Detoxifying PCBs

Everything from microbes to vitamin C is being considered in new approaches to degrade PCBs

By JANET RALOFF

Officials at the New York Department of Environmental Conservation estimate it will cost the state at least $40 million to dredge up and bury just 12.5 of the more than 70 tons of the polychlorinated biphenyls (PCBs) that contaminate the Hudson River. However, at about the same time as New York officials were giving taxpayers this bad news in May, researchers working for General Electric Co., one of the companies responsible for the Hudson's PCB contamination, were reporting some good news about this toxic cache: They've found that microbes in the river's sediment are munching away on buried PCBs, breaking them down into nontoxic substances.

While these yet-unidentified bacteria are dining slowly – too slowly to satisfy state and federal environmental-cleanup specialists – they do point toward a potential solution to the toxic pollution.

And the hunt for such solutions is intensifying. While PCB production was banned in 1979, an estimated 250 million pounds of these oily fluids are still in service – largely as nonflammable and insulating heat-dissipators in capacitors and transformers – and must be disposed of within the next three years. Moreover, the Environmental Protection Agency (EPA) has identified many sites where the chemicals have been illegally dumped or accidentally spilled. As a result, safe disposal of these suspected carcinogens is becoming not only big business but also an environmental imperative.

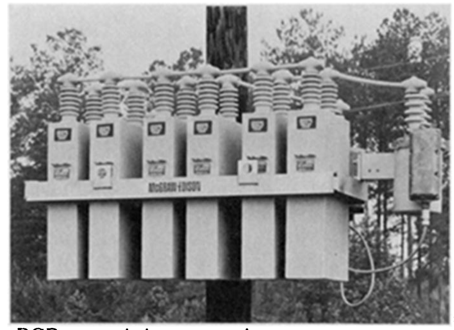
And that may explain why there are probably 100 or more different U.S. research efforts aimed at developing better PCB detoxification, destruction or cleanup technologies. These programs embody concepts as simple as sprinkling a nontoxic chemical over the soil, then periodically raking the soil for enhanced sunlight-driven dechlorination, to subjecting PCBs to detoxifying chemical baths.

PCBs are a family of 209 species, each containing a pair of linked, ring-shaped structures. As many as 10 chlorine atoms may dangle off a PCB's rings. How toxic and persistent any one of them will be in the human body is determined by how many chlorines it has and where they reside.

In the May 8 Science, John F. Brown Jr. and his co-workers at the General Electric Research and Development Center in Schenectady, N.Y., described the activity of PCB-degrading anaerobic bacteria in aquatic sediment. Brown, manager of health research, reports that the more highly chlorinated PCBs – those with four or more chlorines – tend to be more toxic. However, he notes, even among the more highly chlorinated ones, those of greatest toxicological concern to humans are the species that contain chlorines linked in the "para," or 4, positions, on the ends of the molecule.

"If you remove even one of those para chlorines and leave everything else," he says, "you have a PCB that will not be persistent in humans or other warm-blooded animals, and will no longer belong to this restrictive group of [species] that have toxic activity."

And, according to his research, that is the key to the success of the Hudson River bacteria. Bacteria feeding on PCBs at the bottom of the Hudson appear to have a particularly avid appetite for just those critical para-position chlorines. What's more, the microbes are not unique to the Hudson. "In every area where there's been a major PCB spill that's gotten into aquatic sediment" – and that includes seven other waterways that Brown has studied – "we have found evidence of a [natural] dechlorination process occurring," he told Science News.



PCB-containing capacitor.

The mere presence of PCBs in water, however, is not sufficient for attracting the degrading microbes. In fact, the GE research indicates that it's not until the PCBs settle out into the sediment and eventually become buried that they become susceptible to anaerobic detoxification. Moreover, the buried PCBs must reside in sufficient quantity to attract and support a population capable of carrying out the dechlorination. To date, Brown's lab has confirmed the presence of several different populations of dechlorinating anaerobes – some preferring four- to six-chlorine PCBs and at least one with a preference for more heavily chlorinated ones.

Because most of the PCB "hotspots" Brown has examined result from contamination that occurred decades before his sampling began, he says it's still unknown how long it takes the chemical to become buried to the critical depth (roughly 2 to 6 inches) and whether there is also some typical threshold period – a time before which colonization and dechlorination begin. However, he says, once these microbes begin to chow down on the PCBs, the pollutant cache appears to become detoxified at a rate of approximately 50 percent every three to five years.

Brown, a chemist, is most interested in continuing to map the extent of this phenomenon. He notes that others (some under contract to GE) are studying the growth conditions of the dechlorinating "bugs" and attempting to identify them. These studies should prove useful to those who have already expressed interest in growing and harnessing these microbes for the commercial cleanup of PCB-contaminated water or sediment.

One of them is Sandra Woods, a civil engineer at Oregon State University in Corvallis. The porous-membrane bioreactor system she is developing to treat wastewater – like that generated by a process that washes PCBs from contaminated soils – would use Brown's PCB-dechlorinating anaerobes, together with aerobes, for commercial PCB detoxification. Woods is now attempting to grow these bacteria on a gas-permeable membrane. Though she is optimistic her bioreactor will work, she has yet to demonstrate microbe-mediated dechlorination with it.

