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# DIOXINS

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having histories of silvex and/or 2,4-D applications. The EPA will analyze the samples for dioxins or herbicide residues. Results are not yet available (Hanna and Goldberg, n.d.).

### Transport in Water

Contamination of streams and lakes by 2,3,7,8-TCDD has also been of concern, especially because of the spraying of 2,4,5-T on forests to control underbrush. Possible routes of water contamination from spraying are direct application, drift of the spray, and overland transport after heavy rains. The latter, however, seldom occurs on forest lands because the infiltration capacity of forest floors is usually much greater than precipitation rates (Miller, Norris, and Hawkes 1973).

The transport of dioxin-contaminated soil into lakes or streams by erosion constitutes another possible route of contamination. This is evidenced by the detection of 2,3,7,8-TCDD in water samples from a Florida pond adjacent to a highly contaminated land area (Bartleson, Harrison, and Morgan 1975). Additionally, several laboratory studies have shown that lakes or rivers could become contaminated with minute quantities (ppt) of 2,3,7,8-TCDD and possibly other dioxins through leaching from contaminated sediments. In a study reported by Isensee and Jones (1975), 2,3,7,8-TCDD was adsorbed to soils, which were then placed in aquariums filled with water and various aquatic organisms. Concentrations of the dioxin in the water ranged from 0.05 to 1330 ppt. These values corresponded to initial concentrations of 2,3,7,8-TCDD in the soil ranging from 0.001 to 7.45 ppm. The investigators concluded that dioxin adsorbed to soil as a result of normal application of 2,4,5-T would lead to significant concentrations of 2,3,7,8-TCDD in water only if the dioxin-laden soil was washed into a small pond or other small body of water.

Other investigations have shown similar results. Using radiolabeled 2,3,7,8-TCDD, Matsumura and Ward (1976) showed that, after separation from lake-bottom sediment, water contained 0.3 to 9 percent of the original dioxin concentration added to the sediment. Results of another test indicated that a total of about 0.3 percent of the applied dioxin concentration passed through sand with water eluate (Matsumura and Benezet 1973). In some cases, the observed concentration of TCDD's in the water was greater than its water solubility (0.2 ppb). The 1976 report suggests that some of the radioactivity apparent in the aqueous phase was probably due to a combination of lack of dioxin degradation, presence of 2,3,7,8-TCDD metabolites, and binding or adsorption of TCDD's onto organic matter or sediment particles suspended in the water.

In another study, application of <sup>14</sup>C-TCDD to a silt loam soil at concentrations of 0.1 ppm led to <sup>14</sup>C-TCDD concentrations in the water ranging from 2.4 to 4.2 ppt over a period of 32 days (Yockim, Isensee, and Jones 1978).

The findings of such investigations are consistent with recent reports that TCDD's are migrating to nearby water bodies from industrial chlorophenol wastes buried or stored in various landfills. At Niagara Falls, New York, for example, 1.5 ppb TCDD's have been detected at an onsite lagoon at the Hyde Park dump where 3300 tons of 2,4,5-TCP wastes are buried (Chemical Week 1979a; Wright State University 1979a,b). Sediment from a creek adjacent to the Hyde Park fill (also in the Niagara Falls area) is also contaminated with ppb levels of the dioxin (Chemical Week 1979a, 1979d). In Jacksonville, Arkansas, there is growing evidence that TCDD's may have migrated from process waste containers in the landfill of a former 2,4,5-T production site. The dioxins have been found both in a large pool of surface water on the site (at 500 ppb) and downstream of the facility in the local sewage treatment plant, in bayou-bottom sediments, and in the flesh of

Wainman et al. 1980). TCDD's apparently are also being released into groundwaters from an 880-acre dump site of the Hooker Chemical Company at Montague, Michigan (Chemical Week 1979c; Chemical Regulation Reporter 1979b). Dioxins were found at the site at levels approaching 800 ppt.

### Transport in Air

One study has been identified in which levels of 2,3,7,8-TCDD in air have been measured (Nash and Beall 1978). Femtogram ( $10^{-15}$  g) quantities of the dioxin were detected in the air after granular and emulsifiable silvex formulations containing radiolabeled 2,3,7,8-TCDD had been applied to microagroecosystems. Air concentrations of the dioxin decreased appreciably with time following application. The data appear to confirm that TCDD has a very low vapor pressure and that loss due to volatilization is extremely low, especially when low levels of 2,3,7,8-TCDD are involved and granular formulations containing the dioxin are used.

Results of other investigations indicate that water-mediated evaporation of TCDD's may take place (Matsumura and Ward 1976).

