Dioxin: Paper's Trace

Chlorine bleaching of wood pulp appears to leave a toxic legacy in much of the paper we encounter



By JANET RALOFF

Coffee filters, disposable diapers, paper towels, milk cartons, newspaper and facial tissues. Researchers sampling bleached-paper products have recently found these contain minute quantities of dioxins or furans (dioxins' nearly-astoxic chemical cousins). Together the chemicals make up a class of chlorinated compounds the EPA considers "one of the potentially most dangerous" to pollute the environment.

Over the past 12 months, this paperdioxin link has triggered not only a major federal inquiry into paper's dioxin risks to health, but also a host of new scientific studies and even congressional hearings. The second in a series of hearings is slated for this summer. Just this week the issue prompted petitions to the Department of Agriculture by Greenpeace USA, a Washington, D.C.-based environmental group. One asks the agency to require that the billions of cartons of milk it subsidizes each year in school and childhealth programs be furnished in dioxinfree recyclable containers. The second requests an assessment of the environmental impact posed by disposing of dioxin-tainted milk cartons.

In response to growing concern over the paper-dioxin connection, the New York City-based American Paper Institute, representing the paper-making industry, announced in November that its members would voluntarily institute changes at wood-pulp mills — such as limiting the chlorine used in bleaching — to reduce the formation of dioxins and furans. Still, environmentalists express doubts these industrial-production changes are occurring as quickly and achieving as much as they could, given what's known about the toxicity of dioxins and furans.

Technically, a dioxin is any of 75 structurally related chlorinated compounds

(see box, p.106). However, people commonly use the term "dioxin" to refer to the most toxic member of that family -2.3.7.8-tetrachlorodibenzo-p-dioxin (TCDD). Moreover, because dioxins so often keep dangerous company, scientists seldom consider them in isolation. Processes yielding dioxins often create comparable levels of furans with the same number of chlorine atoms. That's why 2.3.7.8-TCDD frequently accompanies the most toxic furan -2.3.7.8-tetrachlorodibenzo furan (TCDF).

Four years ago, a series of chemical analyses uncovered evidence that low levels of dioxins and furans contaminate all members of Western industrialized societies (SN: 7/13/85, p.26). The finding spurred an immediate search for the sources most responsible.

Incinerators of municipal and hazardous wastes are among the best-known sources (SN: 7/8/78, p.21). EPA's David Cleverly told Science News, "We've estimated that the air emissions [of dioxins and furans from U.S. municipal-waste incinerators] contribute from two to 40 cancer cases per year." Dioxins also form as unwanted byproducts during the manufacture of many chlorinated chemicalssuch as the phenoxy herbicides (including Agent Orange) used widely through the 1960s and '70s. Ironically, contends Ellen K. Silbergeld, director of the Environmental Defense Fund's toxic chemicals program in Washington, D.C., if there's any surprise about dioxin, it's that the chemical's formation during papermaking went unrecognized for so long. "We've known for decades," she says, "that dioxins can form in processes involving chlorine, wood lignin and heat."

Paper-making's role

Yet that link was not established until about 18 months ago, when EPA and the

paper industry released initial findings of a dioxin-screening study they conducted jointly at five mills employing the "kraft" pulping process and chlorine bleaching. TCDD appeared in pulps at four of five mills, and in wastewaters or sludges from each. TCDF contaminated pulps and wastewaters at all mills, and the sludges from four.

Sampling at these and several other mills showed TCDD and TCDF accounted for 93 to 99 percent of the dioxin/furan toxicity in bleached pulps and wastes, according to Gary A. Amendola, one of the study's researchers at EPA's Westlake, Ohio, laboratory. It was unnecessary to screen papers made from the dioxintainted mill pulp, he says, "because whatever is in the pulp will end up in the products [made from it]."

Others, however, have gone that extra step, confirming the presence of dioxins in paper. Among the first to formally publish data were West German scientists working at the Max von Pettenkofer Institut in Berlin. Their paper in the January 1988 Chemosphere reported dioxins and furans contaminated a range of commercial paper products—from newsprint and coffee filters to facial tissue.

