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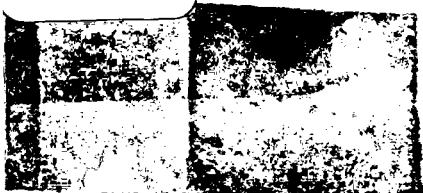
DIOXINS IN THE VICINITY OF TWO ATLANTIC REGION WOOD PRESERVING OPERATIONS

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DIOXINS IN THE VICINITY OF TWO
ATLANTIC REGION WOOD PRESERVING OPERATIONS

by

D.J. Baker and R.A.F. Matheson

Environmental Protection Service
Atlantic Region
Dartmouth, Nova Scotia
Canada

August, 1981

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ABSTRACT

Samples collected in the vicinity of two Atlantic Region wood preserving plants using pentachlorophenol were analyzed for dioxin content. Octachlorodibenzo-p-dioxin, and in some instances heptachlorodibenzo-p-dioxin and hexachlorodibenzo-p-dioxin, were identified in effluent, sediment, soil and product samples. No 2,3,7,8-tetrachlorodibenzo-p-dioxin was detected. Recommendations for future action are discussed.

RESUME

On a fait l'analyse d'échantillons provenant des environs de deux usines de produits préservateurs pour le bois. Les échantillons de pentachlorophenol furent analysés pour le dioxin. Le octachlorodibenzo-p-dioxin et dans quelques cas, le heptachlorodibenzo-p-dioxin et le hexachlorodibenzo-p-dioxin furent identifiés dans les échantillons des produits, du sol, des sédiments et d'effluent. Nul 2,3,7,8-tetrachloro-p-dioxin n'a été identifié. Des recommandations pour la marche à suivre sont faites.

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1

INTRODUCTION

Chlorinated phenols are included on the DOE/NHW List of Priority Chemicals. This list is intended to focus upon those substances for which regulations are being developed under the Environmental Contaminants Act (ECA) and upon those substances about which further information must be obtained to determine whether regulation is necessary. Materials are evaluated on the basis of toxic effects, persistence, and quantity and use criteria. Chlorinated phenols appear in Category II of the List, indicating that investigations are being conducted to determine the nature and the extent of the danger to human health or the environment and the appropriate means of alleviating that danger.

Polychlorinated dibenzo-p-dioxins have been identified as common impurities in chlorinated phenols resulting in part from the elevated temperatures used in the process chemistry. Hexa, hepta, and octachloro-dibenzo-p-dioxins have been detected in commercial pentachlorophenol preparations.

In September, 1978, the Atlantic Regional Environmental Contaminants Committee (RECC), in discussing possible projects for funding in 1979/1980 under the auspices of the Environmental Contaminants Contract Fund (ECCF), noted that two wood preserving plants in the Region known to be releasing pentachlorophenol into their immediate environment could pose a dioxin contamination problem. At the suggestion of the RECC, EPS drafted a proposal for a preliminary investigation at both sites to determine whether a dioxin problem existed. This proposal was submitted as the highest rated priority for the

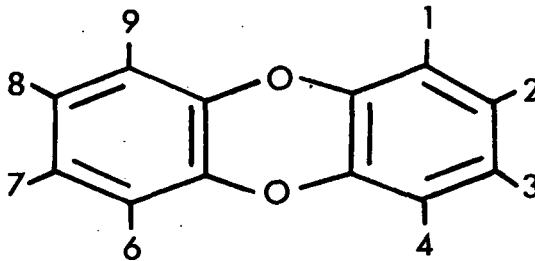
Atlantic Region and ECCF funding was approved. Wellington Science Associates Inc. were contracted to conduct the survey and their results form the basis of this report.

2 POLYCHLORINATED DIBENZO-p-DIOXINS IN THE ENVIRONMENT

2.1 Background

Polychlorinated dibenzo-p-dioxins (PCDDs)* are a class of chlorinated tricyclic aromatic hydrocarbons of current concern. A total of 75 PCDD isomers and congeners are possible ranging from the mono to the octa-substituted compound. The structure and numbering system is illustrated in Figure 1.

FIGURE 1 STRUCTURE AND NUMBERING SYSTEM FOR POLYCHLORINATED DIBENZO-p-DIOXINS



* In this report the term polychlorinated dibenzo-p-dioxins (PCDDs) includes the monochlorodibenzodioxins.

The individual PCDDs are colourless solids at room temperature and, as with most high molecular weight halogenated aromatics, are extremely insoluble in water and only sparingly soluble in most organic solvents. At room temperature and atmospheric pressure they have no appreciable vapour pressure. Physical and chemical properties of some typical PCDDs are given in Tables 1 and 2.

2.2 Polychlorinated Dibenzo-p-dioxins Associated with Chlorophenols

2.2.1 Production of Chlorophenols

Chlorophenols (CPs) are industrially produced either by direct chlorination of phenol or by hydrolysis of chlorobenzene, depending upon the isomer desired. The former process is used to manufacture 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TTCP) and under forced conditions pentachlorophenol (PCP). The hydrolysis of chlorobenzene is mainly used for production of 2,4,5-TCP and PCP and is especially conducive to dioxin formation. PCDDs are produced in side reactions, facilitated by high temperatures, during the synthesis of commercial CPs. Reactions responsible for the formation of PCDDs have been summarized by Buser (1978).

2.2.2 Use of Chlorophenols

The annual world production of CPs is in the range of $90-180 \times 10^6$ kg (Nilsson, et. al., 1978). They are used as insecticides, fungicides, mold inhibitors and disinfectants with effectiveness generally increasing with increased chlorination.

TABLE 1 PROPERTIES OF SEVERAL CHLORINATED DIOXINS (Firestone, 1977)

CHLORODIOXIN	MOLECULAR WEIGHT	MELTING POINT °C	"P" VALUE ¹	ESTIMATED VAPOUR PRESSURE ²	MOLAR REFRACTION ³	UV MAX. (CHCl ₃) _{nm}
2,7-dichloro	253.08	-	0.76	6.0 x 10 ⁻⁶	-	302
2,3,7-trichloro	287.53	162	0.86	3.6 x 10 ⁻⁶	-	305
2,3,7,8-tetrachloro	321.87	306	0.51	1.7 x 10 ⁻⁶	71.4	310
1,2,4,7,8-pentachloro	356.42	206	-	-	72.6	307
1,2,3,7,8-pentachloro	356.42	241	-	-	-	308
1,2,4,6,7,9-hexachloro	390.86	240	0.94 ⁴	6.6 x 10 ⁻⁷	-	310
1,2,3,6,8,9-hexachloro	390.86	-	-	-	-	81.1
1,2,3,6,7,8-hexachloro	390.86	285	-	-	-	317
1,2,3,7,8,9-hexachloro	390.86	243	-	-	-	317
1,2,3,4,6,7,9-heptachloro	425.31	-	0.90	3.0 x 10 ⁻⁷	85.9	-
1,2,3,4,6,7,8-heptachloro	425.31	-	0.90	-	-	-
1,2,3,4,6,7,8,9-octachloro	459.75	331	0.90	1.8 x 10 ⁻⁷	90.7	318

1 "P" value determined for dioxin between hexane and acetonitrile (Beroza and Bowman, 1965).

2 Vapour pressure estimated from GLC data of Woolson, *et. al.*, 1972.

3 Estimated by summing atomic refractions.

4 "P" value determined for mixture of hexachlorodioxin isomers.

TABLE 2 SOLUBILITY (mg/l) OF CHLORODIOXINS IN VARIOUS SOLVENTS¹ (Firestone, 1977)

SOLVENT	2,3,7,8-TCDD	HxCDD ²	OCDD
Acetone	90	-	5
Anisole	-	2 600	1 700
Benzene	470	1 600	1 000
Chloroform	550	-	560
Methanol	10	-	-
Toluene	-	1 800	1 600
o-Xylene	-	-	3 600
Water	0.0002	-	-

1 Firestone (unpublished data, 1976) observed that 1,2,3,6,7,8-HxCDD is considerably less soluble in organic solvents than other HxCDD isomers. The solubility of the 1,2,3,6,7,8-isomer in isooctane is about 20 mg/l.

2 Dow standard 82-A, a mixture of 71% 1,2,3,6,7,8-HxCDD and 29% of a combination of 1,2,3,6,7,9-HxCDD and 1,2,3,6,8,9-HxCDD.

Of a possible 19 CP isomers, only those listed in Table 3 have commercial application and all are marketed and used in Canada. The most important use of 2,3,4,6-TTCP and PCP and their corresponding sodium or potassium salts is for wood preservation. Approximately 2.8×10^6 kg, or 80% of the annual Canadian consumption of 3.5×10^6 kg, is used yearly for this purpose. PCP is also used as a fungicide for slime control in pulp and paper manufacture and in a variety of other products such as cutting oils, leather, paint, glue and textiles. Most of the 2,4-DCP production is used for the manufacture of the phenoxy acid herbicide, 2,4-D.