Transport of dioxins by way of airborne particulates has recently received much attention. Several studies have shown the presence of dioxins in fly ash from municipal incinerators (Nilsson et al. 1974; Olie, Vermuelen, and Hutzinger 1977; Buser and Rappe 1978; Dow Chemical Company 1978; Tiernan and Taylor 1980). A recent report of Dow Chemical Company (1978) contends that particulates from various combustion sources may contain dioxins and that these dioxin-laden particulates are a significant source of dioxins in the environment. More details on these studies are presented in Section 3.

It has also been recently reported that dioxins from buried chlorophenol wastes are being mobilized by means of airborne dust particles (Chemical Regulation Reporter 1980a).

## BIOLOGICAL TRANSPORT

This section discusses the potential for dioxins to accumulate and to become concentrated and magnified in biological tissues. In the past, pesticides (most notably DDT) have been found to accumulate in organisms at almost every trophic level. In some organisms, these chemicals have been concentrated in the tissues. When an animal in a higher trophic level feeds on organisms that accumulate these chemicals, the animal receives several "doses" of the chemical, resulting in what is termed biomagnification. If this process proceeds to higher levels in the food chain, the chemicals may become concentrated hundreds or thousands of times, with possibly disastrous consequences.

The ability for a chemical to accumulate and to become concentrated or participate in biomagnification depends primarily on its availability to organisms, its affinity for biological tissues, and its resistance to breakdown and degradation in the organism.

### Bioaccumulation, Bioconcentration, and Biomagnification in Animals

The biological activity of dioxins with respect to accumulation, concentration, and magnification has been addressed by several researchers. Briefly, bioaccumulation is the uptake and retention of a pollutant by an organism. The pollutant is said to be bioconcentrated when it has accumulated in biological segments of the environment. The increase of pollutant concentrations in the tissues of organisms at successively higher trophic levels is biomagnification.

Several investigators (Fanelli et al. 1979, 1980; Frigerio 1978) have studied the levels of TCDD's in animals captured in the dioxin-contaminated area near Seveso, Italy. Data shown in Table 53 indicate that TCDD's accumulate in environmentally exposed wildlife. All field mice were found to contain TCDD's at whole-body concentrations ranging from 0.07 to 49 ppb (mean value 4.5 ppb). The mice were collected from an area where the soil contamination (upper 7 cm) varied from 0.01 to 12 ppb (mean value 3.5 ppb). These data are in agreement with Air Force studies by Young et al. (described below), which indicate that rodents living on dioxin-contaminated land concentrate TCDD's in their bodies only to the same order of magnitude as the soil itself; biomagnification does not occur. Several rabbits and one snake have been found to concentrate TCDD's in the liver. The snake also had accumulated a very high level of TCDD's in the adipose (fat) tissue. Liver samples from domestic birds were analyzed for TCDD's with negative results.

TABLE 53. TCDD LEVELS IN WILDLIFE<sup>a</sup>

Animal	No. of samples analyzed	Tissue	Positive	TCDD level (ng/g) (ppb)	
				Average	Range
Field mouse	14	Whole body	14/14	4.5	0.07-49
Hare	5	Liver	3/5	7.7	2.70-13
Toad	1	Whole body	1/1	0.2	
Snake	1	Liver	1/1	2.7	
		Adipose tissue	-	16.0	
Earthworm	2 <sup>b</sup>	Whole body	1/2	12.0	

a—Source: Fanelli et al. 1980.

b—Each sample represents a 5-g pool of earthworms.

Earlier studies by the Air Force evaluated alternative methods for disposal of an excess of 2.3 million gallons of Herbicide Orange left from the defoliation program in Southeast Asia. The studies took place at the test site at Eglin Air Force Base in Florida (Figure 64) and at test areas in Utah and Kansas.

In June and October of 1973, samples of liver and fat tissue of rats and mice collected from grids on a 3-mile-square test area (TA C-52A) at Eglin Air Force Base were analyzed for the presence of TCDD's (Young 1974). The samples contained concentrations of TCDD's ranging from 210 to 542 ppt. Tissue of control animals contained less than 20 ppt TCDD's. Because most of the concentrations of TCDD's in the group of animals tested were higher than those found in the soil, it was suggested that biomagnification might have occurred; however, because the animals studied failed to show teratogenic or pathologic abnormalities, the presence of a substance similar to TCDD's but with a lower biologic activity was postulated.

Another Air Force report gives results of additional studies conducted at Eglin Air Force TA C-52A (Young, Thalken, and Ward 1975). In an effort to test the possible correlation between levels of TCDD's in the livers of beach mice and in soil, experiments were conducted to determine the possible exposure routes. Because contamination by TCDD's could be detected only in the top 6 in. of soil, it

was thought that a food source might be responsible for the presence of the dioxin in animal tissue. Analysis of seeds (a food source for beach mice) collected in the area revealed no TCDD's (at 1 ppt detection level); therefore, another route of contamination was suggested. Since the beach mouse spends as much as 50 percent of its time grooming, investigators postulated that the soil adhering to the fur of the mice as they move to and from their burrows was being ingested. As a test of this hypothesis, a dozen beach mice were dusted 10 times over a 28-day period with alumina gel containing TCDD's. Analysis of pooled samples of liver tissue from controls indicated concentrations of TCDD's of less than 8 ppt (detection limit), whereas concentrations in samples of tissue from the dusted mice reached 125 ppt.

