MICHIGAN FARMER
TWICE MO.

FEB 7 1976

1800

As society "chemicalizes," Geagley Lab feels the pressure

By DICK LEHNERT

Was the insecticide DDT guilty of the crimes with which it was charged? Or was the miracle chemical of the fifties and sixties unfairly banned in Michigan (the first state to to so) in a case of mistaken identity?

A scientist at the Basel, Switzerland, corporate headquarters of Ciba-Geigy, the chemical company that invented DDT back in 1939, says some of the things of which DDT was accused were instead caused by PCBs (polychlorinated biphenyls), and the people doing the testing for DDT residues couldn't tell the difference.

"You're saying it wasn't DDT that was thinning the shells of peregrine falcon eggs, embedding itself in the fat of penguins at the South Pole, polluting the milk of nursing mothers, killing off the trout in Lake Michigan, and otherwise messing up the globe?" I asked, aghast at the magnitude of such an error and all it implied.

"I'm saying," he replied, "that mix-ups could be made, and probably were, in determining what the residues in some of these samples were."

The young German-Swiss chemist, whose name I never captured, went on to explain exactly how such errors could occur, and how only in recent years has the gas liquid chromatograph been hooked in tandem with the mass spectrograph to produce positive identification of these miniscule residues.

On my trip home, I mulled over the sobering implications of what the chemist had said.

Chemists today are key figures in our chemicalized society. They deal in an alphabet soup of chemical names and abbreviations. The average man — the average farmer, the average farm writer — would rather not try to tangle with this frustrating and complicated world, but what can we do?

DES causes cancer, says a chemist somewhere, and the feeding practices and profit potentials of thousands of cattlemen is changed. PBB is accidentally mixed into livestock feed, and a whole state's agriculture and its biggest farmer cooperative are embroiled in a multimillion-dollar tragedy.

PCBs are found in silos, and dairymen's milk is taken off the market. DDT is discovered "everywhere," and a chemical that has saved millions of lives is suddenly deadly to life.

TCDD, a deadly dioxin, is found in minute quantities in the herbicide 2,4,5-T. TCDD is linked to birth defects in Vietnamese children in the country where the herbicide was applied during a war. Only recently another chemist found a way to remove TCDD from 2,4,5-T.

Normally, chemists don't like to talk to laymen about how they find out what is contaminating what; they assume nobody but chemists understand, or even want to.

So when I called up officials at the Michigan Department of Agriculture's William C. Geagley Laboratory in East Lansing and told them I wanted to look over their tests for DDT residues, they were skeptically curious. As the MDA's official laboratory, they generated some analyses that provided ammunition against DDT.

They've also run 18,000 samples over the last year or so in connection with the PBB incident, and are currently investigating a case in which fields of corn in southern Michigan near Sherwood were damaged, allegedly by a contaminant in liquid fertilizer.

Geagley lab chemists also routinely check milk, animal feed, fertilizer, drugs, alcoholic beverages, and the urine of race horses, as well as doing the special work of detecting residues in possible pesticide contamination cases.

When I told them what the Swiss chemist had told me, and asked them if it could be true, it was like reminding an old friend of a good story. For as it turned out, the very problem I was concerned about had been observed and reported by them already in 1964 — perhaps before anyone else had recognized it.

Donald A. Muentener, acting chief, and Wendell Brewbaker, coordinating

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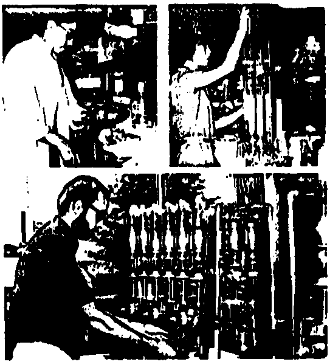

Starting with crude but effective tools, samples are ground (by Rita Serens), extracted (Maureen McCully), boiled in solvents (Neil Jones), and ultimately tested, in this case for PBB contamination. At right, Wendell Brewbaker injects a sample into the gas liquid chromatograph (GLC). A mass spectrometer and a computer will double check and analyze the findings. Hanging on the wall above his head are U-tubes for the GLC.