2.2.3 Chlorophenol Impurities

All commercial CPs, including TCP, TTCP and PCP, contain significant quantities of other isomers. For example, PCP contains TTCP and possibly TCP. In addition, smaller quantities of a number of other impurities, including polychlorinated dibenzo-p-dioxins, chlorinated phenoxy phenols (potential dioxin precursors), chlorinated diphenyl ethers, chlorinated dibenzofurans and dihydroxybiphenyls have been reported. (For the purposes of this report only PCDD impurities of CPs will be discussed.)

PCDDs have been detected quantitatively in commercial CPs by a number of researchers. The amount of PCDD present varies considerably among different CP formulations with typical values for fungicides used in wood treatment ranging from <1-2 000 mg/l (Nilsson, et. al., 1978).

For most CPs tested, relative PCDD content is in the order of tetra < penta < hexa < hepta < octa (Buser and Bosshardt, 1976). Goldstein, et. al., (1977)

TABLE 3 COMMERCIAL CHLOROPHENOLS MARKETED AND USED IN CANADA

CHLOROPHENOL NAME	CANADIAN MANUFACTURER ¹	LOCATION ²
<u>o</u> -chlorophenol (2-CP)	Imported	N/A
<u>p</u> -chlorophenol (4-CP)	Imported	N/A
2,4-dichlorophenol (2,4-DCP)	Uniroyal Ltd.	Clover Bar, Alta.
2,4,5-trichlorophenol (2,4,5-TCP)	Imported	N/A
2,4,6-trichlorophenol (2,4,6-TCP)	Imported	N/A
2,3,4,6-tetrachlorophenol (2,3,4,6-TTCP)	Uniroyal Ltd.	Clover Bar, Alta.
Pentachlorophenol (PCP)	Uniroyal Ltd.	Clover Bar, Alta.
Sodium pentachlorophenate (NaPCP)	Imported & Domestic	Unknown

1 All Canadian manufacture is via catalytic chlorination of phenol.

2 N/A = not applicable.

quantitatively analyzed a sample of technical PCP from Monsanto and found the hexa, hepta and octa-isomers present at 8, 520 and 1 380 mg/l respectively. Pentachloro- and tetrachlorodibenzo-p-dioxin were not found above the detection limit of 0.1 mg/l. In other studies hexa, hepta and octa-isomers have been reported in TCP, TTCP and PCP at levels ranging from approximately 0.001 mg/l for one of the hexachlorinated compounds to 1 000 mg/l for octachlorodibenzo-p-dioxin.

Additional quantitative data on the chlorodioxin content of various North American commercial CPs are presented in Table 4.

It is important to note that the most toxic dioxin, 2,3,7,8-TCDD, has not been detected in TTCP or PCP, the most widely used CPs. This isomer has, however, been reported in 2,4,5-TCP at levels ranging from 0.09-6.2 mg/l. TCP is often a trace contaminant of other CPs, including TTCP and PCP, and consequently TCDD could occur as a trace impurity in these materials.

2.3 Dioxins in the Environment

2.3.1 Routes of Entry

The release of CPs into the environment has become substantial in recent years and these materials are now ubiquitous in the Canadian ecosystem. The presence of PCDD impurities in CPs is the suspected major source of dioxin contamination of environmental matrices such as sediment, soil, and biota. Other dioxin routes of entry

TABLE 4 POLYCHLORINATED DIBENZO-p-DIOXINS (ppm) REPORTED IN CHLOROPHENOLS (USEPA, 1980)

CHLOROPHENOL SAMPLE	Chlorodioxins ¹								Reference
	mono-CDDs	di-CDDs	tri-CDDs	tetra-CDDs	penta-CDDs	hexa-CDDs	hepta-CDDs	octa-CDDs	
Monochlorophenol									
2-chlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	Firestone, <u>et. al.</u> , 1972 Chemical Week, 1979
<u>o</u> -chlorophenol	-	-	-	0.037(2,3,7,8) ²	-	-	-	-	
Dichlorophenol									
2,4-dichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	Firestone, <u>et. al.</u> , 1972 "
2,6-dichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	
Trichlorophenol									
2,4,5-trichlorophenol (1969)	ND	ND	ND	0.30(1,3,6,8) 6.20(2,3,7,8)	ND	ND	ND	ND	"
2,4,5-trichlorophenol (1970)	ND	ND	ND	ND	1.5	ND	ND	ND	"
2,4,5-trichlorophenol (1970)	ND	ND	ND	ND	ND	ND	ND	ND	"
2,4,5-trichlorophenol (1970)	ND	ND	ND	0.07(2,3,7,8)	ND	ND	ND	ND	"
Na-2,4,5-trichlorophenol (1967)	ND	ND	ND	ND	ND	ND	ND	ND	"
Na-2,4,5-trichlorophenol (1969)	ND	0.72 (2,7)	ND	1.40(2,3,7,8)	ND	ND	ND	ND	"
2,4,5-trichlorophenol	-	-	-	0.30(2,3,7,8)	-	-	-	-	Elvidge, 1971 Firestone, <u>et. al.</u> , 1971
2,4,6-trichlorophenol	ND	ND	93 (2,3,7)	49(1,3,6,8)	ND	ND	ND	ND	
trichlorophenol	-	-	-	ND	-	0.5- 1.0	0.5- 1.0	0.5- 1.0	Woolson, <u>et.al.</u> , 1972

...Cont'd

TABLE 4 (Cont'd)

CHLOROPHENOL SAMPLE	Chlorodioxins ¹								Reference
	mono-CDDs	di-CDDs	tri-CDDs	tetra-CDDs	penta-CDDs	hexa-CDDs	hepta-CDDs	octa-CDDs	
Tetrachlorophenol									
2,3,4,6-tetrachlorophenol (Dowicide 6)	-	-	-	-	-	6	-	-	Buser, 1975
2,3,4,6-tetrachlorophenol	ND	ND	ND	ND	ND	29	5.1	0.17	Firestone, et. al., 1972
2,3,4,6-tetrachlorophenol (1967)	ND	ND	ND	ND	ND	4.1	ND	ND	"
2,3,4,6-tetrachlorophenol tetrachlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	"
	-	-	-	ND	-	10-100	10-100	10-100	Woolson, et. al., 1972
Pentachlorophenol									
PCP (Dowicide 7)	-	-	-	-	-	9	235	250	Buser, 1975
PCP	-	-	-	ND	-	10-100	100-1000	100-1000	Woolson, 1972
Na-PCP (1967)	ND	ND	ND	ND	ND	14	14.5	3.8	Firestone, et. al., 1972
Na-PCP (1969)	ND	ND	ND	ND	ND	20	11.3	3.3	"
PCP (1970)	ND	ND	ND	ND	ND	39	49	15	"
PCP (1970)	ND	ND	ND	ND	ND	35	23	ND	"
PCP (1967)	ND	ND	ND	ND	ND	0.17	ND	ND	"
PCP (1969)	ND	ND	ND	ND	ND	13	47	ND	"
PCP (1970)	ND	ND	ND	ND	ND	0.91	2.1	5.3	"
PCP (1970)	ND	ND	ND	ND	ND	15	23	15	"
PCP (1978)	-	-	-	ND	-	19	140	432	Dioxin in Industrial Sludges, 1978
Pentachlorophenate	-	-	-	-	-	-	+	+	Jensen and Renberg, 1972
PCP formulation	-	-	-	-	-	-	870	50-3300	Jensen and Renberg, 1972

...Cont'd

TABLE 4 (Cont'd)

CHLOROPHENOL SAMPLE	Chlorodioxins ¹								Reference
	mono-CDDs	di-CDDs	tri-CDDs	tetra-CDDs	penta-CDDs	hexa-CDDs	hepta-CDDs	octa-CDDs	
PCP (technical grade)	-	-	-	ND	-	33-42	19-24	7-11	Villanueva, et. al., 1973
PCP (reagent grade)	-	-	-	ND	-	0.02-0.03	0.04-0.09	0.02-0.03	
PCP (many samples)	-	-	-	ND	-	9-27	90-135	575-2510	PCP- A Wood Preservative, 1977
PCP's (17)	-	-	-	-	-	0-23	-	0-3600	Crummett, 1973
PCP or PCP-NA(7)	-	-	-	<0.01-0.23 ³	<0.03-0.08	0.03-10	0.6-180	5.5-370	Buser and Bosshardt, 1976
PCP (Dowicide 7 1970)	-	-	-	-	-	4	125	2500	PCP Ad Hoc Study Report, 12/78 SAB
PCP (Dowicide 7 1970) (distilled)	-	-	-	-	-	1.0	6.5	15	PCP Ad Hoc Study Report 12/78 SAB
PCP	-	-	-	-	-	9-27	-	575-2510	Johnson, 1973
Na-PCP (Dowicide G 1978)	-	-	-	-	-	ND-2	1-12	4-173	Dow Chemical Company, 1978
PCP(25 samples; various formulations) ⁴	-	-	-	-	-	10	142	300	Cochrane, 1981

1 Key to abbreviations and symbols: ND = Not detected (minimum detection level, ppm). Other numbers in parentheses indicate year chlorophenol sample was obtained, or specific dioxin detected.