Further analysis was done on samples of liver tissue from beach mice collected from Grid 1 of TA C-52A. A composite sample of male and female liver tissue contained TCDD's at levels of 520 ppt, and a composite sample of male tissue contained 1300 ppt. In contrast, the liver tissue of mice collected from control field sites contained TCDD's in concentrations ranging from 20 ppt (male and female composite) to 83 ppt (female composite). Air Force researchers concluded that although bioaccumulation was evident, there were no data to support biomagnification because the levels of TCDD's in the liver tissue of beach mice were in general no greater than levels found in the soil on Grid 1 (ranging from <10 to 1500 ppt).

In evaluation of this Air Force study Commoner and Scott (1976) again reached a different conclusion. Because dioxin concentrations in the pooled liver samples represented an average value for the mice, they believed that this value should be compared with average value for TCDD's in the soil of Grid 1, which was 339 ppt. They concluded that biomagnification was evidenced by the significantly higher levels of TCDD's in mouse liver than in soil.

Analysis for TCDD's in the six-lined racerunner, a lizard found in the area, showed concentrations of 360 ppt in a pooled sample of viscera tissue and 370 ppt in a pooled sample of tissue from the trunks of specimens captured in TA C-52A. Specimens captured at a control site showed concentrations of TCDD's less than 50 ppt (detection limit).

Early studies of aquatic specimens obtained from ponds and streams associated with TA C-52A showed no TCDD's at a detection limit of less than 10 ppt (Young 1974). In further studies, however, three fish species showed detectable (ppt) levels of TCDD's (Young, Thalken, and Ward 1975). Pooled samples of skin, gonads, muscle, and gut from a species of bluegill, *Lepomis punctatus*, contained 4, 18, 4, and 85 ppt TCDD's, respectively. All of these specimens were obtained from the Grid 1 pond on TA C-52A, where bluegill was at the top of the food chain. Two other fish species, *Notropis lypselopterus* (sailfin shiner) and *Gambusia affinis* (mosquito fish), also showed 12 ppt of TCDD's. These specimens were collected from Trout Creek, a stream draining Grid 1. (Mosquito fish samples consisted of bodies minus heads, tails, and viscera, whereas shiner samples consisted of gut.) Inspection of gut contents of *Lepomis* specimens from Trout Creek showed that the food source of this fish consisted mostly of terrestrial insects. The source of the TCDD's was not identified, however.

In another Air Force study, tests were done on 22 biological samples from TA C-52A and 6 samples (all fish) from the pond at the hardstand-7 loading area designated as HS-7 (Bartleson, Harrison, and Morgan 1975). A composite of whole bodies of 20 mosquito fish *Gambusia* collected from the HS-7 pond and 600 feet downstream showed a concentration of 150 ppt TCDD's. Liver samples from a small sunfish from the HS-7 pond also showed 150 ppt TCDD's, whereas samples of the livers and fat of 12 medium-sized sunfish from the HS-7 pond showed concentrations of 0.74 ppb. Because the solubility of 2,3,7,8-TCDD in water is far below these levels (0.2 ppb), the data seem to indicate biomagnification in addition to bioaccumulation. The stream that drains the HS-7 pond flows north into a larger pond known as Beaver Pond. Composite samples of four whole large

fish from Beaver Pond showed a concentration of 14 ppt TCDD's. The livers of 25 large fish and fillets of 8 large fish from Beaver Pond showed no TCDD's at a detection limit of 5 ppt. A followup study conducted from 1976 to 1978 showed that TCDD's were present in turtle fat and beach mouse liver and skin (Harrison, Miller, and Crews 1979).

In the same study, samples obtained from deer, meadowlark, dove, opossum, rabbit, grasshopper, six-lined racerunner, sparrow, and miscellaneous insects from TA C-52A were analyzed for TCDD's. TCDD's were detected in the livers and stomach contents of all of the birds. One composite sample of meadowlark livers contained 1020 ppt TCDD's, the highest level found in all samples. No TCDD's were detected in samples from deer, opossum, or grasshopper. The sample from miscellaneous insects contained 40 ppt TCDD's, and the composite sample from racerunners, 430 ppt TCDD. The authors concluded that this study demonstrated bioaccumulation. The data also indicate that biomagnification may have occurred. Commoner and Scott (1976b) point out that the average concentration of TCDD's in soil from TA C-52A was 46 ppt. It should also be noted that the composite insect sample most likely included insects that are eaten by the birds. In all cases the concentration of TCDD's in animal liver samples was greater than that in the insect sample, an indication of the possibility of biomagnification. Because none of the Air Force studies analyzed for TCDD's in a series of trophic levels, biomagnification was not clearly demonstrated.

