ENVIRONMENTAL SCIENCE & TECHNOLOGY

FEATURE ARTICLE
August 1, 1998/ Volume 32, Issue 15 / pp. 360 A-363 A

"Natural" Remediation of DDT, PCBs Debated

The dispute over chlorinated contaminant cleanups is heating up amid claims about benefits of natural processes.

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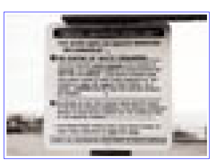
The controversy over whether persistent organic pollutants can be naturally degraded by microbial action has been heightened by new claims from researchers that for DDT and its toxic byproducts this indeed occurs. Research recently reported in *Science* (1), indicates that naturally occurring organisms in sediments play an important role in breaking down the chlorinated compounds. Although Montrose Chemical Corporation--the company largely responsible for a massive DDT-contaminated Superfund site off the California coast--hailed the findings as good news that natural processes are underway to clean up the contamination, others believe that the findings are preliminary and largely irrelevant. At stake are remediation decisions that affect millions of people and could cost hundreds of millions of dollars.

The finding that DDE (1,1-dichloro-2,2-bis(chlorophenyl)-ethylene), a toxic byproduct of the pesticide DDT, can naturally degrade comes from laboratory experiments performed by researchers from Michigan State University's (MSU's) Center for Microbial Ecology in East Lansing. They used marine sediments collected from a Superfund site off the coast of southern California on the Palos Verdes Shelf, the subject of one of the largest Natural Resources Damage Assessment cases in the United States (see photo at left). The findings are important because they suggest that problem byproducts and breakdown products from DDT use may not persist forever, said center director James Tiedje. He raised the possibility that natural processes might be significantly reducing the risk posed by these contaminated sediments.

EPA contractors collected coring samples of contaminated sediments in the upper Hudson River as part of EPA's study of PCBs in the Hudson River. (Courtesy TAMS Consultants, Inc., Bloomfield, N.J.)

Whether these findings and further research will have an impact on how the site is ultimately remediated remains an open question. Fred Schauffler, EPA project manager for the Palos Verdes Superfund site, discounted the significance of the research. More than 20 years after they were deposited, DDT compounds are still present in surface sediments at levels harmful to benthic organisms, he said. In addition, a commercial fishing ban and fish consumption advisories are still in effect. If biodegradation were occurring in the field as rapidly as it did in the experiments, the deposit would be long gone. "Regardless of whether biodegradation is occurring, there are clearly conditions out there that maintain harmful levels of contaminant exposure," Schauffler said.



As a result of PCB and DDT contamination of ocean waters and sediments off the southern California coast, the Los Angeles Department of Health Services has posted fish consumption warning signs. (Courtesy John Cubit, National Oceanic and Atmospheric Administration, Long Beach, Calif.)

But according to John Quensen, the Michigan State University microbiologist who performed the DDE experiments, the new results are broadly consistent with environmental data. He acknowledges, however, that the experiments do not prove dechlorination is taking place at a significant rate in the sediments at the site. They do demonstrate that there are sediment microbes that can dechlorinate what was previously considered a terminal product.

If natural processes are reducing the risk from the Palos Verdes contamination, the implications for remedial actions are vast. With an estimated 100 metric tons of DDT and its byproducts spread over 17 square miles, the Palos Verdes Shelf (see figure at right) is one of the most extensive DDT-contaminated sites in the world. In the ongoing Natural Resources Damage Assessment action, the federal government and the state of California are seeking hundreds of millions of dollars in damages from Montrose, other companies, and municipalities responsible for the discharges. In addition, EPA's most likely plan for the Superfund site is to cover part of the ocean floor with a cap of thick sand, a project that could cost as much as $300 million.

New research on DDT-laden sediments

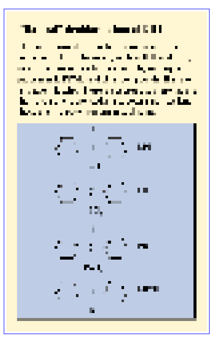
PCB Hudson River cleanup

Increasingly, potentially responsible parties are becoming advocates of a view that natural conditions or processes reduce the need for costly cleanup of contaminated sediments. For example, EPA is currently at loggerheads with General Electric (GE) over cleanup of PCB contamination in the upper Hudson River. The company contends that natural processes, including reductive dechlorination, have substantially reduced the risk to humans and the environment and that these processes should be allowed to continue. The agency is considering a Superfund cleanup of the contaminated sediments, and a massive Natural Resources Damage Assessment case is in the offing.