- = Not analyzed or not reported.

2 Presence of 2,3,7,8-TCDD confirmed but not quantitatively reported.

3 1,2,3,4-TCDD.

4 Average values. Average ratio of hexa:hepta:octa for all samples is 1:15:60. Uniroyal's PCP, used at both plants surveyed in this report, approximates the average.

into the environment are accidental release and the application of the phenoxy acid herbicides 2,4,5-T and Fenoprop.

PCP wood preservatives are generally considered the major source of higher chlorinated dioxins, in particular OCDD, in the environment. The higher chlorinated isomers usually predominate in environmental samples (Dow, 1978). In addition to direct release, some PCDDs are generated as a result of photochemical, thermal and/or pyrolytic reaction of CPs and related compounds prior to and following their discharge to the environment.

2.3.1.1 Photolytic Generation

Photochemical generation of PCDDs has been shown to occur from pentachloro-2-phenoxy phenol (Nilsson *et. al.*, 1974), sodium pentachlorophenate (Stehl *et. al.*, 1973) and chlorinated dibenzo-p-dioxins themselves. In the latter case, higher chlorinated dioxins have been found to yield lower chlorinated ones upon photolytic exposure (Buser, 1976; Buser, 1979a).

2.3.1.2 Thermal Generation

A review of the early literature on thermal generation of dioxins has been prepared by Kulka (1961). Substances that have been converted to PCDD by thermal reaction include PCP (Kulka, 1961), chlorophenoxy phenol (Rappe and Nilsson, 1972) and sodium pentachlorophenate (Langer, *et. al.*, 1973).

2.3.1.3 Pyrolytic Generation

The pyrolytic generation of PCDDs has been demonstrated to occur from PCP treated scrap wood (Crosby et. al., 1973) and chlorophenate impregnated vegetation (Rappe, et. al., 1978b). Dow Chemical Company's Chlorinated Dioxin Task Force (1978) has advanced a controversial theory that trace chemical reactions in all normal combustion processes such as occur in garbage incinerators, gasoline and diesel engines, fireplaces, charcoal grills and cigarettes give rise to particulate matter containing dioxins.

2.3.2 Environmental Levels

The quantity of dioxins entering the environment is a matter of much speculation. However, substantial dioxin contamination of air borne particulates, soil, biota and food has been demonstrated. Tables 5-9 list data on PCDD content for a number of these matrices.

2.4 Toxicology of Polychlorinated Dibenzo-p-dioxins

Concern about PCDDs in the environment stems primarily from the extremely high toxicity of 2,3,7,8-TCDD. Other dioxins are less toxic; however, toxicological responses have been associated with a number of these compounds.

TABLE 5 POLYCHLORINATED-DIBENZO-p-DIOXINS (ng/g) IN AIR BORNE PARTICULATES¹

SOURCE	LOCATION	UNSPECIFIED PCDDs	TCDD	HxCDD	HpCDD	OCDD	REFERENCE
Fly ash from a municipal incinerator	Switzerland	200	-	-	-	-	Buser, <u>et. al.</u> , 1978
Fly ash from an industrial heating facility	Switzerland	600	-	-	-	-	Buser, <u>et. al.</u> , 1978
Fly ash from a municipal incinerator	Ontario	-	0.4-4.0	-	-	-	Elceman <u>et. al.</u> , 1979

1 See also Table 6 - Section 2.3.4.

TABLE 6 POLYCHLORINATED DIBENZO-*p*-DIOXINS ($\mu\text{g/g}$) IN DUST

SOURCE	LOCATION	TCDD	HxCDD	HpCDD	OCDD	REFERENCE
Dow Chemical Laboratory	Midland, Michigan	-	9-35	140-1200	650-7500	Dow Chemical Co., 1980
Midland, Michigan	Midland, Michigan	0.03-0.04	0.2-0.4	2-4	20-30	"
Metropolitan area	Detroit, Michigan	ND-0.03	ND-0.3	0.3-4	0.1-4	"
Metropolitan area	St. Louis, Missouri	0.03	2	34	210	"
Metropolitan area	Chicago, Illinois	0.04	ND-0.3	0.6-3	3-8	"

TABLE 7 - POLYCHLORINATED DIBENZO-p-DIOXINS ($\mu\text{g/g}$) IN SOIL

SOURCE	LOCATION	UNSPECIFIED PCDDs	TCDD	HxCDD	HpCDD	OCDD	REFERENCE
Riding arena soil sprayed with dioxin contaminated waste oil	Missouri	-	~ 32	-	-	-	Kimbrough, <u>et al.</u> , 1977
Farm road soil sprayed with dioxin contaminated waste oil	Missouri	-	0.61	-	-	-	"
Soil at site of <u>o</u> -chlorophenol spill	Sturgeon, Missouri	-	<0.01	-	-	-	Anonymous, 1979c
Near TCP plant explosion	Seveso, Italy	5477 $\mu\text{g/m}^2$	-	-	-	-	Bonaccorsi, <u>et al.</u> , 1978
From rural area	Gaylord, Michigan	-	ND	ND	ND-0.05	ND-0.2	Dow Chemical Co., 1980
From urban area	Lansing and East Lansing, Michigan	-	ND	0.03-1.2	0.03-2	0.05-2	"
From major metropolitan area	Chicago, Illinois	-	0.005-0.03	0.03-0.3	0.1-3	0.4-22	"
From Dow Chemical Company plant property	Midland, Michigan	-	1-120	7-280	70-280	490-20000	"

TABLE 8 POLYCHLORINATED DIBENZO-*p*-DIOXINS (ng/g) IN ANIMALS

ANIMAL AND PCDD SOURCE	LOCATION	UNSPECIFIED PCDDs	TCDD	HxCDD	HpCDD	OCDD	REFERENCE
Prawn collected near heavy 2,4,5-T spraying	Vietnam	-	0.018	-	-	-	Baughman and Meselson, 1973b
River prawn collected near heavy 2,4,5-T spraying	Vietnam	-	0.042	-	-	-	"
Spotted sunfish near 2,4,5-T spraying (muscle, gonads, gut)	Florida	-	4 18 65	-	-	-	Young, <u>et. al.</u> , 1975
Brown trout Small mouth bass	Lake Ontario	6.5 4.6		-	-	-	New York State Dept. of Health, 1979
Fish downstream from Dow Chemical plant	Tittabawassee River, Michigan	-	0.01- 0.02	-	-	-	Anonymous, 1978
Carp, catfish, croakers in area exposed to 2,4,5-T	Vietnam	-	0.049- 0.80	-	-	-	Shadoff, <u>et. al.</u> , 1977
Beach mice from herbicide test area (liver, pelts)	Florida	-	0.010- 0.71 0.13- 0.14	-	-	-	Young, <u>et. al.</u> , 1975
Reptiles herbicide test area (visceral mass)	Florida	-	0.36	-	-	-	Young, <u>et. al.</u> , 1975

Cont'd

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TABLE 8 Cont'd

ANIMAL AND PCDD SOURCE	LOCATION	UNSPECIFIED PCDDs	TCDD	HxCDD	HpCDD	OCDD	REFERENCE
Cows contaminated with PCP (liver samples)	Michigan	-	-	-	-	16000-50000	Anonymous, 1977d
Cows (beef fat samples)	U.S. Midwest	-	0.020-0.060	-	-	-	Shadoff and Hummel, 1979
Rabbits (liver samples)	Sevesco, Italy	-	0.27-0.33	-	-	-	Bonaccorsi, <u>et. al.</u> , 1978
Humans exposed to o-chlorophenol spill	Sturgeon, Missouri	.007-.031	-	-	-	-	Anonymous, 1979e
Herring gull eggs	Great Lakes	-	0.010	-	-	-	Hallet and Norstrom, 1980
Herring gull eggs	Lake Ontario	-	0.044-0.068	-	-	-	Hallet and Norstrom, 1980
	Lake Huron	-	0.043-0.090	-	-	-	
Herring gull eggs near Kent Island	Bay of Fundy	-	0.003	-	-	-	Hallet and Norstrom, 1980

TABLE 9 POLYCHLORINATED DIBENZO-p-DIOXINS (ng/g) IN FOOD

TYPE OF FOOD	LOCATION	UNSPECIFIED PCDDs	TCDD	HxCDD	HpCDD	OCDD	REFERENCE
Milk from cows fed TCDD contaminated fodder	Seveso, Italy	-	7 μ g/l	-	-	-	Bonaccorsi, <u>et. al.</u> , 1978
Human milk from women exposed to 2,4,5-T	Vietnam	-	0.040-0.050	-	-	-	Baughman, 1974
Beef fat	United States	>0.1	-	-	-	-	Tiernan and Taylor, 1978
Gelatin from supermarkets	United States	0.1-28	-	-	-	-	Firestone, 1977
Charcoal broiled steaks		-	-	-	-	30	Dow, 1978

2.4.1 Factors Influencing Toxicity

The acute toxicity, biological activity and enzyme inducibility have been shown to vary greatly for closely related PCDD isomers. For example, 2,3,7,8-TCDD is 3-1 000 times more toxic than other tetra-chlorinated isomers (Dow, 1978).