Woolson and Ensor (1972) analyzed tissues from 19 bald eagles collected in various regions of the country in an effort to determine whether dioxins were present at the top of a food chain. At a detection limit of 50 ppb, no dioxins were found.

Another study failed to show dioxin contamination in tissues of Maine fish and birds (Zitco, Hutzinger, and Choi 1972).

In a similar study 45 herring gull eggs and pooled samples of sea lion blubber and liver were analyzed for dioxins and various other substances (Bowes et al. 1973). Analysis by gas chromatography with electron capture and high-resolution mass spectrophotometry revealed no dioxins.

Fish and crustaceans collected in 1970 from South Vietnam were analyzed for TCDD's in an effort to determine whether the spraying of Herbicide Orange had led to accumulation of TCDD's in the environment (Baughman and Meselson 1973). Samples of carp, catfish, river prawn, croaker, and prawn were collected from interior rivers and along the seacoast of South Vietnam and were immediately frozen in solid CO<sub>2</sub>. Butterfish collected at Cape Cod, Massachusetts, were analyzed as controls. Samples of fish from the Dong Nai River (catfish and carp) showed the highest levels of TCDD's, ranging from 320 to 1020 ppt. Samples of catfish and river prawn from the Saigon River showed levels ranging from 34 to 89 ppt. Samples of croaker and prawn collected along the seacoast showed levels of 14 and 110 ppm of TCDD's, whereas in samples of butterfish from Cape Cod the mean concentration of TCDD's was under 3 ppt (detection limit). The authors concluded that TCDD's had possibly accumulated to significant environmental levels in some food chains in South Vietnam.

Other investigators have studied the accumulation of TCDD's in mountain beavers after normal application of a butyl ester of 2,4-D and 2,4,5-T to brushfields in western Oregon (Newton and Snyder 1978). They reported that the home range of the mountain beavers was small and that among all animals collected inside the treatment areas the home ranges centered at least 300 feet from the edge of the treatment area. Thus their food supplies, consisting primarily of sword fern, vine maple, and salmonberry, had definitely been exposed to the herbicide. Analysis of 11 livers from the beavers showed no TCDD's in 10 of the samples at detection limits of 3 to 17 ppt. One sample was questionable; the concentration was calculated at 3 ppt TCDD's.

Investigators in another study analyzed milk from cows that grazed on pasture

and drank from ponds that had received applications of 2,4,5-T (Getzendaner, Mahle, and Higgins 1977). Sample collection ranged from 5 days to 48 months after application; 14 samples were collected within 1 year after application. Application rates ranged from 1 to 3 pounds per acre. Milk purchased from a supermarket was used as the control. The control samples contained levels of TCDD's ranging from nondetectable to 1 ppt. No milk samples from cows grazing on treated pasture contained levels of TCDD's above 1 ppt.

In a similar study, milk samples were collected throughout the Seveso area just after the ICMESA accident occurred (Fanelli et al. 1980). The samples were analyzed for TCDD's by GC-MS methods. Results are given in Table 54. Figure 66 shows the sites where the milk samples were collected. Dioxin levels were highest in samples from farms close to the ICMESA plant. The high levels of TCDD's found in the milk samples strongly suggest that human exposure via oral intake must have occurred after the accident through consumption of dairy products. A milk monitoring program that has been sampling milk from outside Zone R since 1978 no longer detects TCDD's in any of the samples.

Three research teams have analyzed fat from cattle that had grazed on land where 2,4,5-T herbicides were applied. In one study, five of eight samples collected from the Texas A & M University Range Science Department in Mertzon, Texas, showed the possible presence of TCDD's at low ppt levels when analyzed by gas chromatography/low-resolution mass spectrometry (Kocher et al. 1978).

TABLE 54. TCDD LEVELS IN MILK SAMPLES COLLECTED NEAR SEVESO IN JULY-AUGUST 1976<sup>a</sup>

Map number <sup>b</sup>	Date of collection	TCDD concentration (ng/liter) (ppt)
1	7/28	76
2	7/28	7919
	8/2	5128
	8/10	2483
3	7/28	469
	8/2	1593
	8/10	496
4	8/10	1000
5	7/29	116
6	7/29	59
7	8/3	80
8	8/3	94
9	7/27	180
	8/3	75
10	8/5	<40

<sup>a</sup>—Source: Fanelli et al. 1980.