Despite 10 years of General Electric-funded efforts to convert research results into a cleanup method, the agency has concluded that dechlorination will not naturally remediate contaminated sediments. Now even GE no longer looks to bioremediation as the sole answer to the problems of the

Hudson River, according to GE engineering project manager John Haggard. Instead, he contends, there are a number of natural processes, which when viewed together, dramatically reduce the risk from contaminated sediments: Anaerobic dechlorination reduces toxicity; aerobic degradation reduces the overall mass; and sorption onto organic particles reduces bioavailability.

The breakdown of persistent chlorinated aromatic compounds by anaerobic bacteria through a process called reductive dechlorination makes a tantalizing research target because these bacteria have demonstrated the potential to destroy troublesome, harmful contaminants. DDE (see figure on page 362A) now joins the list of persistent organic pollutants that, depending on field or test conditions, can be degraded by such microbial action. The Michigan researchers demonstrated this in laboratory experiments in which ^{14}C-labeled DDE was added to sediments from three different locations.



"Natural" declorination of DDT

In 32 weeks, microbes transformed some of the DDE to DDMU in each of the sediments and under both methanogenic and sufidogenic conditions. DDMU, which has one less chlorine atom, does not bioaccumulate as readily as its parent, and it is also subject to reductive dechlorination.

But the relevance of these experiments to the contamination off the coast of Los Angeles is likely to be the subject of intense study and debate. A major difference between the laboratory experiments and the conditions at the site is that the DDE added in the experiments may be more bioavailable than it is at the site. The presence of sulfide and the lower temperature at the ocean bottom would also slow the reaction in the field, he said. To quantify these effects, the MSU group is running additional experiments that more closely replicate conditions on the ocean floor. They are also planning to work with material from other sites in an attempt to identify which composition factors affect the process.

One important point of comparison is the experimental rates. These are consistent with field observations, if laboratory conditions are factored in, according to Quensen. The most rapid dechlorination rate observed corresponds to a half-life of 17 weeks. This occurred in the absence of sulfate and at room temperature. For the slowest rate, in the presence of sulfate and at room temperature, the half-life is about three years. Accounting for temperature differences gives an expected rate of degradation at the Palos Verdes Shelf of about six years, he said.

The evidence for the fate of DDE in the Palos Verdes sediments comes from core data collected over the last two decades by the Los Angeles County Sanitation District and the U.S. Geological Survey. These data show that the mass of DDE is decreasing with time and that the breakdown product, DDMU, is also found in the sediments, according to Quensen. Moreover, the constant concentration of trace metals with time suggests that some process, possibly anaerobic dechlorination is selectively removing the DDE. Quensen estimates that the decrease in the mass of DDE in the field suggests a half-life of about a decade.

Other scientists who study the Palos Verdes Shelf say that the DDE field data are far from clear because the picture is different depending on the site. Some locations show an apparent decrease in DDE, but concentrations appear to be constant at other locations. Also, U.S. Geological Survey efforts to integrate the mass of DDE over the entire site show no apparent changes from one year to the next.

The debate about the implications of the Michigan State laboratory result is similar to the controversy that has accompanied other attempts to use microbial processes to remediate persistent organic pollutants. Although there have been numerous laboratory investigations to identify beneficial microbial processes, demonstrations of their effectiveness in the field have been few, especially for the difficult problem of contaminated sediments in freshwater and marine environments.

Bacterial complexities

There are currently widely divergent views about the future promise of natural dechlorination as a remediation technique.

The problem, according to Eugene Madsen, a Cornell University microbiologist, is that the process is not always reliable, in part because the dechlorinating microbes lead such complex lives, participating in chemical scenarios too improbable even for science fiction novels.

A number of different groups of bacteria that use hydrogen and acetate as food live in the oxygen-free depths of sediments. These anaerobes appear to breathe substances such as sulfate, iron (III), carbon dioxide, or chlorinated organic compounds. In the process, they reduce these electron receptors, converting them to sulfide, iron (II), methane--or in the case of chlorinated organics--to less toxic compounds. These unusual bacteria are at the end of a strange food chain in which other organisms break down and ferment organic matter to generate the hydrogen and acetate.

In this competitive environment, the "dechlorinators" are often less successful than other bacteria, so that their use in remediating contaminants must be evaluated carefully. To make reductive dechlorination work as a cleanup method, researchers either have to limit their choices to sites with the right conditions to give the dechlorinators a natural advantage or they have to figure out how to give the dechlorinators an artificial advantage. Approaches include finding a way to make them more competitive than other organisms or adjusting field conditions in their favor. Environmental conditions and bacterial types vary at every site, however, and obtaining desired results is difficult.