The position of the chlorine atoms in the molecule is usually considered the single most important factor affecting toxicological activity. Lateral symmetry, chlorination of two adjacent carbon atoms, the availability of unsubstituted positions and the absence of steric hindrance all enhance toxicity. The toxicity is also highly dependent on the extent of chlorine substitution. A chlorine content from 4 to 6 produces the most highly toxic compounds, while less than 4 or more than 6 chlorine atoms results in a significant decrease in toxicity. Accordingly, the four most toxic chlorinated dibenzo-*p*-dioxins are 2,3,7,8-TCDD, 1,2,3,7,8-PnCDD and 1,2,3,5,7,8- and 1,2,3,7,8,9-HxCDD.

Of these four dioxins, 2,3,7,8-TCDD is considered the most acutely toxic member of the dioxin family as it is capable of producing toxic effects at extremely low levels. Consequently, the majority of toxicological literature on biomass deals with this particular isomer.

2.4.2 Acute Toxicity of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin

The LD50 values for 2,3,7,8-TCDD in rats, guinea pigs and rabbits are presented in Table 10. The male guinea pig is the most sensitive test species having

TABLE 10. ACUTE TOXICITY OF 2,3,7,8-TCDD FOR SEVERAL SPECIES

SPECIES	SEX	ROUTE OF EXPOSURE	LD50 ng/g	REFERENCE
Rat	male	oral	22	Schwetz, <u>et. al.</u> , 1973
	female	oral	45	Schwetz, <u>et. al.</u> , 1973
Guinea pig	male	oral	0.6	Schwetz, <u>et. al.</u> , 1973
	male	oral	2.1	Schwetz, <u>et. al.</u> , 1972
	female	oral		Harris, <u>et. al.</u> , 1973
Rabbit	female and male	oral	115	Schwetz, <u>et. al.</u> , 1973
	female and male	dermal	272	Schwetz, <u>et. al.</u> , 1973
	female and male	interperitoneal	252	Schwetz, <u>et. al.</u> , 1973
	?	oral	10	Schulz, 1968
	?	oral	10	Milnes, 1971
Mouse	male	oral	114	Vos, <u>et. al.</u> , 1974
Dog	male and female	oral	300 LD50 3000	Schwetz, <u>et. al.</u> , 1973
Monkeys	?	oral	50-70	McConnell, <u>et. al.</u> , 1978

an LD50 of 0.6 ng/g. The LD50 values in monkeys, exposed to a single oral dose, range from 50-70 ng/g body weight (McConnell, et. al., 1978a), while in mice the LD50 is 284 ng/g (McConnell, et. al., 1978b).

Aside from an obvious inter-species difference, a marked intra-species individual variation in sensitivity to 2,3,7,8-TCDD has been reported (Schwetz, et. al., 1973, Greig, et. al., 1973). There also appears to be a significant difference in tissue distribution among various animal species. Toxic symptoms are characterized by severe thymus involution, testicular degeneration, gastrointestinal hemorrhage, hyperplasia, skin lesions, terminal jaundice, ascites and loss of weight (Schwetz, et. al., 1973; Harris, et. al., 1973; Vos, et. al., 1974; Moore, et. al., 1976).

2.4.3 Acute Toxicity of Other Polychlorinated Dibenzo-p-dioxins

Table 11 lists the LD50 values for various other substituted dibenzo-p-dioxins in guinea pigs, mice and rats.

2.4.4 Chronic Toxicity of Polychlorinated Dibenzo-p-dioxins

Not only are several of the PCDDs acutely toxic but they also have an extremely high potential for producing adverse effects under conditions of chronic exposure. This is especially true of 2,3,7,8-TCDD.

Chloracne is the most common indicator of 2,3,7,8-TCDD exposure in humans and certain animal species. However, chronic exposure to this dioxin can affect many other organ systems.

TABLE 11 ACUTE TOXICITIES OF POLYCHLORINATED DIBENZO-*p*-DIOXINS
OTHER THAN 2,3,7,8-TCDD^{1,2}

COMPOUND	LD50 (μ g/kg)		
	GUINEA PIGS	MOUSE	RAT
2,3-DCDD			<1x10 ⁶
2,7-DCDD			-2 000*
2,8-DCDD	>300 000.0		
2,3,7-Tri-CDD	29 444.0	>3 000.0	<1 000*
1,2,3,4-TCDD			<1 000*
1,2,6,8-TCDD			<100*
1,2,4,7,8-PnCDD	1 125.0	>5 000	
1,2,3,4,7,8-HxCDD	72.5	825.0	
1,2,3,6,7,8-HxCDD	70-100	1 250.0	
1,2,3,7,8,9-HxCDD	60-100	>1 440.0	
HxCDD (mixture)			-100*
1,2,3,4,6,7,8-HpCDD	>600		
1,2,3,4,6,7,8,9-OCDD		>4 x 10 ⁶	-2 000*

1 All values taken from McConnell, 1978b except those asterisked (*) which are taken from Saint-Ruf, 1978.

2 All values are for doses given orally.

Hepatic (Gupta, et. al., 1973; Van Miller, et. al., 1977), renal (Anazai and Cohen, 1979, Hook, et. al., 1978), endocrine (Piper, 1979; Barsotti, et. al., 1979; Gustafsson, and Ingelman-Sundberg, 1979), immunologic (Faith and Luster, 1977; Vos, et. al., 1978, Luster, 1979a); hematologic (Allen, 1967; Weissberg and Zinkl, 1973, Zincke, et. al., 1973); gastrointestinal (Ball and Chhabra, 1977, Madge, 1977) and neuropsychiatric effects (Purkyne et. al., 1974, Elovaara, et. al., 1977, Creso, et. al., 1978) have all been observed upon exposure of various test animals to 2,3,7,8-TCDD. In addition, it has been shown to cause a number of adverse developmental effects such as teratogenicity (Neubert and Dillman, 1972; Moore, et. al., 1973; Smith, et. al., 1976), carcinogenicity (Van Miller, et. al., 1977, Kociba, et. al., 1978; Toth, et. al., 1979), and mutagenicity (Hussain, et. al., 1972; Seiler, 1973, Michigan Critical Materials Register, 1979).

While all these effects have been demonstrated for 2,3,7,8-TCDD, several other PCDDs also produce some of the same toxic responses. Table 12 summarizes some of the chronic effects produced by several of these PCDDs.

2.4.5 Environmental Toxicology of Polychlorinated Dibenzo-p-dioxins

2.4.5.1 Human Exposure

Several incidences of accidental release have afforded an insight into the ramifications of human exposure to PCDDs (May, 1973; Kimmig and Schulz, 1957), in particular 2,3,7,8-TCDD.

TABLE 12 BIOLOGICAL PROPERTIES OF POLYCHLORINATED DIBENZO-*p*-DIOXINS¹
(Saint-Ruf, 1978)

COMPOUND	CHLORACNE APTITUDE	TERATOGENIC EFFECT	EMBRYOTOXIC EFFECT
2,3-DCDD	0	0	0
2,7-DCDD	0	<u>+</u>	<u>+</u>
2,3,7-Tri-CDD			
1,2,3,4-TCDD	0	0	0
1,3,6,8-TCDD	0	0	0
2,3,7,8-TCDD	+++	+++	+++
HxCDD (mixture)	+	++	++
1,2,3,4,6,7,8,9-OCDD	0	<u>+</u>	+

1 Definitions for symbols were not reported but are assumed to be:

0 = no effect

+ = possible effect

+

++ = moderate effect

+++ = severe effect.

While the numbers of humans involved in most of these accidents was small, an industrial explosion in Seveso, Italy in 1976 resulted in the exposure of several thousands of people to TCDD. Those closest to the plant became ill almost immediately with headaches, nausea and vomiting (Rawls and O'Sullivan, 1976). Within a short time, chloracne developed. A few days later less severely affected individuals began to develop symptoms which included skin burns and stomach pains. Children were hospitalized with skin disorders and a decrease in the lymphocytes of the peripheral blood. Chloracne developed in three to four months.

The use of phenoxy acid herbicides has also been a source of human exposure to TCDD. The herbicide Agent Orange, containing levels of TCDD from 0.5-47 mg/l, was used extensively as a defoliating agent by the U.S. Armed Forces in Vietnam. There are reports of chloracne, nausea, vomiting, diarrhea, fatigue, dizziness, and abortions in humans living in the sprayed areas (Rose and Rose, 1972). Data show an increase in infant mortality from 30 to 47 per thousand.