<sup>b</sup>—Locations shown in Figure 66.

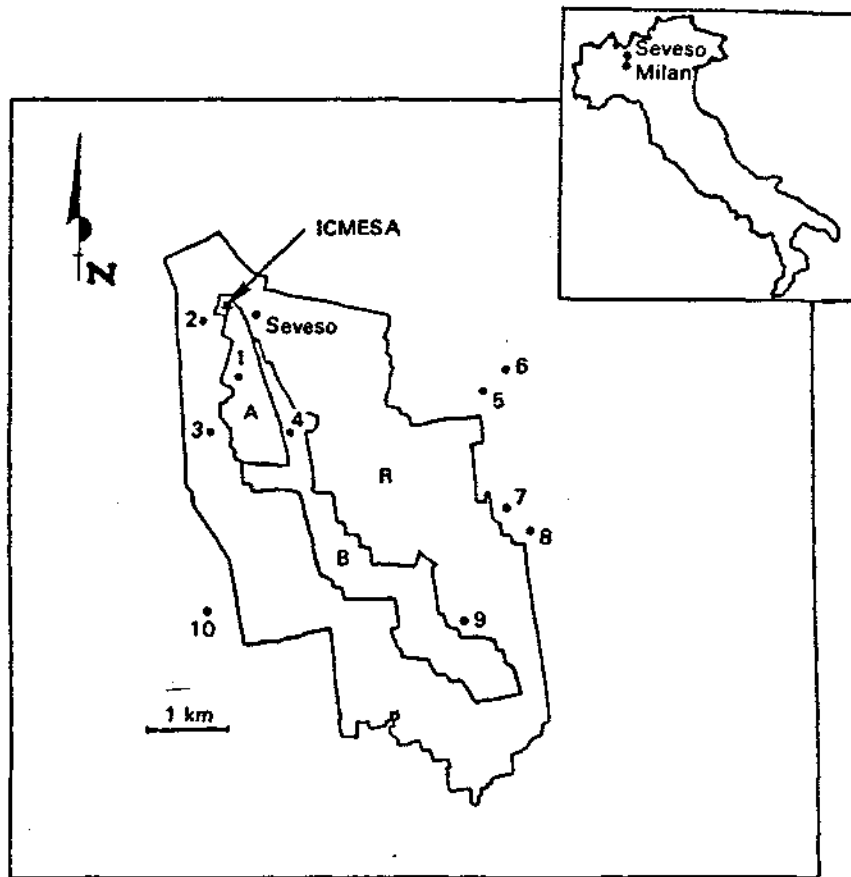


Figure 66. Location of farms near Seveso at which cow's milk samples were collected for TCDD analysis in 1976 (July-August).

Source: Fanelli et al. 1980.

Apparent TCDD concentrations ranged from 4 to 15 ppt at detection limits ranging from 3 to 6 ppt. In the second study, 11 of 14 samples analyzed contained TCDD's (Meselson, O'Keefe, and Baughman 1978). The four highest levels reported were 12, 20, 24, and 70 ppt TCDD. In the third study, Solch et al. (1978, 1980) detected TCDD's in 13 of 102 samples of beef fat at levels ranging from 10 to 54 ppt.

Shadoff and co-workers could find no evidence that TCDD's are bioconcentrated in the fat of cattle (Shadoff et al. 1977). The animals were fed ronnel insecticide contaminated with trace amounts of TCDD's for 147 days. Sample cleanup was extensive to permit low-level detection of the dioxin. Analysis was by combined gas chromatography/mass spectrometry (both high and low resolution). No TCDD's were detected at a lower detection limit of 5 to 10 ppt.

Samples of human milk obtained from women living in areas where 2,4,5-T is used have also been analyzed for dioxins. In one study, four of eight samples were reported to contain about 1 ppt TCDD's (Meselson, O'Keefe, and Baughman 1978). In a subsequent study, no evidence of 2,3,7,8-TCDD contamination was found in 103 samples of human milk collected in western states (Chemical

Regulation Reporter 1980). The lower level of detection in the latter study ranged from 1 to 4 ppt.

Model ecosystems have been developed in aquariums to study the bioaccumulation and concentration of several pesticides including TCDD's (Matsumura and Benzet 1973). Concentration factors for TCDD's calculated from these studies were:

Daphnia: 2198  
Ostracoda: 107

Mosquito larvae: 2846  
Northernbrook silverside fish: 54

The authors concluded that the biological and physical characteristics of organisms played an important role in the bioaccumulation and concentration of TCDD's and the other pesticides studied. They also indicated that because of the low solubility of TCDD's in water and liquids and their low partition coefficient in liquids, TCDD's are not likely to accumulate in biological systems as readily as DDT.