At West Virginia University in Morgantown, scientists are trying to coax sunlight and chemicals into emulating the dechlorination activity of the Hudson microbes for the low-cost, environmentally benign detoxification of contaminated soils. "By replacing a chlorine with a hydrogen atom," explains chemist John Penn, the PCB "becomes much less toxic." Sunlight is capable of fostering this reaction (SN: 12/17/83, p.390). However, Penn notes, sunlight is slow. Since electrons help cleave chlorine atoms, Penn throws in an electron-donating chemical to encourage the hydrogens to substitute for the chlorines. This step alone speeds the sunlight-driven dechlorination process 50-fold, Penn says. But his research shows that adding water accelerates the process more dramatically still. Working with a PCB-surrogate molecule, his addition of 3 percent water increased the dechlorination rate 1-million-fold over what would occur with sunlight alone. This suggests, he says, that detoxification of PCBs could probably be accomplished in less than one day.

Today, decontaminating soils usually involves excavating the polluted ground and running this soil through an expensive incineration process or a sodium/polymer dechlorinating reactor. Penn envisions being able to achieve the same PCB-detoxification by merely sprinkling an electron donor – perhaps something as innocuous as vitamin C – onto the contaminated ground, then periodically raking the soil to expose initially buried PCBs to light. It probably wouldn't even be necessary to add extra water, he notes, since most soils already contain more than his studies indicate would be needed to speed the reaction.

The process has already been demonstrated in a solvent-based system involving PCB surrogates – such as chloronaphthalene. If all goes well, Penn expects to establish its utility on PCBs in soil within three years.

Chemists at the University of Connecticut in Storrs are pursuing a radically different route to detoxifying PCBs – but one that also benefits from sunlight. Their approach uses a catalyst to transfer an electron from an electrode to a PCB. "This initiates a reaction that eventually leads to the loss of the PCB's chlorines," explains James F. Rusling, who is directing the work.

Originally working with PCBs in organic solvents, Rusling and his colleagues have recently adapted this electrocatalysis for a water-based system by using surfactant (soap-like) molecules to dissolve and attract both the oily PCBs and the catalyst (a polyaromatic-hydrocarbon derivative) into tiny, concentrated "microcatalytic packages." Though this process might be used for PCBs in a number of environments, if used on dredged-up PCB-contaminated river sediment, its surfactant might take on an additional cleaning role – dissolving PCBs off contaminated sediment particles.

In fine-tuning their system, the researchers have identified several tricks for speeding the electrochemical reaction rate. Rusling points out that any reaction involving an electrode will slow down once the reactant in the area adjacent to the electrode is depleted. It's possible to replenish the near-electrode environment by stirring things up – something the Connecticut chemists accomplish with ultrasound. Ultrasound waves create high-pressure bubbles in the solution. "When they burst," Rusling says, "things scatter all over the place," stirring the PCB-contaminated bath very efficiently.

More recently, he and his co-workers have shown that they can speed the electrochemical dechlorination even more – by 10 to 20 times – simply by shining sunlight or other visible light on the electrode. This "excites" the catalyst, dramatically improving its efficiency.

Ultrasound, light and ozone are the main ingredients in another PCB detoxification concept, which a new EPA report ranks as especially promising for the treatment of sediment.

For many years, EPA has permitted the use of ozone and ultraviolet light for the breakdown of PCBs in dilute (parts per billion) liquid concentrations. Ultraviolet light activates the PCB molecule by transferring energy to it. Once activated, ozone (O_3) is able to initiate an oxidative attack on the PCBs: Not only does it strip off their chlorines, but it will also "go on to oxidize the remaining biphenyls," explains Ben H. Carpenter of Research Triangle Institute in Research Triangle Park, N.C. He says research suggests the final product of biphenyl oxidation may be just carbon dioxide and water.

Together Carpenter and Edward Pedzy, president of Ozonics Technology Inc. in Closter, N.J., came up with a way to adapt this ozone treatment for sediment. A detergent is used not only to dissolve PCBs off sediment particles and into a water bath, but also to increase the amount of PCBs that will stay dissolved in the bath. Then the PCB-water slurry is hit with the ultraviolet-ozone combination. It will take the addition of ultrasound, however, to make this process truly effective, Carpenter believes.

When ozone is bubbled through a solution containing PCBs, the bubbles tend to coalesce into increasingly larger ones, decreasing the surface area of the bubbles available for reaction with passing PCBs. Pedzy's studies have shown that by subjecting the ozonated PCB-water bath to ultrasound, he can largely prevent the bubbles from coalescing. The result should be an increase in detoxification efficiency and efficacy, Carpenter says.

While a workable system is still under development, Carpenter says, "we're close to a viable process." And, he adds, "cost estimates are very good for it" – roughly one-seventh that of high-temperature incineration, the only other technology EPA has approved for destruction of PCBs in soils or sediment.

