system can not be held responsible. On the other hand, the system is responsible for what was done about Mirex discharges since 1974. This report showed major faults in the performance of the NPDES system. Some of them can be blamed on the EPA which administers the system. Some are being corrected by the New York State DEC. Most of the faults can be traced to decisions made by the U.S. Congress, and will require correction by Congress.

The National Pollutant Discharge Elimination program has been behind schedule from the start, because the EPA was allotted barely enough resources to review discharge applications and grant the initial permits. Many important control activities based on the permits were consequently set aside.

The initial permits set limits for discharges on the basis of the best practicable technology for cleaning up chemicals at a plant. Next, the EPA started listing the most toxic industrial chemicals, so as to put them under much tighter limits (14) or ban discharges if needed. EPA stopped adding new chemicals to this list before Mirex was recognized as a threat to water, partly for lack of funds and partly because of pending legislation (the Toxic Substances Control Act).

This sequence of events explains why the Hooker Corp. had a permit to discharge a fairly large amount of chlorinated hydrocarbons, with no special restriction on Mirex. In hindsight, the EPA should have moved promptly to limit discharges of Mirex as soon as tests for it became available and its toxicity in food was officially recognized by the FDA. In practice, adequate control may not be possible until Congress gives the EPA the mandate and money to control toxic chemicals under a new Toxic Chemicals Control Act.

The "practicable" discharge limits initially set by the EPA are supposed to be replaced, in the long run, by new limits that prevent ecological damage (This is what the law means by "elimination of pollutant discharges"). In theory, these limits are calculated from "balance sheets" for each chemical in each watershed: water flows and chemical concentrations are tested, and the limits for releases from all sources are adjusted to keep the final concentration in the water at a permissible, non-polluting level. In practice, the EPA hardly got started on this task.

In the case of Mirex, for example, the EPA was not even able to produce a definitive list of all sources of discharge of Mirex or Dechlorane into the Lake Ontario watershed. Hooker Corporation's discharge of Mirex was limited only by the permit for total chlorinated hydrocarbons. This permit would have allowed the release of much more Mirex than was actually released since 1974: at a rough estimate, over 200 times more. Clearly, a changeover to ecological standards is necessary, but it will not be done unless Congress allots the necessary funds for EPA's enforcement branch. Environmental organizations, led by the National Resources Defense Council, charged recently that both Congress and the President's Office of Management and Budget have been systematically weakening EPA's enforcement powers instead of strengthening them (15).

On September 14, measures were announced by the New York State Commissioner of Environmental Conservation which approach the long-range aims of the permit system:

1. A computer analysis is being undertaken of all industries which discharge chlorinated hydrocarbons.
2. Requirements are imposed on the dischargers to identify the type as well as the amount of specific compounds by analysis of a 24-hour continuous sample.

In addition, Commissioner Berle of the DEC announced in a news release of September 14, 1976 that he asked 1,500 industrial dischargers in New York State to tell the DEC whether they have purchased or used chlorinated hydrocarbons in the past year. If they did, they must report the chemical identity and amount, so that the DEC may monitor their releases and if necessary adjust their discharge permits.

#### References

- (1) News Release by New York State Department of Health, Albany. Sept. 14, 1976
- (2) "*Insecticide Mirex Found in Lake Ontario Fish*", News release by Ontario Ministry of the Environment, Toronto. July 16, 1976
- (3) Mehendale, N. M. et al, "*Fate of Mirex <sup>14</sup>C in the Rat and Plants*", Bull. Environ. Contamination and Toxicology 8:20, 1972
- (4) Baetcke, K. P., J. D. Cain and W. E. Poe, "*Residues in Fish, Wildlife and Estuaries*", Pesticides Monitoring J., 6:14, 1972
- (5) Alley, E. G., "*The Use of Mirex in Control of the Imported Fire Ant*", J. Environ. Quality 2:52, 1973
- (6) Rochester Times-Union, Sept. 14, 1976
- (7) List received by RCSI from NYS Department of Environmental Conservation, August 13, 1976



- (8) "Mirex in Lake Ontario Fish (August - November 1975)". Report by Buffalo Laboratory, Bureau of Foods, U.S. Food and Drug Administration. Feb. 2, 1976
- (9) Fox, G. A. et al, "Herring Gull Productivity and Toxic Chemicals in the Great Lakes in 1975". Toxic Chemicals Division, Canadian Wildlife Service, Ottawa, 1976
- (10) Kaiser, Klaus, "Mirex: An Unrecognized Contaminant of Fishes From Lake Ontario". Science 185:523, 1974
- (11) Rochester Times-Union, Sept. 2, 1976
- (12) News release by New York State Department of Environmental Conservation, Albany, Sept. 14, 1976
- (13) Hetzel, Peter, "Control of Pollution Discharges in Monroe County (NY)," RCSI Bulletin #188, July 1975
- (14) Federal Register 39:164 pt. 4, August 22, 1974, 30465-30471 and 38:241 pt. 2, Dec. 17, 1973, 34706-34716
- (15) Flattau, E., "EPA Follows Orders of Budget Bureau", The Times-Union, September 17, 1976, p. 10A

END NOTE

*Chemical and Engineering News (September 13, 1976, pg. 9) reports that the State of Mississippi has petitioned the EPA to end all aerial spraying of Mirex in the South by December, 1977.*

Late information received September 22 by RCSI:

- 1) Hooker Corp. manufactured another chemical (not Mirex) under the name of Dechlorane.
- 2) 1962-1967 were the years of heaviest production of Mirex by Hooker Corp. at Niagara Falls.

MIREX (ppb)

- not detected
- ◻ 0-5
- ◻ 5-10
- ◻ >10