The National Council of the Paper Industry for Air and Stream Improvement (NCASI), a research arm of the American Paper Institute, found TCDD in paper towels, paper plates, bond paper, coffee filters, the coated packaging used for frozen foods and the uncoated packaging used for such things as cereal boxes. Furans showed up in all papers tested. While the tests identified no TCDD in disposable baby diapers, "we did find 2,3,7,8-TCDF," notes American Paper Institute Vice President Carol L. Raulston of Washington, D.C. This furan's toxicity is about one-tenth that of 2,3,7,8-TCDD.

Thomas Tiernan, an analytical chemist

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at Wright State University in Dayton, Ohio, also detected 2,3,7,8-TCDF—and no TCDD—in disposable diapers, sanitary napkins and coffee filters he tested for the Canadian Broadcasting Corp. His analyses of paper towels, paper plates and facial tissue identified both TCDF and TCDD. Finally, Triangle Laboratories Inc. in Research Triangle Park, N.C.—working under contract to WJLA, a television station in Washington, D.C.—found TCDFs in milk, whipping cream, a diaper, and the meat from a microwave dinner.

A question of safety

Where dioxins or furans have been detected, the contamination has been in trace quantities only — the parts-pertrillion (ppt) range. Just for perspective, notes American Paper Institute President

Red Cavaney, 1 ppt is equal to 1 second in 32,000 years. Indeed, Cavaney told the House Subcommittee on Health and the Environment on Dec. 8, "the bottom line confirms that these paper products are safe."

On this, however, there is considerable controversy.

"With regard to a carcinogen, we would not use the word 'safe,'" says Charles Elkins, director of EPA's Office of Toxic Substances. "We believe that there is a possible risk all the way down to zero [exposure]."

EPA does attempt to assess whether certain environmental agents pose "an unreasonable risk to health." And where exposures are preventable, it will usually consider regulating exposure to hazards that pose a one-in-a-million lifetime risk

of cancer. In testimony before the House subcommittee last December, Elkins noted that at least one preliminary analysis already indicates that the cancer risk from dioxin in paper may fall within that crucial one-in-a-million range.

By contrast, Richard J. Ronk, acting director of the FDA's Centers for Food Safety and Applied Nutrition, testified that "we do not believe that the very low levels of dioxins and furans that have been reported in paper products represent a significant health risk." However, he added, "simple prudence dictates that if a single source can be readily reduced, it should be." He says it's "very likely" changes to reduce dioxin from consumer products — especially milk cartons — will be required.

Still others, like Silbergeld, consider

How much dioxin did you consume today?

No one knows what share of the dioxin in foods, the environment and human bodies comes from any particular source — incinerators, industrial chemicals or paper. How-

ever, many environmentalists now suspect that dioxins formed by pulp bleaching will prove an important contributor.

While inhaling incinerator emissions offers one route by which dioxins may enter the body, researchers generally consider tainted foods the more important source of exposure for the general population.

Fish constitute the most publicized food source contaminated by dioxins. Since finding dioxins and furans in Great Lakes fish in 1980, the FDA has routinely sampled edible species—now about 250 fish annually, at a cost of about \$1,000 per assay. While fish from several of the Great Lakes continue to show contamination, "in general, levels appear to be below [25 ppt] and going down," notes David Firestone, FDA's analytical chemist overseeing these assays.

What makes fish a potentially serious hazard is their ability to accumulate remarkably high quantities of the chlorinated chemicals in their fat. Though rates vary, an EPA draft report issued last March cited a 1987 study showing one species – the fathead minnow accumulated dioxin levels 159,000 times greater than those present in water or sediment. This bioaccumulation potential has made fish classic sentinels of many industrial pollutants. Indeed, federal scientists first suspected the dioxin/paper link after discovering unexpectedly high levels of the chemicals in walleye pike, bass, catfish, carp and other fish downstream of pulp and

paper mills.

Less well known is dioxin's ability to contaminate crops. But in the February 1988 CHEMOSPHERE, Katherine Davies of the Toronto Department of Public Health reported trace contamination of a number of foods in her study of locally grown produce from area stores. She found a range of dioxin and furan species, although no TCDD, in a sample of the edible portions from a mix of fresh fruits - largely apples and plums. By contrast, a sample combining popular leafy vegetables contained barely detectable levels of TCDD only. Various 4and 8-chlorine dioxins and furans turned up in a combined sample of meat and eggs, in milk and in a sample of root vegetables, including potatoes.