Researchers at EPA's Hazardous Waste Engineering Research Laboratory in Cincinnati are spearheading studies of potassium polyethylene glycolate (KPEG) as a PCB-dechlorinating agent. Explains Donald L. Wilson, a physical scientist involved in the research, KPEG treatment knocks the chlorines off PCBs (or related chlorinated compounds, like dioxin) and replaces them with part of the KPEG molecule. Both the former PCB and the resulting byproducts are nontoxic, Wilson says, adding that the treatment costs considerably less than incineration or most other conventional technologies in which PCBs are concentrated in oils or other liquids.

At IIT Research Institute in Chicago, scientists are attempting to marry KPEG and radio-frequency heating for the treatment of PCB-contaminated soils. A radio-frequency (6- to 45-megahertz) alternating current applied to rows of electrodes implanted into the ground causes a warming of the earth through a process similar to the one that heats foods in a microwave oven. Temperatures to 400°C in blocks of earth up to 880 cubic feet are possible. This heating not only speeds the KPEG-dechlorinating reaction, but also drives off some of the soil water, a factor that improves the chemical's efficiency.

In small-scale IIT experiments involving just 25 grams of soil premixed with KPEG, 99.9 percent decontamination of the PCBs occurred with an 8-hour heating. According to IIT cost estimates, *in situ* radio-frequency decontamination might be achieved for just $30 to $60 per ton of soil (not counting the cost of the KPEG) – a figure IIT says not only would be competitive with most soil-incineration techniques, but also would eliminate the need for excavation. IIT has just applied for a patent on the technique, and field testing is planned for later this year.

Unison, a wholly owned subsidiary of Union Carbide Corp. in Tarrytown, N.Y., is developing strategies for dechlorinating PCBs in transformer fluids. Currently, incineration is the preferred destruction technique for transformer PCBs. However, says Eugene C. Ward, incineration "is not very cost effective," and there are only about four EPA-approved incinerators in service today – far from enough to provide sufficient processing capacity for all the PCB-transformer fluids that must be taken out

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of service by 1990. At the recent American Chemical Society meeting in Denver, Ward described one process his firm is working on that involves a pair of solvents.

According to Ward, several alcohols — such as isopropyl, propanol and methanol — dechlorinate PCBs, leaving behind nontoxic biphenyls. However, the process they use is slow and inefficient. Dimethyl formamide, on the other hand, rapidly produces the same biphenyls, but leaves them linked as an undesirable, sludge-like polymer. By pairing the solvents, says Ward, "we get the best of two worlds" — a quick reaction that leaves individual biphenyls. Stripped-off chlorines are recovered in a nontoxic salt.

This is not only useful for detoxifying pure PCBs, Ward says, but also for treating PCBs that occur as dilute contaminants in other transformer oils. Currently, it's hard to extract the PCBs out, he says, meaning that cleanup of contaminated fluids, like the relatively expensive silicone — might require destroying the silicone along with the PCBs. With the new Unison treatment, these oils could be treated and then recycled back into the transformer.

The Electric Power Research Institute in Palo Alto, Calif., has developed a solvent-extraction process removing PCBs from contaminated mineral oil, another of the fluids being used in many transformers. A recyclable solvent, methylcarbitol, dissolves the PCBs out of the oil and into a waste stream, from which they will be captured and destroyed. Then the mineral oil can be cleaned up and put back into the transformers. "The alternative to this is to treat the PCB-contaminated oil with a reagent containing sodium that destroys the PCBs," explains Gil Addis, who has been managing the institute's role in the project. "We are hoping that [our new process] will be at least as competitive as and possibly less hazardous than dealing with sodium," he told SCIENCE NEWS. He says the Atlanta-based Georgia Power Co. has successfully tested this process in the first commercial-scale, 500,000-gallon-per-year plant.

While the total quantity of PCBs as minute contaminants in U.S. transformer fluids is small — perhaps some 100,000 pounds — the market for dealing with them is large. Notes Martin Halper of EPA, "There are 22 million potentially contaminated transformers in the United States" containing just 50 to 500 parts per million PCBs.

Taken together, these projects offer a glimpse of the breadth of research efforts under way to detoxify PCBs. But this list is far from exhaustive. For example, a June assessment for EPA of potential alternatives to landfill burial and incineration — just for dealing with PCB-contaminated river sediments — identified at least 64 different experimental technologies. Others are being explored for dealing with the high-concentration PCB liquids now filling some 100,000 electrical transformers and 8 million capacitors.

Which will win out as commercial leaders in the burgeoning PCB-destruction marketplace is anyone's guess, although safety, cost and reliability will undoubtedly be major determining factors. How any will score in those categories is difficult to predict at the experimental stage.

Explains Halper: "We put people through lots of hoops to get a permit. And we see a fairly significant number of failures — more than you'd believe." In part, he says, it indicates how hard it is to scale up a working bench-scale experimental process into a commercial-size plant. Even EPA's own mobile incinerator system (SN: 7/20/85, p.39) has failed Halper's tests to obtain a permit for use on contaminated soils — twice. As a result of such setbacks, Halper says, "A lot of people with wonderful ideas drop by the wayside." □