2.4.5.2 Animal Exposure

The industrial accident which occurred in Seveso, Italy, also resulted in animal exposure to TCDD which was linked with increased death rates in wild and domestic animals.

A farm road sprayed with dioxin contaminated waste oil resulted in the exposure and death of 70 chickens within 2 weeks of spraying (Carter, et. al., 1975).

In Vietnam large numbers of fish in Agent Orange sprayed ponds and rivers died and death of domestic animals, especially cows and pigs, was common. Cattle experienced convulsions and skin disorders. Abortions and monstrous births were observed in many of the animal species (Rose and Rose, 1972).

2.4.6 Other Environmental Concerns

Concern about environmental dioxin contamination stems not only from their toxicity but also from their persistence and potential for biological magnification.

PCDDs have been given the highest rating for environmental persistence in hazard assessment studies conducted by the Department of Natural Resources, State of Michigan (Michigan Critical Material Register, 1979). The half life ($t_{1/2}$) of pure 2,3,7,8-TCDD in soils is approximately 1 year (Michigan Critical Materials Register, 1979).

In assessing the persistence of a substance in the environment, the susceptibility of that substance to biodegradation is of primary concern. Based on the results of several studies on the biodegradability of dioxins, USEPA (1980) concluded that dioxins are essentially non-biodegradable.

Other PCDD removal mechanisms include photolysis and pyrolysis. Photolysis appears to be the most significant. Studies have clearly shown that dioxins may be photolytically degraded in the environment by natural sunlight. Reaction is dependent on a number of factors including the degree of chlorination. The higher chlorinated isomers are generally more stable to photolytic degradation than the lower chlorinated ones.

Several investigators have studied the level of TCDD in animals captured in dioxin contaminated areas and have shown that TCDD has accumulated in a number of animals such as mice, rabbits, toads, snakes and earthworms (Fanelli, et. al., 1979; Fanelli, et. al., 1980a; Frigerio, 1978; Young, et. al., 1975). In all cases TCDD body burdens were of the same order of magnitude as environmental levels suggesting that no biomagnification occurred.

Studies indicate that only very small amounts of dioxins are accumulated in plants (Kearney et. al., 1973a). In Seveso, Italy, samples of fruit trees and garden plants, taken a year after the TCP plant explosion, contained only ng/g levels of dioxins (Cocucci, et. al., 1979).

3 WOOD PRESERVATION IN CANADA

After the production of food crops, wood constitutes Canada's most valuable renewable resource (Smith, 1977) and ranks first in export dollars earned. In 1976, the value of forest products exported totalled 6.5 billion dollars (Hansard, 1979).

Wood destined to be utilized for long term purposes generally requires some form of protection against biological attack in order to maintain structural strength and thereby prolong the effective period of service. The type of wood preservative used depends upon the particular end use of the product.

In 1977 there were approximately forty wood preserving plants in operation in Canada. Of these, five are located in the Atlantic Provinces and three use PCP as a preservative. These are located at Truro, Nova Scotia, Newcastle, New Brunswick and Clarendville, Newfoundland. In addition to PCP these plants also use coal tar creosote, creosote solution and ammoniacal copper arsenate as preservatives.

For the purpose of this report only PCP and PCP wood treatment processes are discussed.

3.1 Pentachlorophenol as a Wood Preservative

PCP, as commercially specified for wood preservation, must contain 95% PCP, calculated on the basis of alkali-titratable hydroxyl. It must have a minimum melting point of 78.8°C and must contain less than 1% matter insoluble in 1N NaOH solution. Prior to application it is dissolved in a suitable petroleum oil

solvent until a 5% PCP solution is obtained. The Domtar, Truro plant utilizes approximately 1 550 000 litres of this 5% solution annually, mainly for the treatment of utility poles. The Newcastle plant uses approximately 1 100 000 litres of the same 5% solution.

3.1.1 Pentachlorophenol Treatment Processes

Numerous processes have been developed for PCP pressure treatment of wood; the basic commercial methods employed at the Domtar plants are the full cell and empty cell processes.

3.1.1.1 Full Cell Process

The objective of this process is to fill the cells of the wood to capacity. Prepared wood which has been peeled, dried, incised and has had all boring, framing and cutting operations performed, is placed in a retort cylinder and a vacuum is applied to remove air from the wood cells. The preservative is introduced into the cylinder until the cylinder is completely filled. Pressure is then applied to force the preservative into the wood until the desired amount is absorbed. Pressure is then released and a final vacuum is applied to clean the wood surface.

3.1.1.2 Empty Cell Process

In the empty cell process air is initially compressed within the wood structure so that at the end of the cycle when the preservative pressure is released the air expands and forces excess preservative out of the wood. Prepared wood is placed in a steel cylinder filled with preservative. Pressure is then applied to force the preservative into the wood until the desired absorption level is obtained. Excess preservative is removed by applying a final vacuum.

4 METHODS AND MATERIALS

4.1 Project Background

On June 21, 1979 Wellington Science Associates Inc. were awarded a contract, funded through the Environmental Contaminants Contract Fund, to measure dioxin levels in products and environmental samples in the vicinity of two Atlantic Region wood preserving operations using pentachlorophenol. The plants are located at Truro, Nova Scotia and Newcastle, New Brunswick.

Liquid effluent samples were collected at the outfalls and a number of sediment cores were obtained at regularly spaced intervals at distances up to 1 km from the point of discharge. In addition, representative finished products, residues removed by waste treatment systems, soils within the plant confines where gross contamination was indicated and commercial pentachlorophenol mixtures being used were also sampled.

The methods and materials used in the data collection phase of this study follow.

4.2 Apparatus

1. Gas chromatography, Hewlett-Packard 5713A equipped with a Ni-63 electron capture detector and a 1.0 mv single pen recorder.

2. Gas chromatograph-mass spectrometer system (GC/MS), Hewlett-Packard 5992B mass spectrometer interfaced with a computerized data system used in either the total or selected ion monitoring modes.

3. Gas chromatographic columns, 120 cm long x 4 mm ID.

4. Column packing (GC/MS system); 3% OV-17 on 100/120 Gas Chrom Q.

5. Column packing (electron capture system); 1.5% OV-17/2% OV-210 on 100/120 Gas Chrom Q.

4.3 Reagents

All solvents were glass distilled.

1. Methanol
2. Methylene chloride
3. Pentane
4. Isooctane
5. Aluminum oxide, basic, activity 1, 80/200 mesh
6. Sodium sulfate-anhydrous, reagent grade, heated for 8 hr. at 600°C and stored in a closed glass container. Washed with benzene prior to use.
7. Celite - Fisher 545.
8. Silica gel, 60/200 mesh-activated at 250°C for 8 hr., deactivated with 5% water (by weight), shaken for 2 hr., stored in a dessicator.

4.4 Sample Collection

The sampling sites are listed in Tables 13 (Truro) and 14 (Newcastle) and are indicated diagrammatically in Figures 2 (Truro) and 3 (Newcastle).

Water samples were collected in foil-capped solvent bottles; all other samples were collected in clean glass preserving jars. Sediment and soil samples were obtained to a depth of approximately 15 cm using a coring device. The sample bottles were sealed and stored in the dark for transportation to the laboratory. Samples were refrigerated until extracted and analyzed.

4.5 Preparation of Standards

4.5.1 1,2,4,6,7,9-Hexachlorodibenzo-p-dioxin (HxCDD)

1,2,4,6,7,9-Hexachlorodibenzo-p-dioxin was prepared using the method described by Buser (1975). Using this procedure 2,3,5,6-tetrachlorophenol was first reacted with potassium hydroxide (1N) in methanol to produce the corresponding potassium salt. Following pyrolysis at 300°C and atmospheric pressure the HxCDD was isolated by extraction with methylene chloride (CH₂Cl₂) and alumina column chromatography. The final product was approximately 85% pure based on gas chromatographic (GLC) measurement.

4.5.2 Octachlorodibenzo-p-dioxin (OCDD)

OCDD was prepared by perchlorination of dibenzo-p-dioxin using the BMC reagent as described by Hutzinger, et. al. (1973). The final product was purified by alumina column chromatography and was 98% pure by GLC.