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chemist in the laboratory division, quickly agreed: It is possible to confuse PCBs and DDT when making lab tests.

"Mixups of the two can be made," Brewbaker said, "and in fact it was done here — once, for four hours." That, he said, was in 1964.

"We are not a research laboratory," Muentener said, "so we reported that unidentified peaks were showing up close to those of DDT on the gas liquid chromatograms. Samples containing these unidentified peaks were submitted to FDA labs in Detroit, where they were tentatively identified as 'halogenated hydrocarbons.' Later, chemists in England identified them as PCBs."

Even if DDT were in fact unfairly banned, the flow of history is such that once banned it would likely never be resurrected. Farmers and other pesticide users have replaced DDT.

But if DDT got an unfair hearing, what about other pesticides? Chlordane and heptachlor, for example, are now under attack by the Environmental Protection Agency, which has issued "intent to suspend."

Just how good are those techniques chemists use to determine pesticide residues?

The question is provocative, for Michigan farmers have been having intimate disagreements with several chemicals in recent years, and chemists at Geagley Laboratory look for these residues. The DDT versus PCB story is interesting because farmers have been involved with both of them.

One of PCB's many uses is as a sealant for concrete. A year ago, milk from some dairy farms was found contaminated with PCBs after cows ate silage from concrete silos sealed with a sealant containing PCBs as much as 25 years before.

PCBs are related closely to another chemical that has messed up Michigan agriculture — PBBs. For nearly two years, polybrominated biphenyls accidentally mixed into feeds by Farm Bureau Services have been having resounding repercussions.

RESIDUE TESTING

Restrictions on chemicals, including pesticides, often come when their residues are found in parts of the environment where they should not be. By the time DDT was banned in Michigan, that chemical and its degradation products had been reported in the fat of birds and fish, in the milk of nursing mothers, and even in the bodies of animals as isolated and far away as at the South Pole.

It was believed that, while DDT apparently did very little harm to humans and other mammalian animals, it was deadly to fish and birds. DDT accumulations in the silt at the bottom of the Great Lakes, at the base of the chain of life, led to increasingly higher bodily accumulations farther up the food chain. This was ultimately basic to Michigan's ban on DDT — to save the commercial fisheries of the state. The DDT was not only accumulating in the fish, it was reducing survival of fish eggs and fry.

All this talk about residues and residue levels is underscored by one fact: *No one can see a residue*. You can see DDT in a quart bottle, and perhaps tell what it is by the smell, but you can't see it as a residue, or smell it, or in any other way detect it without laboratory analysis. Even when DDT is concentrated 85,000 times by fish, or 34,000 times by snails, as can happen, actual levels seldom reach much above 100 parts per million.

To find such levels, you must enter the chemist's world and there follow his rules and methods.

TESTS EVOLVE

At one time, according to Brewbaker and Muentener, a test for DDT might have been merely a total chlorine analysis. Analysis of unknown compound was made to see if it contained chlorine. If it did, it *could be* DDT. But PCBs — and a lot of other organic molecules — contain chlorine.

With the advent of thin layer chromotography, it became much easier to identify small residues of materials. Here's how:

Near the bottom of a sheet of special paper, a drop of "unknown" chemical is placed. This end of the sheet is placed into a solvent. The solvent gradually wets the paper as it migrates by capillary action. It carries with it some of the unknown chemical. The distance the unknown chemical moves with solvent depends on what the chemical is and what the solvent is. When the paper is later "developed," a series of spots at certain distances from the initial drop of chemical become visible. DDT, for example, makes two spots, reflecting the two kinds of DDT — parapara DDT and ortho-para DDT. (Ortho and para refer to the position of chlorines on the basic benzene ring molecular structure of DDT.)