Another aquatic study involved a recirculating static model ecosystem in which fish were separated from all the other organisms (algae, snails, daphnia) by a screened partition (Yockim, Isensee, and Jones 1978). In this study <sup>14</sup>C-TCDD was added to 400 g of Metapeake silt loam clay to yield TCDD's at a concentration of 0.1 ppm. Treated soils were placed in the large chambers of the ecosystem tanks and flooded with 16 l of water. One day after the water addition, all organisms except the catfish were added. Samples of organisms and water were collected on days 1, 3, 7, 15, and 32. On day 15 a second group of 15 mosquito fish was added. On day 32 all organisms remaining were collected and counted. Also on day 32, nine channel catfish were added to the large chambers of the tanks containing the soil. Catfish were collected 1, 3, 7, and 15 days later. Of the two collected on each day, one was sacrificed for analysis and one was placed in untreated water.

Bioaccumulation ratios (tissue concentration of TCDD's divided by water concentration) for the algae ranged from 6 to 2083, the maximum exhibited after 7 days. Bioaccumulation ratios for the snails ranged from 735 to 3731, with the maximum at 15 days. The ratios in daphnia ranged from 1762 to 7125, with the maximum at 7 days. The accumulation ratios in the mosquito fish ranged from 676 at day 1 to 4875 after 7 days. All mosquito fish were dead after 15 days, and their tissues showed an average of 72 ppb TCDD's. No bioaccumulation ratios were calculated for the catfish, but levels of TCDD's in the tissues ranged from 0.9 ppt after day 1 to 5.9 ppt after day 15. By day 32 of exposure, all catfish had died. The average concentration of TCDD's in the tissue at this time was 4.4 ppb.

It was concluded that under normal use of 2,4,5-T, concentration of TCDD's in sediments of natural water bodies would probably be 10<sup>4</sup> to 10<sup>6</sup> times lower than the concentration used in this experiment, and although the TCDD's could be a potential environmental hazard, the magnitude of the hazard would depend on biological availability and persistence in the aquatic ecosystem under conditions of normal use.

In previously mentioned studies with microagroecosystems, earthworms contained 0.2 and 0.3 ppt 2,3,7,8-TCDD and/or breakdown products of TCDD's following two silvex applications to soil (Nash and Beall 1978). The silvex contained 44 ppb TCDD's.

Another study not yet completed concerns the possible accumulation of dioxins in vegetation and earthworms in turf and sod of areas having a history of silvex and/or 2,4-D applications (Hanna and Goldberg, n.d.).

Isensee and Jones (1975) performed three experiments using algae, duckweed, snails, mosquito fish, daphnia, channel catfish and other organisms. Radiolabeled dioxin (<sup>14</sup>C-TCDD) was adsorbed to two types of soil, which were then placed in glass aquariums and covered with water. One day later, daphnia, algae, snails, and various diatoms, protozoa, and rotifers were added. In one experiment duckweed plants were also added on the second day. After 30 days, some daphnia were

analyzed and two mosquito fish were added to each tank. Three days later, all organisms were harvested; in Experiments II and III, two fingerling channel catfish were added to each tank and exposed for 6 days. At the conclusion of each experiment the concentrations of <sup>14</sup>C-TCDD in the water and in the organisms were determined and the concentration factors calculated. Table 55 summarizes soil application rates in each experiment and type of soil used.

TABLE 55. SOIL APPLICATION RATES AND REPLICATIONS<sup>a</sup>

Total <sup>14</sup> C-TCDD added per tank (μg)	Type of soil <sup>b</sup> and amount of <sup>14</sup> C-TCDD added (g)	Final concentrations of <sup>14</sup> C-TCDD (ppm) <sup>c</sup>	No. of replicates
	Experiment I		
149	L-20	7.45	3
0	L-20	0.00	1
	Experiment II		
63	L-20	3.17	2
63	L-20 + M-100	0.53	2
63	L-20 + M-200	0.29	2
63	L-20 + M-400	0.15	2
0	L-20	0.00	2
	Experiment III		
10	M-100	0.10	2
1	M-100	0.01	2
0.1	M-100	0.001	2
0.01	M-100	0.0001	2
0	M-100	0.00	2

a—Isensee and Jones 1975.

b—L = Lakeland sandy loam; M = Metapeake silt loam. In Experiment II, L was first treated with <sup>14</sup>C-TCDD, then dry-mixed with M in treatment tanks.

c—Soil concentrations based on total quantity of soil in tanks.