TABLE 13 SAMPLES COLLECTED AT THE DOMTAR WOOD TREATMENT FACILITY IN TRURO, NOVA SCOTIA

SAMPLE TYPE	LOCATION	CODE USED IN DIAGRAM
Sediment	near mouth of discharge stream	T1
Sediment	~0.5 km downstream from discharge stream at bridge	T2
Sediment	~1 km upstream from discharge stream	T3
Soil	riverbank (under TCH bridge)	T4
Sediment	~2 m downstream from discharge stream	T5
Sediment	~4 m below discharge pipe in discharge stream	T6
Sediment	~2 m below discharge pipe in discharge stream	T7
Sediment	at mouth of discharge stream	T8
Sediment	~2 m upstream from discharge stream	T9
Sediment	at mouth of discharge pipe	T10
Soil	inside plant boundaries	T11
Carbon	used for effluent treatment	T12
Wood	treated wood	T13
Wood	treated wood	T14
Carbon	used for effluent treatment	T15
PCP	in oil for wood treatment	T16
Water	effluent at mouth of discharge pipe	T17
Water	effluent at mouth of discharge pipe	T18
PCP	product prior to preparation of treatment mixture	T19

TABLE 14 SAMPLES COLLECTED AT THE DOMTAR WOOD TREATMENT FACILITY IN NEWCASTLE, NEW BRUNSWICK

SAMPLE TYPE	LOCATION	CODE USED IN DIAGRAM
Sediment	brook at "Meat Market" (North side)	N1
Sediment	brook at a location above industrial park entrance	N2
Sediment	~100 m from final outfall	N3
Sediment	~15 m from final outfall	N4
Sediment	~4 m from final outfall	N5
Sediment	at final outfall	N6
Soil	plant entrance	N7
Sediment	brook at "Meat Market" (South side marsh)	N8
Sediment	under railroad bridge	N9
Soil	at excavation site	N10
Soil	within plant (near resort)	N11
Filter	polyurethane foam used for water treatment	N12
Wood	treated wood	N13
Wood	treated wood	N14
Filter	polyurethane foam used for water treatment	N15
PCP	in oil for wood treatment	N16
Water	final effluent	N17
Water	final effluent	N18
PCP	pure product prior to preparation of treatment mixture	N19

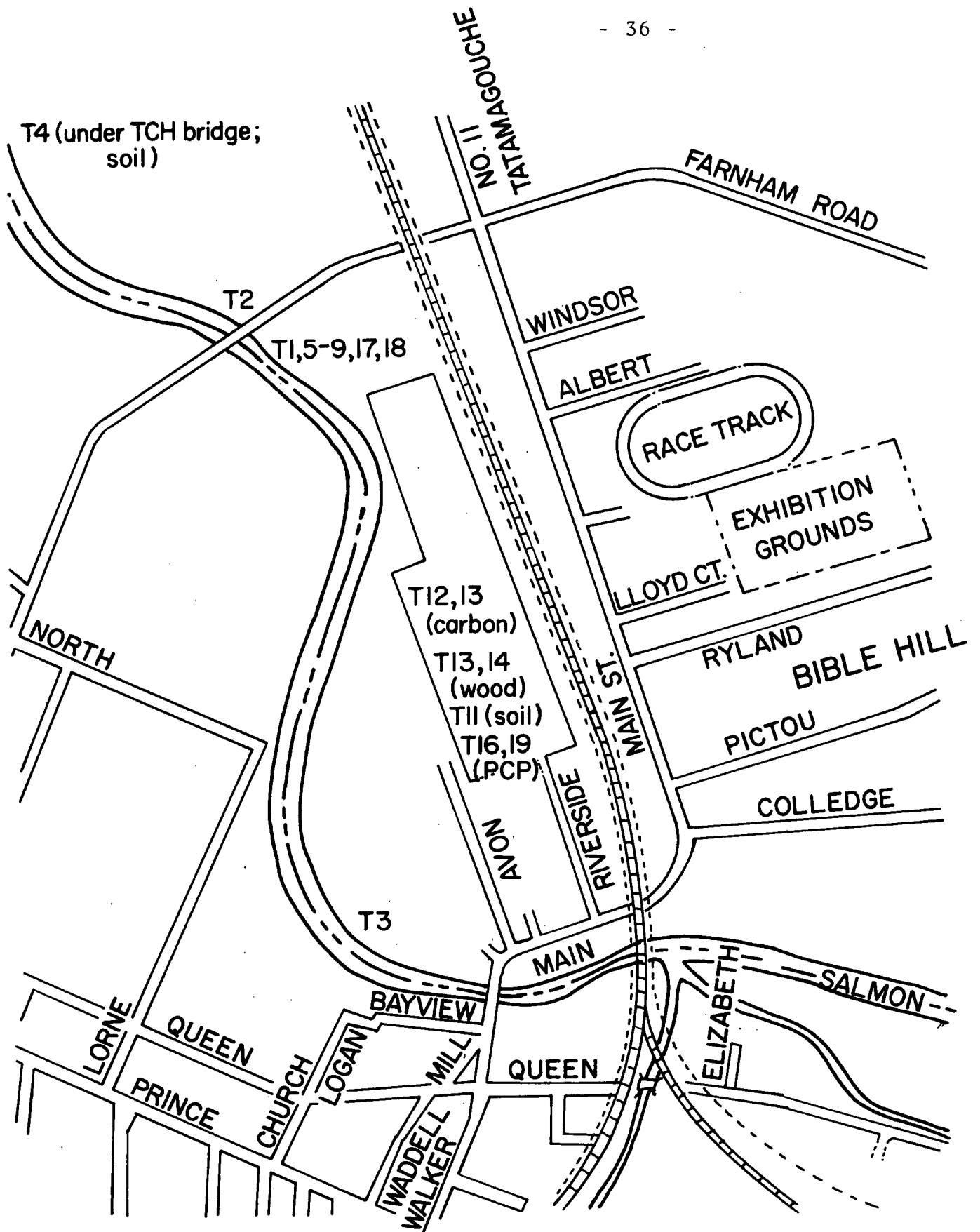


FIGURE 2 - SAMPLING SITES, TRURO

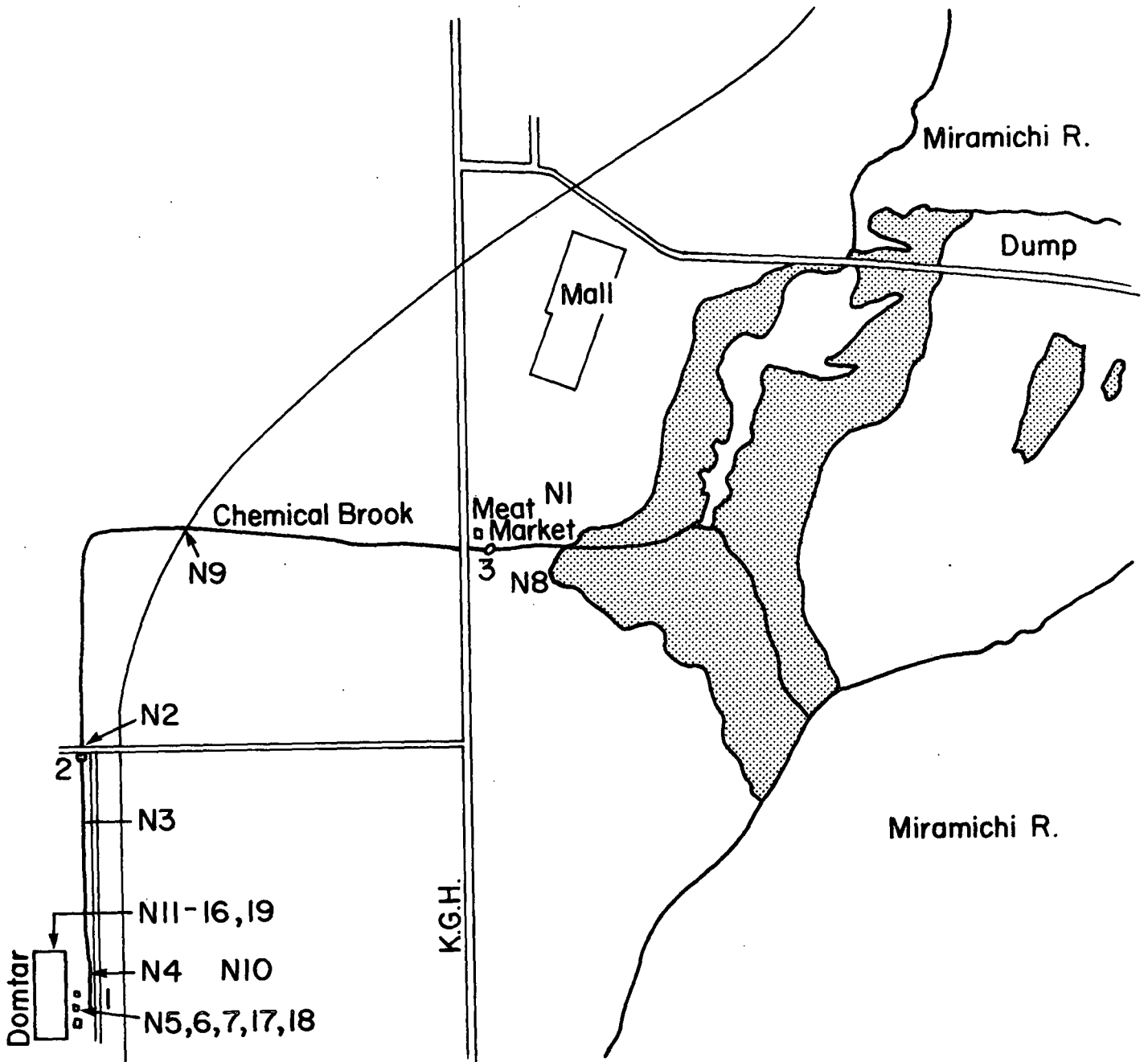


FIGURE 3 - SAMPLING SITES, NEWCASTLE

4.5.3 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)

The TCDD standard was provided by Dr. D. Firestone (USFDA).