EPA's March 1988 draft report, "Estimating Exposure to 2,3,7,8-TCDD," cites a wealth of recent research indicating how such contamination can occur. Five studies, for example, show that when grown in contaminated soils, root crops—such as carrots, potatoes and onions—can develop TCDD levels that equal or exceed those in the soil.

Though dioxins emitted by incinerators are the most likely source of crop exposure, land spreading of papermill sludge to improve crop soils can provide more severe contamination. Toxicologist John Olson at Wisconsin's Department of Health and Social Services in Madison is developing a formula to estimate possible human exposures from landspreading this sludge - a practice begun around 1980 in Maine. For 150-ppt contamination of papermill sludge, a level measured in Wisconsin, his preliminary estimates for the worstcase scenario - a subsistance farmer living off crops, dairy products and grass-fed cattle - yield average daily doses of more than 50 picograms of

TCDD per kilogram (pg/kg) of body weight, well above the U.S. average of 1 pg/kg daily.

Data accumulating over the past year also suggest tainted papers may leach measurable levels of these toxic chemicals into foods or beverages. Says Robert J. Scheuplein, acting director of toxicological sciences at the FDA, "I think we've identified the two major sources here" - milk cartons and coffee filters. His very rough estimates suggest young children getting all their milk from contaminated cartons might double their daily dioxin intake, to a level of 2 pg/kg. Heavy coffee drinkers consuming most of their brew from pots with bleached-paper filters might increase their daily dioxin intake 5 or 10 percent above the average U.S. level, Scheuplein speculates.

Another indication of the papermigration hazard comes from a single pair of data points collected by WJLA, a Washington, D.C. television station. According to Roberta Baskin, the station's consumer affairs reporter, WJLA's data show that the meat from a microwave dinner increased its furan levels 1.7 ppt during cooking. Presumably, the almost 32 percent increase was due to migration of furans from the paper tray on which the meat cooked, although the investigators never tested the tray to show it had contained any of the furan detected in the meat. Nonetheless, researchers with the federal government's dioxin-assessment program already cite WJLA's data scanty as they are - as an impetus for having the paper industry investigate further

try investigate further the likelihood of dioxin/ furan migration during microwave cooking.

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dioxin a clearly demonstrated human health risk—at levels to which the general population is already exposed. Ten weeks ago, EPA's science advisory board recommended the agency continue to view a daily dioxin dose of 0.006 picogram per kilogram (pg/kg) of body weight as posing a one-in-a-million lifetime increased risk of developing cancer, says Silbergeld, an advisory board member. According to the FDA, the average American already receives a daily dose of 1 pg/kg daily—166 times that level.

A dearth of data

A lack of solid data feeds this controversy. For example:

- To date, dioxin-production data collected at five mills are being extrapolated to the 104 U.S. kraft-pulp mills that now use chlorine bleaching. Because the processes and pulp stock vary considerably among the mills, their dioxin/furan production probably does also.
- None of the analyses of bleachedpaper products tested for dioxins and furans involved enough samples to be statistically significant. For example, NCASI's tests consisted of a single, composite sample for each type of product tested. Its data on disposable diapers come from a single sample containing a mix of papers from five different off-theshelf brands. The Triangle Laboratories data are even more limited. Only one item provided the data for each type of product – such as diapers – tested.

The main reason for federal regulators' rapt attention to such weak data, two U.S. officials told Science News, is that these few, very limited tests represent virtually the entire universe of "hard, measured data" now available to their agencies.

- · Data on the ability of dioxins and furans to migrate out of paper and into food or the human body are even sparser - if perhaps statistically a little stronger. "We know [from NCASI tests] that somewhere between 40 and 70 percent of the dioxin in coffee filters can be extracted," notes EPA's Dwaine Winters, who's heading up the U.S. government's dioxin/furan risk assessment for paper. A recent Canadian study - involving about 20 samples of milk and five of cartons - reported an apparent migration of dioxin from cardboard into milk (SN: 10/29/88, p.279). For dioxin migration, Winters says, these data about sum up available measurements.
- Though some scientists have calculated theoretical migration rates, "theory isn't the best guide," Winters says, pointing to theoretical analyses that initially suggested a plastic barrier coating the inside of milk cartons would prevent the contamination of milk. Based on the Canadian data, Winters says, "it now looks like the process of laying the coating onto paper may actually help extract dioxin and transfer it to the coating," and thus to the milk.

