ebate continues over Dow's dioxin theory

sults of several recent dies don't jibe with Dow's ntention that dioxins enter vironment from combustion; l, agreement is emerging

1979
Washington, D.C.

king potshots at Dow Chemical's ory that polychlorinated di- nzo-*p*-dioxins are formed by all ts of combustion processes and are, refore, ubiquitous in the environ- nt has become a popular sport ong some analytical chemists, pecially when there are reporters esent The most recent opportunity this activity, the symposium and ess conference on the chemistry of benzodioxins and dibenzofurans, onsored jointly by the divisions of sticide Chemistry and of Chemical alth & Safety (Probationary), had share of shooters But the sessions o seemed to show, perhaps for the st time, an emerging common und shared by scientists on all es of the issue

The issue is Dow's theory, first posed last November, that poly- lorinated dibenzo-*p*-dioxins, di- nzofurans, and biphenyls are med in trace amounts in all forms combustion. Therefore, they are t only ubiquitous in the environ- ent, but have been there since the vent of fire It is only their detec- n that is recent, due to advances in alytical techniques (C&EN, Feb. , page 23)

The theory has gained so much at- ntion because one of the polychlo- nated dibenzo-*p*-dioxins, the 3,7,8 tetrachloro species (2,3,7,8- CDD), is an extremely toxic com- ound that also is a carcinogen and a ratogen in laboratory animals This mpound is a trace contaminant in e herbicide 2,4,5-trichlorophenox cetic acid (2,4,5-T) produced by ow and others.

The herbicide is currently under an emergency suspension for many uses from the Environmental Protection Agency because of an alleged association between its use and increased miscarriages in a group of women living near forests that had been sprayed with the herbicide in Alsea, Ore Detectable levels of 2,3,7,8-TCDD also have been found in fish taken from the Tittabawassee River, which flows by Dow's production plant for the herbicide in Midland, Mich. Presence of the compound in fish led Michigan's Department of Natural Resources to suspect the company of illegally contaminating the river with this compound.

So Dow's theory that combustion is a major source of polychlorinated dioxins in the environment is more than interesting chemistry If true, it goes a long way toward absolving the company's product and its manufacturing process from responsibility for contamination of the environment by these very toxic compounds.

Among the potshots the theory received at the symposium, two are most prominant: Brenda J Kimble of the Department of Energy's Radiobiology Laboratory at the University of California, Davis, and Michael L. Gross, director of the Midwest Center for Mass Spectrometry at the University of Nebraska, Lincoln, have analyzed the smokestack emissions of a coal-fired power plant in California They find no TCDD's in the emissions, down to their detection level of 0.6 ppt of fly ash The Dow study looked specifically at the smokestack emissions of a power plant and concluded that this was a source of dioxins.

Also, David L. Stalling of the U S Fish & Wildlife Service and associates analyzed 16 samples of fish and other aquatic animals for polychlorinated dibenzofurans and dibenzodioxins They found dibenzo-*p*-dioxins in only two samples, both from the Tittabawassee River Further, 2,3,7,8-TCDD was the most common isomer in these samples, an isomer distribution that would not be expected if the source of the isomer were ordinary combustion The most likely explanation, Stalling says, is that the Dow plant is the source of the isomer found in the fish

C&EN staff photo



Crummett: complex and expensive

Even these reports may be at least partially compatible with Dow's findings. For example, Warren B Crummett, a research scientist with Dow's analytical laboratories, explained that the power plant where Dow found dioxins in the stack emissions was on Dow's Midland facility During the sampling period it was burning primarily fuel oil, with a small amount of coal. Various scientists at the press conference suggested that possibly the fuel oil, or even the air in Midland, contains chemical precursors to the dioxins found in the stack emissions that are not found in the California power plant