4.6 Extraction and Cleanup of Samples

Initially the extraction and cleanup procedure involved solvent extraction of the sample followed by alkaline partitioning and finally, an alumina column cleanup. Large amounts of creosote in the samples, however, necessitated the use of an additional celite-sulfuric acid/silica gel/sodium sulfate multilayer column.

4.6.1 Extraction of Soil, Sediment, Wood and Effluent Sorbent Samples

All samples, except the sediments, were used as received. The sediment samples contained appreciable amounts of water which were removed by decantation after the sediment was allowed to settle.

An aliquot (10-100 g) of the sample was weighed into a 600 ml beaker. This sub-sample was extracted first with methanol (2 x 100 ml) and then with methylene chloride (2 x 100 ml) with thorough mixing using a glass rod for approximately 10 min. After sedimentation each extract was filtered into a 1 litre separatory funnel. To these combined extracts, water (150 ml) and 1.5 N NaOH (15 ml) were added and the separatory funnel shaken. After the phases had separated, the methylene chloride was then drained into a 250 ml erlenmeyer flask. The extract was filtered through anhydrous sodium sulfate in a sintered glass funnel into a 250 ml round-bottom

flask. The methylene chloride extract was then evaporated just to dryness and the residue re-dissolved in approximately 20 ml of pentane. The pentane solution was then chromatographed using columns A and B (Section 4.6.4).

4.6.2 Extraction of Aqueous Samples

Effluent and water samples (250 ml) were first poured into a 1 litre separatory funnel to which methanol (75 ml) and 1.5 N NaOH (25 ml) were added. The resulting solution was then extracted with pentane (2 x 150 ml). The combined pentane extracts were washed with a combination of water (125 ml) and 2.5 N NaOH (5 ml), and then with water (125 ml) alone. The extracts were then dried over anhydrous sodium sulfate, filtered into a round-bottom flask and concentrated to approximately 20 ml. This solution was then partitioned on an alumina column (column B, Section 4.6.4).

4.6.3 Extraction of Pentachlorophenol and Pentachlorophenol/Oil Samples

Samples (10 g) of PCP used in the wood treatment facilities were first dissolved in methanol (60 ml) in a 1 litre separatory funnel. To this was added 2.5 N NaOH (25 ml) and water (200 ml) and the resultant solution was extracted with pentane using the method described for water samples (4.6.2). For PCP samples the final concentrate was partitioned using column B while for PCP in oil samples, both columns A and B were used.

4.6.4 Cleanup Procedures - Column Partitioning

In instances of extreme contamination, sample extracts were partitioned first on column A and then on column B in the manner described below.

Column A

Column A was a 30 cm x 10 mm I.D. glass column packed with, from the bottom,

5 cm silica gel

5 cm celite/sulfuric acid; 20:5

5 cm anhydrous sodium sulfate

The column was first washed with pentane (25 ml). Pentane solutions from the extractions described in section 4.6.1 were then added to the top of the column using a pasteur pipette. The column was eluted with pentane (50 ml) and the eluate evaporated just to dryness. The residue was then reconstituted with 2% methylene chloride/pentane (5 ml) and partitioned using column B.

Column B

Column B was a 25 cm x 5 mm I.D. glass column packed with alumina to a depth of 15 cm.

The column was prewashed with 2% methylene chloride/pentane (10 ml). The methylene chloride/pentane solution from column A was added to the top of the column using a pasteur pipette. The column was eluted with 2% methylene chloride/pentane (15 ml) and then with methylene chloride/pentane (1:1; 15 ml). (The first fraction will contain potential interfering substances such as PCBs and

DDT while PCDDs and polychlorinated dibenzofurans (PCDFs), if present, will be in the second fraction.)

The second fraction from this column was evaporated just to dryness, reconstituted with pentane (5 ml) and re-evaporated to dryness. The residue was reconstituted with toluene to an appropriate volume and analyzed by electron-capture gas chromatography (EC/GC) and, in some instances, by combined gas chromatography/mass spectrometry (GC/MS).

4.7 Analysis of Extracts

4.7.1 Standard Solutions

Stock solutions of the three PCDDs were prepared by dissolving known weights of compounds in 100 ml of isooctane. A PCDD standard isomer mix was prepared by combining aliquots of these stock solutions and diluting the mixture to a known volume with isooctane. The final concentration of this mixture (the working standard) was:

2,3,7,8-tetrachlorodibenzo-p-dioxin(TCDD)= 16 mg/l
1,2,3,6,7,9-hexachlorodibenzo-p-dioxin(HxCDD)= 6.9 mg/l
1,2,3,4,6,7,8,9-octachlorodibenzo-p-dioxin(OCDD)= 2 mg/l.

4.7.2 Calibration Curves

Calibration curves, to be used for quantitation, were prepared by graphing peak areas obtained by EC/GC against quantities injected.

An EC/GC chromatogram of the PCDD isomer mix is shown in Figure 4.

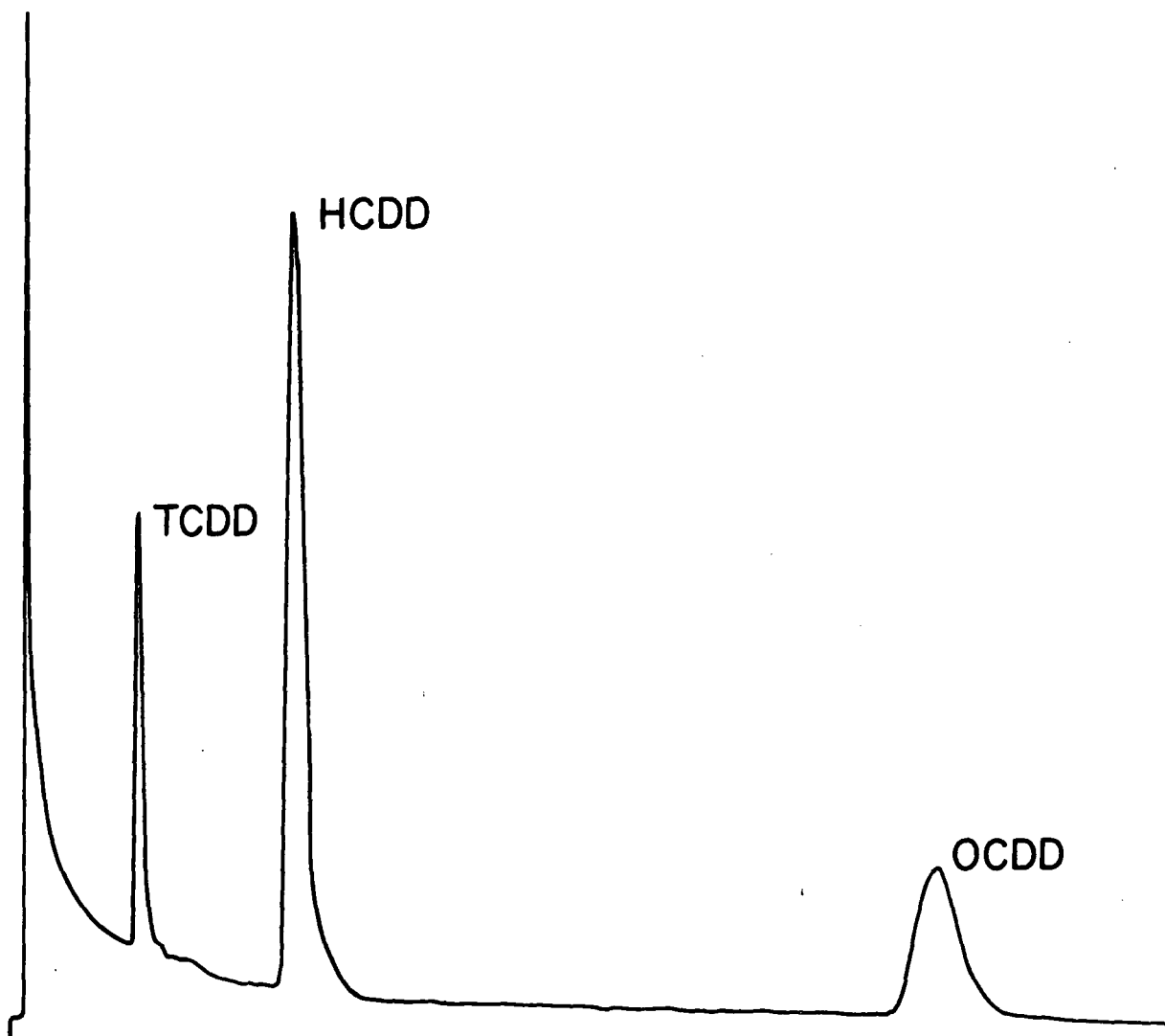


FIGURE 4 - EC/GC CHROMATOGRAM OF A 2,3,7,8-TCDD,
1,2,4,6,7,9-HCDD AND OCDD STANDARD MIXTURE

4.7.3 Gas Chromatographic Analysis

A Hewlett-Packard 5713A gas chromatograph equipped with a Ni-63 electron capture detector (ECD) and a 1.2 m x 4 mm I.D. glass column packed with OV-17 (1.5%)/OV-210 (2%) on Gas Chrom Q (100-120 mesh) was used for analyses. Argon/methane (5%) at 60 ml/min was the carrier gas. The detector, oven and injection port temperatures were 300°C, 240°C and 240°C respectively.