At soil concentrations as low as 0.1 ppb, <sup>14</sup>C-TCDD was leached into the water and accumulated in the organisms. Bioaccumulation factors at this soil concentration and a water concentration of 0.05 ppt were 2,000 for algae, 4,000 for duck weed, 24,000 for snails, 48,000 for daphnia, 24,000 for mosquito fish, and 2,000 for catfish, corresponding to concentrations of 0.1, 0.2, 1.2, 2.4, and 0.1 ppb of <sup>14</sup>C-TCDD in the tissues. Although some biomagnification was evident, results were highly variable. The differences in bioaccumulation factors found in this study relative to those of Yockim et al. (1978) were attributed to system design, differences in the organisms, and the fact that bioaccumulation factors in the other study were based on fresh weight whereas those in this study were based on dry weight.

The authors conclude that since some bioaccumulation ratios were relatively high (as compared with those observed with other pesticides), especially in daphnia and mosquito fish, the potential of TCDD's to accumulate in the environment is considerable. They further project, however, that at suggested application rates of 2,4,5-T, concentrations of TCDD's in the soil would probably not result in accumulation in biological systems unless erosion or runoff from recently sprayed areas is discharged to a small body of water (e.g., a pond).

Dow Chemical Company reported in 1978 on a series of studies to determine whether dioxins are present in the Tittabawassee River, into which Dow discharges treated wastes. In one study, rainbow trout were placed in cages at various locations above and below the Dow Midland plant, in a tertiary effluent stream, and in clear well water. Five of six fish placed in the tertiary effluent stream showed levels of TCDD's ranging from 0.2 to 0.05 ppb. Analysis of whole fish exposed for 30 days at a point 6 miles downstream of the effluent discharge showed concentrations of 0.01 and 0.02 ppb TCDD's. Analysis of whole fish from the tertiary effluent showed levels ranging from 0.05 to 0.07 ppb.

In a laboratory experiment with <sup>14</sup>C-2,3,7,8-TCDD, Dow (1978) determined that the bioconcentration factor in rainbow trout was about 6600. Dow also analyzed native catfish taken randomly from various locations in the Tittabawassee River and tributaries. The analyses showed levels of TCDD's ranging from 0.07 to 0.23 ppb, levels of OCDD from 0.04 to 0.15 ppb, and one sample with 0.09 ppb of hexa-CDD. Highest levels of TCDD's and OCDD were found in fish collected from the Tittabawassee at points approximately 1 to 2 miles downstream from Dow. Dow noted that caustic digestion used in sample preparation may have degraded octa-, and hexachlorodioxins. No other fish analyzed contained detectable levels of TCDD's (Dow Chemical Company 1978).

Subsequent to the Dow studies, the U.S. EPA collected and analyzed fish samples from the Tittabawassee, Grand, and Saginaw Rivers in Michigan (Harless 1980). TCDD's were found in 26 of 35 samples (74 percent) at levels ranging from 4 to 690 ppt. Catfish and carp contained the highest concentrations, while perch and bass had the lowest. Additional information concerning dioxin in fish from different sources can be found on pages 175 and 178.

#### Accumulation in Plants

Because dioxins are sometimes used in herbicides applied on and near areas where food plants may be growing, it is important to determine whether the dioxins may be incorporated into the plants. Thus far, few studies have been done to determine whether dioxins might accumulate in plants. In the few studies that have considered this question, results seem to indicate that very small amounts are accumulated in plants.

Kearney et al. (1973a) studied the uptake of DCDD's and TCDD's from soil by soybeans and oats. Soil applications of <sup>14</sup>C-DCDD (0.10 ppm) and <sup>14</sup>C-TCDD (0.06 ppm) were made, and a maximum of 0.15 percent of the dioxins was detected in the above-ground portion of the oats and soybeans. No dioxins were found in the grains harvested at maturity. Application of a solution of Tween 80 (a surfactant) and TCDD's or DCDD's to the leaves of young oat and soybean plants showed no translocation to other plant parts after 21 days.

Studies of the absorption and transportation of TCDD's by plants in the contaminated area near Seveso have been reported (Cocucci et al. 1979). Samples of fruits, new leaves, and, in some cases, twigs and cork were taken from various types of fruit trees a year after the dioxin contamination occurred. TCDD's were found in all samples at μg/kg levels. Concentrations in the leaves were 3 to 5 times higher than in the fruits, which had the lowest concentrations. Levels in the cork samples were generally higher than in the leaves, but not as high as in the twigs. The findings show that the dioxin is translocated from the soil by plants in newly formed organs and suggest that the lower concentrations in fruits and leaves may be due to some form of elimination such as transpiration or ultraviolet photodegradation. The latter possibility would agree with the photolysis results reported by Crosby and Wong in 1977.

Cocucci and co-workers also examined specimens of garden plants such as the carrot, potato, onion, and narcissus. Again μg/kg levels of TCDD's were found. In all plants, the new aerial portions appeared to contain less dioxin than the

underground portions. Concentrations of TCDD's differed in the inner and outer portions of potato tubers and carrot taproots; the variation was attributed to the prevalence of conductive tissues in these plant parts. The authors again suggested that the relatively low concentrations in the aerial parts of these garden plants were due to an elimination process such as transpiration or photodegradation, or possibly to metabolism of the dioxin by the plants. The elimination hypothesis was supported by the further observation that when contaminated plants were transplanted in unpolluted soil, the dioxin content disappeared.