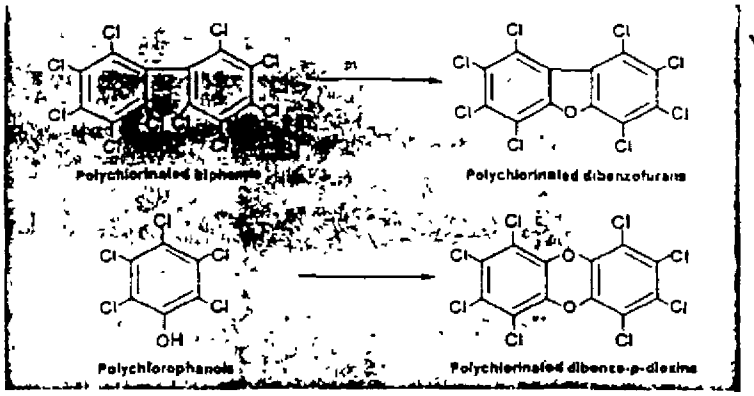
Crummett criticized the California study in two ways He says the samples were taken from too low in the smokestacks and that the particulates that were analyzed were primarily siliceous, whereas Dow had found that the dioxins in such emissions were associated with carbonaceous particulates

"The particulates we sampled were the same as those that come out the top of the smokestack," Kimble says The Dow study made sweeping claims about power plants being sources of environmental dioxins based on extremely limited evidence, she says What she and Gross have shown is that at least one important class of power plants, those that burn western coal, can be free of dioxin contamination

The question of the need to have

MONS 213527

Dioxins, dibenzofurans can form from burning precursors



Note: These polychlorinated compounds contain one or more, but not necessarily all of the chlorine atoms pictured in these structures.

precursors present in the material being burned in order to generate chlorinated dioxins or dibenzofurans in combustion has become a central point of dispute. Something, of course, has to provide the atoms that eventually end up in the dioxins and dibenzofurans. Dow contends, based on its widespread finding of these compounds in combustion products, that just about anything that will burn can serve as a precursor. Others, particularly Christoffer Rappe of the University of Umea, Sweden, and Hans-Rudolf Buser of the Swiss Federal Research Station, Wädenswil, think that synthetic chlorinated compounds must be present before combustion will yield chlorinated dioxins and dibenzofurans.

Here, too, there seems to be some middle ground emerging. Crummett, for instance, seems to acknowledge that some materials produce more dioxins when they are burned than do others. He maintains, however, that precursor compounds are so widespread in the environment that tracking them down via combustion data is a task of such complexity and expense as to be infeasible. He reported two new examples of how widespread 2,3,7,8-TCDD is in the environment. Detectable levels of this compound now have been found in commercial sludge fertilizer made from treated sewage. It also has been detected in the National Bureau of Standards' standard sample of urban particulate matter.

Buser and Rappe now say that the synthetic chemical precursors for both dioxins and dibenzofurans can be found "practically everywhere" in the environment at low levels. They maintain, however, that, except in special circumstances, such as the combustion of chemical wastes or accidental fires involving stores of certain kinds of chemicals, such combustion presents very little health hazard. And, like Dow, they think that the use of 2,4,5-T is a very much less important contributor of dioxins to the environment than is combustion.

Even the dioxins that enter the environment from pesticide use seem to be much less hazardous than laboratory tests would lead one to believe, says Capt. Alvin L. Young of the U.S. Air Force's Occupational & Environmental Health Laboratory, Brooks Air Force Base, Tex. Young and his associates have analyzed the soil and animals at Eglin Air Force Base in Florida where 73,000 kg of 2,4,5-T was sprayed between 1962 and 1970. Much of this material contained much higher levels of 2,3,7,8-TCDD than are now found in the herbicide.

Some 2,3,7,8-TCDD was still present in soil samples taken in 1978. Concentrations ranged from less than 10 ppt to 1500 ppt. (Young's analytical method cannot distinguish 2,3,7,8-TCDD from all other chlorinated dibenzo-*p*-dioxins. The concentration he reports is for the combination of isomers that includes the 2,3,7,8-TCDD isomer.)