To determine what an unknown chemical is, you compare it with the

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characteristics spotting of known chemical standards. If no such standard exists, as may be the case with some chemicals, it cannot be identified. Unless it has been tested before, this "fingerprint" is not on record to compare it with.

A method similar to thin layer chromotography is gas liquid chromotography. This method, according to Muentener and Brewbaker, is essentially a fractional still. An unknown chemical is injected with a hypodermic needle into a very hot U-shaped glass column packed with any of several possible materials.

This method requires only a tiny amount of material. One-millionth of a liter is needed to make the test.

The unknown chemical is changed by the heat to a gas. As it travels through the packed U-shaped tube, it begins to separate, as different parts of the gaseous material travel at different rates. By measuring the time at which the different organic compounds are picked up by a detector at the end of the tube, a chemist can identify what the unknown chemical is — again provided it matches a known record.

In DDT, ortho-para DDTcomes off at six minutes and para-para DDT at nine minutes, said Brewbaker, adding the very important qualifier, "the way I pack the column." Different chemists pack the columns differently, so each chemist has his own individual operating parameters.

According to Brewbaker, "The first confusing peak of PCB is almost superimposed upon the para-para DDT peak at nine minutes, being displaced only slightly (about six seconds). Methoxychlor comes off at about 14 minutes, then PCBs have nine or ten more peaks after that."

If a column was packed with a different material, Brewbaker said, the first peak of PCB and the second peak of DDT could fall right on top of each other.

"We first noticed this one afternoon in 1964," Brewbaker said. "At the time, we could not identify what that peak was, but we knew it wasn't DDT. There was some confusion for about four hours.

"Our work here is primarily regulatory. However, when such observations are recognized they cannot be ignored. Our findings were reported. Subsequently, other chemists elsewhere identified it as caused by PCB."

That confusing peak is named, at least among MDA chemists, after the Michigan dairy farmer whose milk, being sampled for DDT residues, gave the PCB peak. Later, it was found the PCB came from the lining in the farmer's concrete silo.

Also, Brewbaker added, during the initial testing of coho and other salmon from Lake Michigan for DDT residues, they had reported the presence of "unidentified halogenated hydrocarbons" now known to have been PCBs.

CAN'T TEST FOR "NOTHING"

At this point we can clear up a misunderstanding about the problems surrounding the initial *identification* of PBB in cattle and poultry feed in Michigan. Remember that no scientific test can identify a residue of something unless that something has been identified *once* before. Labs all over the country failed to detect polybrominated biphenyls in the feed. The gas chromatograph peaks that come through the column at six and nine minutes for DDT, and in that range for PCB, would not have come through Brewbaker's packed column until something like 27 hours after the start of the test.

It was only after a Maryland researcher named George Fries, who had worked with PBBs on a gas chromatograph before, suggested that the feed might be contaminated with PBBs that scientists at other labs were able to find and identify it.

The machines today do not require 27 hours for each PBB test. Instead, a different packing material and oven temperature are used in the U-shaped tubes, which shortens the time to minutes.

MASS SPECTROGRAPH

The Swiss chemist at Ciba-Geigy believed that his company has a machine that made identification less subject to confusion. There, a gas liquid chromatograph is hooked in tandem to a mass spectrograph. That is also the case at Geagley labs.

Geagley labs also use the "mass spec," because, as Brewbaker put it, "we often need the kind of data we can go to court with." The MDA lab findings are sometimes used in the trial and conviction of violators.

The mass spectrograph at Geagley is hooked to a computer and to a gas chromatograph. As the gaseous "unknown" comes from the U-tube into the mass spec, it is bombarded by electrons that fragment it. The mass spectrometer determines the molecular weight of each fragment.

Every chemical fragments in a

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unique way, always emitting fragments of the same molecular weight under the same conditions. "This is a true fingerprint machine, a sure thing," *Brewbaker said.*

DDT, for example, has a chemical formula of $(C_6H_4Cl)_2C_2HCl_3$. When hit by an electron, its first fragment is $(C_{13}H_9Cl_2)^+$ a charged, ionic particle that has no special characteristics — except to be the first fragment of DDT. When combined with second, third, fourth, and additional fragments, *many equally unique,* the identity of DDT is clearly defined.