Young et al. (1976) used specially designed growth boxes to study the uptake of  $^{14}\text{C}$ -TCDD by *Sorghum vulgave* plants. After placing Herbicide Orange containing 14 ppm  $^{14}\text{C}$ -TCDD under the soil in the growth boxes, 100 plants were grown for 64 days. After 64 days the plants were harvested, extracted with hexane, and analyzed for  $^{14}\text{C}$ -TCDD. Some plant samples were also analyzed for  $^{14}\text{C}$ -TCDD before hexane extraction by combustion and collection of the  $\text{CO}_2$ . Analysis before extraction showed a concentration of about 430 ppt  $^{14}\text{C}$ -TCDD in the plant tissue. After hexane extraction, the concentration of  $^{14}\text{C}$ -TCDD in the plant tissue was reported as being not significantly reduced. Young et al. concluded that the relatively high  $^{14}\text{C}$  activity in the plant tissue could have been due to the presence of 1) nonhexane-soluble TCDD, 2) a soil biodegradation product of TCDD's that was taken up, 3) a metabolic breakdown product of TCDD's found after plant uptake of the TCDD's, or 4) a contaminant in the original  $^{14}\text{C}$ -TCDD stock solution that was taken up by the plant.

As mentioned elsewhere, concentration of  $^{14}\text{C}$ -TCDD in algae and duckweed has been observed. Bioaccumulation factors were 2000 and 4000, respectively (Isensee and Jones 1975).

## SECTION 8

### DISPOSAL AND DECONTAMINATION

#### GENERAL CONSIDERATIONS

One of the principal unsolved problems that has followed the discovery of dioxins is development of methods for destroying them once they are produced. Many investigators have studied various methods for disposing of commercial chemicals and production wastes that contain these compounds, and further research is needed. Even more important is the need for methods of destroying dioxins after they are released into the environment.

Simple out-of-sight storage has been used on several occasions to dispose of dioxin-contaminated soils and equipment following industrial accidents from the manufacture of 2,4,5-TCP. Soil contaminated by the application of dioxin-containing wastes at Verona, Missouri, was used as fill under a new concrete highway and was also placed in a sanitary landfill. Some was also used as fill at two residential sites, but was later removed and placed elsewhere (Commoner 1976a). The soil contaminated by the accident at Seveso, Italy, was partially removed from moderately contaminated areas and added to the more heavily contaminated areas, which will remain uninhabitable for an indefinite period of time (Reggiana 1977). Following an explosion at Coalite and Chemical Products, Ltd., in England, portions of the plant equipment were buried in an abandoned coal mine (May 1973). Portions of the Phillips Duphar plant in the Netherlands, following its explosion, were encased in concrete and dumped into the ocean (Hay 1976a).

The quantities of TCDD-containing wastes from the normal manufacture of 2,4,5-TCP that have been buried at various sites in the United States are not well documented, although some published figures are available. One company at Verona, Missouri, reportedly disposed of 16,000 gallons of 2,4,5-TCP distillation residues over an 8-month period (Shea and Lindler 1975). A New York company reportedly disposed of 3700 tons of 2,4,5-TCP production wastes at three dumps in the Niagara Falls area over a 45-year period (Chemical Week 1979a). It is estimated that the 3700 tons of waste produced by this company could contain 100 pounds of TCDD (Chemical Week 1979a). An Arkansas facility has been producing 2,4,5-TCP and related products since 1957 and possibly earlier (Sidwell 1976a). Reports indicate that 3000 barrels of TCP wastes are buried or stored on the manufacturing site (Fadiman 1979; Cincinnati Enquirer 1979). Many of these barrels were leaking and contaminating nearby water bodies (Richards 1979a; Tiernan et al. 1980). There are, at this writing, 3000 barrels now stored in an EPA-approved shelter, and none are presently leaking. The correction of the drum problem was completed by Vertac at a cost of about \$500,000 (Howard 1980).

Continuation of land disposal is still being proposed as at least a temporary measure, however. Other proposals include chemical fixation, deep well disposal, burial in salt mines, and inclusion of these chemicals with nuclear fission by-products in secured cavities.

Although these practices postpone the need for solving the problems of disposal and decontamination, they offer no permanent solutions. Techniques that may be used to decompose dioxins and thereby remove them permanently from the environment are discussed in this section. The most extensively tested method is incineration, which entails a high-temperature oxidation of the dioxin molecules. Physical methods have also been proposed for some applications; these include the