For some chlorinated solvents, the requirements for remediation are becoming clear, according to Madsen. For perchloroethylene and trichloroethylene, which are the most common groundwater contaminants at many hazardous waste sites, there are now good natural attenuation prerequisites. "In certain well-understood geochemical settings where there are no direct threats to humans or ecological resources, natural attenuation can be a good solution," he said.

PCB cleanup questions

But for PCBs, the move from the laboratory to the field has been very slow, as can be seen from the history of attempts to translate research results into cleanup methods for PCB-contaminated sediments in the Hudson River. Ten years ago, researchers at Michigan State University, under contract with GE, identified a reductive dechlorination mechanism for polychlorinated biphenyls. Subsequent research has shown that this dechlorination has little effect on the total mass of PCBs but causes a significant reduction of their overall toxicity. This is because the process selectively affects the most highly chlorinated PCBs, which are also the most toxic (2).

Aerobic degradation of the less chlorinated PCBs has also been demonstrated, and laboratory results have shown that anaerobic degradation followed by aerobic degradation often will eliminate PCBs completely (3). But in the upper Hudson River, the site where these processes have been most extensively studied, the magnitude of biodegradation is hotly disputed.

EPA's decision against a sediment cleanup in 1984, when the river site was first listed under Superfund because of PCB contamination, is now being reconsidered. The study, which has been ongoing for seven years, is scheduled for completion in December 2000. Also, a Natural Resources Damage Assessment is in the offing that seeks compensation for damages to the ecosystem as a whole and to assets such as beaches and fisheries. The Hudson River Superfund site covers about 200 river miles, extending from the upstate town of Hudson Falls to New York City. The sediment contamination is the legacy of four decades of PCB discharges from two GE factories in Hudson Falls and Fort Edward, N.Y. The discharges were banned by New York State in 1976, the same year it banned all fishing in the upper Hudson, closed commercial fisheries, and issued health advisories on fish consumption.

In 1991, GE conducted field experiments in the Hudson River of the aerobic biodegradation of PCBs by naturally occurring microorganisms (4). The results were both a success and a failure. Despite evidence suggesting that nearly all of the material should be biodegradable, only 60% of the PCBs in the Hudson River sediments were degraded. The problem is bioavailability: The aerobic bacteria cannot degrade the more lightly chlorinated PCBs because they are sorbed by organic particles in the sediment.

To improve the effectiveness of the aerobic bacteria that degrade PCBs, researchers at the Center for Microbial Ecology are turning to genetic engineering. Naturally occurring aerobic PCB degraders only partially degrade PCBs and cannot be used as growth substrates. The researchers are trying to create aerobic strains that can grow directly on PCBs and degrade them. Such strains should be more competitive than naturally occurring PCB degraders. Within three or four years, these combined techniques could be used at a demonstration site, according to Tiedje.

But according to EPA's Hudson River project manager, Doug Tomchuk, the combined technique will not be used as a remedy on the Hudson River, nor will natural dechlorination be enough. "Both anaerobic dechlorination and aerobic breakdown do occur in the sediments," he acknowledged. "But, is it a remedy? No." A detailed study of dated sediment cores demonstrates that the processes are neither adequate nor reliable to constitute a remedy, he said.

On the basis of detailed analysis of dated sediment cores, the agency concluded in a February 1997 report (*5*) that sediment inventories will not be naturally remediated via dechlorination. Another study released in July substantiates this conclusion (*6*). Core data show that the extent of dechlorination is limited to less than a 10% mass loss, according to the agency's analysis. Also, there was no correlation between dechlorination and the age of the sediment. Instead, the most contaminated sediments had the highest degree of dechlorination. At PCB concentrations of less than 30 ppm, no predictable degree of dechlorination occurs. The study concluded that dechlorination occurs relatively rapidly in the first 5 to 10 years of deposition, but then effectively ceases.

The jury is still out on the significance of reductive dechlorination for cleaning up the Hudson River. All sides acknowledge that anaerobic dechlorination is not, on its own, a remedy. An engineered solution combining anaerobic and aerobic breakdown now appears to have been dismissed by GE and EPA. According to GE engineering project manager John Haggard, the company accepts the sediment-coring observations that natural dechlorination is slow and occurs only to a limited extent. Although GE believes that dechlorination is one of the natural processes that have already reduced the health and environmental risks from the contamination, EPA contends that its benefits are minor.

For the DDT contamination of the Palos Verdes Shelf, a similar debate appears to be taking shape. Michigan State University scientists are planning additional experiments using sediments from different sites and different geochemical conditions. Whether reductive dechlorination proves to be a natural process that is making a significant impact on the DDT contamination remains to be seen.

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