The problem with the machine is that results are hard to read. With the computer doing the hard computations, it is an easier test. "The computer can read the graphs—and actually print them out. For chemists, it's too time consuming," Brewbaker said..

The machine cannot identify an "unknown" that has never been identified before, for in this case, too, the machine only compares the "fingerprints" of the chemical in question to the fingerprints of all others on record.

GEAGLEY LABS

There are eight laboratory sections under Brewbaker's supervision at the Geagley Laboratory in East Lansing. These include the racing lab, which does urine tests on winning horses in all races at Michigan parimutuel tracks; the food and beverage lab; the dairy lab; the feed and fertilizer lab; the pesticide residue lab; the drugs and toxicology lab; the alcoholic beverage *lab; and a special projects lab. There* are seven laboratory sections under the supervision of veterinarian and pathologist Norman Gatzemeyer. These include serology, pathology, dairy microbiology, food and animal microbiology, seed, and plant pathology. He also supervises the Escanaba branch laboratory.

Many of these labs have been handling milk, animal tissue, water, soil, and manure analyses in connection with the PBB affair. Some 18,000 samples had been run by mid-1975.

PENGUIN FAT

Geagley Labs, of course, is concerned with chemical residues in the environment of Michigan. One of the concerns of the Swiss scientist related directly to the widely publicized theory that DDT was "a global contaminent" found in the fat of penguins at the South Pole and in the eggs of birds in remote parts of the earth.

And while Geagley Labs can say, "It was DDT in salmon in Lake Michigan," what about this other case?

This is a question of concern. If DDT is in fact in animals thousands of miles from farmers and other DDT users, it is truly a global contaminant of monstrous proportions. PCBs, however, may be at the Poles, for they are taken there by man's machines.

BAN ON PCBs

In early May of this year, a report by the Lake Michigan Toxic Substances Committee recommended a near-total ban on all PCBs. These materials have been manufactured since the early 1930s, in the U.S. solely by the Monsanto Chemical Co., but worldwide by many others.

PCB's major use is in transformers and capacitors, where they greatly reduce the threat of fire, explosion, and disruption of electrical service. Other uses include that of an additive to hydraulic fluids and oils; as an adhesive; in textile coatings for flame proofing; in paints, varnishes and epoxy resins for protective coatings on metals; as *sealants and putties where they act as* non-hardening agents; in the printing industry for many purposes; and dozens of other categories of uses.

Its adverse effects on health are also known. Workers in PCB plants develop acne-like lesions from contact, and can develop worse symptoms such as vomiting, swelling, jaundice, baldness, and some nerve damage. In 1968, an accidental poisoning occurred in Japan when 1,000 people ate rice oil contaminated with PCB. Some died.

Fish in the Great Lakes are known to contain PCBs.

With the many uses of PCBs, it is logical they would be found even at the Poles of the earth, for they are used in fuels and oils dispersed over the globe by jet aircraft and ships on the seas.

The use of PCBs is presently being restricted voluntarily by the manufacturer. *The electrical* uses and use in "closed circulation" systems such as hydraulic units are being continued, but some "open-ended" uses where the PCBs end up in the environment are being stopped.

SUMMARY

Many of the tests run by Geagley and other labs are not so esoteric. But as chemicals used by man increase in number and complexity, the chemist is called upon to find smaller quantities of more toxic "needles" diluted in ever bigger haystacks."

The Geagley labs, the ones Michigan farmers and consumers rely on, have established a pretty fair record in *this complicated world.*

They share one problem with all labs: It is extremely difficult to find and identify a contaminating chemical unless they have some idea what they are looking for. Sometimes, they find hundreds of things "it" is not, but not what "it" is. □

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