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Anatomy of a dioxin and a furan

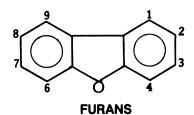
Dioxins and furans belong to a family of 210 related chemicals. The numerical prefixes that identify the different species within this family refer to the positions where their chlorine atoms sit within the molecule. In 2,3,7,8-varieties, chlorines bond at the outermost left and right positions -2,3,7 and 8.

A June 1988 EPA draft document describes 2,3,7,8-TCDD as both "the most potent animal carcinogen ever tested" and "the most potent animal teratogen

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known." EPA considers TCDD not only a "probable human carcinogen" but also a poison capable of inducing reproductive and immune-system effects "at low doses." And 2,3,7,8-TCDD is far from the only dangerous member of its family. One recent study, for example, indicates that while the fully chlorinated dioxin (OCDD) is only 1/1,000 as toxic as TCDD, it's roughly 1,000 times more prevalent in the environment (SN: 4/23/88, p.269).

– J. Raloff



• While animal data prove 2,3,7,8,-TCDD one of the single most toxic chemicals in existence, data on its risks to humans remain less convincing. According to an August 1986 report by EPA's Dioxin Update Committee, human epidemiological studies point "either to a very high risk or very low risk or no risk" — with no study especially compelling.

Filling in the data gaps

Early last year, the U.S. government signed a consent decree with the Environmental Defense Fund and National Wildlife Federation, settling a six-yearold lawsuit on an unrelated dioxin issue. As part of the settlement, EPA agreed to coordinate an interagency federal effort to assess the human-health risks of dioxin in paper. Unless EPA finds that paper's dioxin contamination "presents no unreasonable risks to the public," the agency must announce by April 1990 that it intends to propose regulations limiting dioxin in paper, or that it plans to refer the problem to a more appropriate regulatory agency, such as FDA.

To make this assessment, EPA and its collaborating partners — the FDA and the Consumer Product Safety Commission — need more and better data. With the exception of some milk testing that FDA chemists will start soon, the paper industry will provide the rest of those data.

The first data delivery, due in April, will include dioxin/furan levels for pulp, wastewaters and sludge from all 104 U.S. mills producing chlorine-bleached wood pulp. Over the next 16 months, EPA will also investigate technologies that could reduce dioxin in pulp bleaching. FDA and the Consumer Product Safety Commission are now preparing their wish lists for studies to supply the data they will need to analyze the potential for human ex-

posure from pulp and pulp products.

Making these risk assessments under the consent order's time constraints "will take a heroic effort," Winters says, "but we think we will be able to do it."

Not just dioxins

Chlorine bleaching's toxic legacy encompasses more than dioxins and furans. One review of chlorinated chemicals produced in pulp bleaching last year described some 250 different compounds. Because many of these pollutants have no commercial value and pose apparently little direct threat to workers, few if any have undergone toxicological studies, say University of Toronto scientists who conducted this survey. In Sweden, where several toxicological studies have begun, more than 15 compounds show cancer- or birth-defect-causing properties.

Moreover, the number of potentially toxic chemicals formed by pulp bleaching complicates assessments of whether any need exists to limit them, note Donald Mackay and his University of Toronto colleagues in the July 1988 Chemosphere. They say that while each of the chemicals may appear harmless when considered in isolation, if their effects are additive—or worse, synergistic—this chemical soup could prove many times more toxic than studies of individual ingredients would hint.

This suggests, Silbergeld says, that focusing on dioxins and furans should not obscure the more general problem—the generation of a whole host of potentially toxic compounds through chlorine bleaching of pulp. If process changes or regulations focus only on dioxins and furans, Silbergeld says, "we may not adequately limit the overall environmental and public health impacts of the pulpmaking and bleaching process."