The Air Force chemists did not find detectable levels of 2,3,7,8-TCDD in any plants taken from the site. However, they did find it in nine species of animals, including mammals, birds, fish, and reptiles. Levels varied from several hundred parts per trillion in the livers of beach mice and meadowlarks to 12 ppt in the whole bodies of two kinds of fish.

Beach mice, which contained the highest concentrations of the compound, were singled out for further study. Eighteen types of tissue from 300 animals were examined for toxic effects, but none of the tissues were significantly different from those of control group animals.

Just how important the trace quantities of dioxins that are being found in the environment are likely to be is a point that was raised frequently during the symposium. Rappe, Buser, and Stalling all seemed to agree that the polychlorinated dibenzofurans, though less toxic in an absolute sense than the most toxic dioxins, are of more concern because they are present in higher concentrations. They can be formed by combustion of polychlorinated biphenyls (PCB's), which earlier work has shown are very widespread in the environment.

Stalling, along with Donald W. Kuehl of EPA's Duluth, Minn., research laboratory, Ralph C. Dougherty of Florida State University, and Rappe, finds polychlorinated dibenzofurans and naphthalenes in aquatic animals living in waters that contain PCB's and their breakdown products. The results are somewhat preliminary, since only 16 samples have been analyzed and, so far, no samples have been checked from pristine waters. However, animals taken from the Ohio River and Lake Michigan, where contamination comes from used PCB's, show higher levels and more complex mixtures of these compounds than do fish taken from the Hudson River, which is contaminated by newly manufactured PCB's but contains low levels of PCB combustion products.

Rappe and Buser have been studying the combustion products of chlorophenols, PCB's, and chlorinated diphenyl ethers and benzenes. All of these compounds can be converted to polychlorinated dibenzodioxins and dibenzofurans in high yield, they find. However, 2,3,7,8-TCDD, the most toxic of the dibenzodioxins, is a minor product of combustion under the conditions found in municipal incinerators. 2,3,7,8-tetrachlorodibenzofuran, the most toxic of this class of compounds, is the major isomer formed under these conditions. PCB's can yield chlorinated dibenzofurans as high as 25%, they find.

Nevertheless, except for a few special cases, they do not see even the dibenzofurans as health hazard. They do recommend that polychlorinated phenolic chemical wastes be very carefully incinerated in ovens that allow for high temperature incineration and long residence times to make sure that toxic products are destroyed. And halogenated phenol biphenyls, and diphenyl ethers should not be used as flame retardants because of the high toxicity of their combustion products.

MONS 213528

From the desk of
R. E. KELLER

11-21-78

B&B Kaley

This was sent to Ken Baker, CLN Today. These copies are for your file.

REK

MONS 213529

DETERMINATION OF CHLORINATED DIBENZOFURANS (DBFs) IN PCBs

We do not have a method specifically for the subject analysis. However, the use of an alumina column separation followed by gas chromatography/mass spectrometry in the selected ion monitoring (SIM) mode should work. We would suggest the following approach.

(1) Insert a glass wool plug in the bottom of a 15 cm X 15 mm (od) glass column with a stopcock and solvent reservoir. Dry pack the column with 10 g basic alumina (activity grade Super 1). Tap to settle.

(2) Introduce 200 µl of 50% PCBs in pesticide grade hexane onto the head of the column.

(3) Move PCBs onto column with a few milliliters of hexane, then add ≈150 ml of 2% (V:V) pesticide grade methylene chloride in hexane to reservoir and elute. Discard eluent. This fraction should contain the PCBs.

(4) Elute DBFs with 40 ml 50% (V:V) methylene chloride in hexane. Collect eluent and concentrate in Kuderna-Danish apparatus for analysis.

(5) Analyze concentrates for DBFs by SIM GC/MS by monitoring for the parent ion (M) and M-63 ion for call chlorinated DBF of interest and using external standards. The detection limit for this procedure should be about 1 ppm for each DBF homolog.

(6) Validate procedure analyzing PCBs spiked with known amounts of DBFs.

If you have questions, please contact me.

R. G. Kaley
MIC, St. Louis
11/21/78

MONS 213530