Amounts of the PCDDs in the sample extracts were determined by dissolving the residue in an appropriate volume of isooctane, and then injecting 5 μ l of the solution on the EC/GC. All injections were duplicated and peak areas averaged. The PCDDs were quantitated by comparing peak areas of calibration standards with those of peaks occurring at the same retention times in extract chromatograms. Some typical chromatographic traces are illustrated in Figure 5.

4.7.4 Gas Chromatography/Mass Spectrometry (GC/MS)

GC/MS analysis was performed on a selected number of the sample extracts. A Hewlett-Packard 5992B GC/MS (electron impact) system was used employing the following operating conditions:

Column - 3% OV-17 on Gas Chrom Q,
100/120 mesh, 4 ft x 4 mm I.D.

Oven - 280°C isothermal

Injection port - 250°C

Mass Spectrometer Inlet - Glass Lined
Jet Separator

Carrier gas - Nitrogen; 25 ml/min

Ionizing voltage - 70 ev

Electron multiplier - 2000 V.

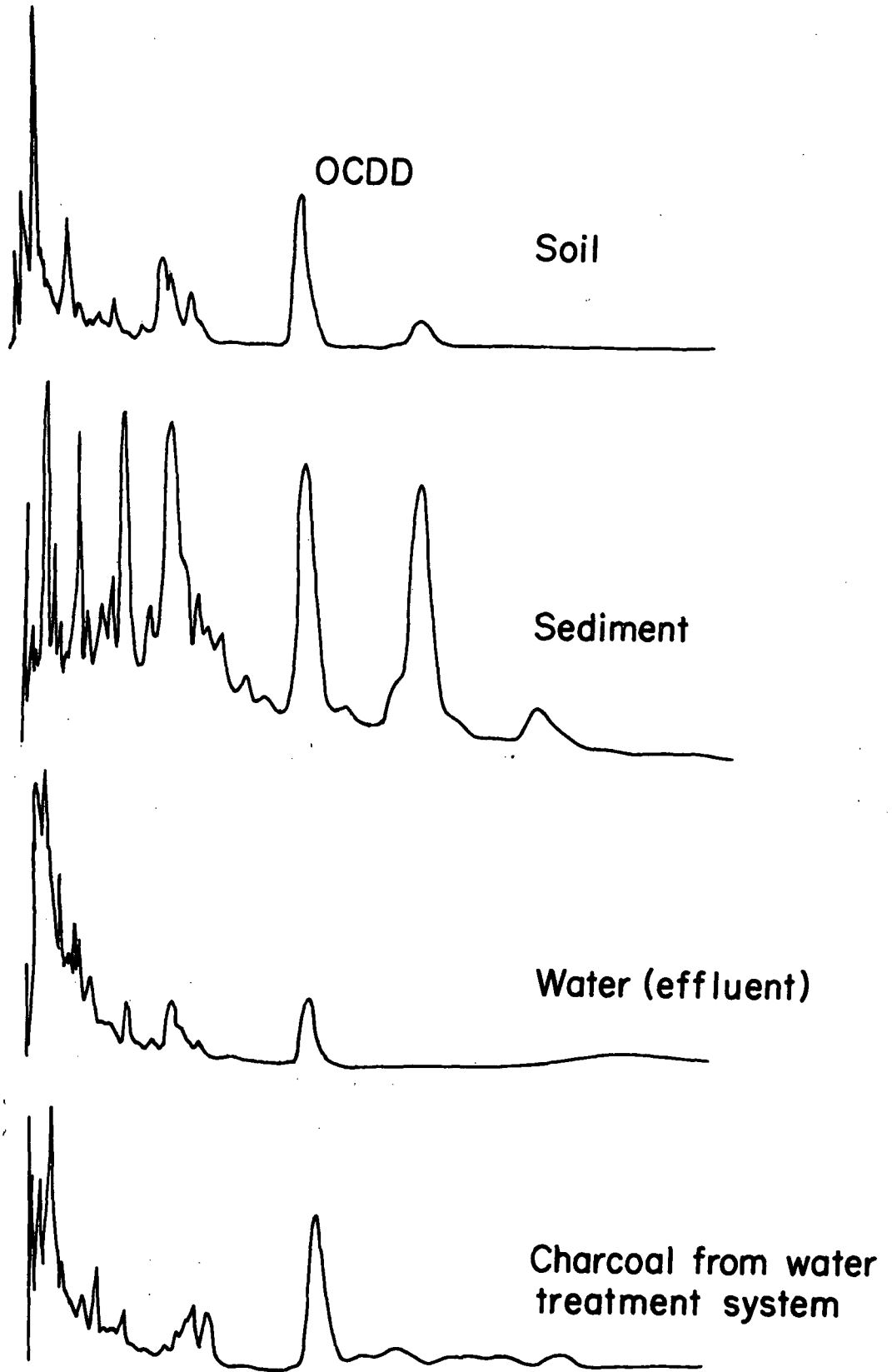


FIGURE 5 - TYPICAL EC/GC CHROMATOGRAMS FOR SOIL, SEDIMENT, EFFLUENT AND EFFLUENT SORBENT

The data system was used in either the total or single ion monitoring mode. Sample extracts analyzed by GC/MS were evaporated to dryness and then reconstituted with an appropriate volume of methanol or diethyl ether prior to a 1 μ l injection.

4.8 Recovery Experiments

The effective recovery of the extraction and cleanup procedure was tested by spiking "background" soil samples with the PCDD isomer mixture. These samples were then analyzed using the analytical procedures described for the environmental samples.

4.9 High Resolution Mass Spectrometric Analysis

Six of the extracts analyzed by Wellington Science were re-analyzed by the Laboratory Services Division (LSD) of Agriculture Canada for OCDD, HpCDD and HxCDD content. A Finnigan 4023 mass spectrometer was used for preliminary dioxin identification and all quantitative measurements. Structural assignments were confirmed using a Krators MS-50 instrument. Instrumental operating conditions were:

Mass Spectrometer - Krators MS-50 with INCOS data system.
(High Resolution)

Mass Spectrometer - Finnigan 4023 with INCOS data system.
(Low Resolution)

Gas Chromatograph - column: SE-30 UP
- Oven Temperature: 250°C
- Injector Temperature: 250°C
- Interface Temperature: 280°C
- Carrier Gas: Helium
- Flow Rate: 30 ml/min.

The analytical results are listed in Table 21.

5 ANALYTICAL RESULTS

5.1 Sample Analysis

All samples were analyzed for TCDD, HxCDD and OCDD using EC/GC. OCDD, however, was the only isomer detected. Concentrations of OCDD in samples collected at the Truro and Newcastle locations are listed in Tables 15-20. Typical EC/GC chromatograms for soil, sediment, effluent and effluent sorbent extracts are diagrammed in Figure 5. The experimental detection limit for OCDD was 10 ppt.

Neither HxCDD nor TCDD could be detected in any of the samples. Interfering peaks in the gas chromatographic traces with retention times similar to both of these dioxins made unambiguous identification impossible at low concentrations. Modifications of the work-up procedure, intended to remove these interferences, were unsuccessful. As a result, qualitative assignment of gas chromatographic peaks to HxCDD and TCDD was only possible when concentrations of these isomers exceeded 400 ppb.

5.2 Dioxin Recoveries

Soil samples having no measurable levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), 1,2,4,6,7,9-hexachlorodibenzo-p-dioxin (HxCDD) or octachlorodibenzo-p-dioxin (OCDD) were spiked with a synthetic mixture of these three compounds. Dioxin content was then determined using the analytical work-up procedures previously described (4.6) with electron-capture gas chromatography (EC/GC) used for quantification. Average recoveries for TCDD, HxCDD and OCDD were 72%, 47% and 37% respectively.

TABLE 15 OCDD IN PENTACHLOROPHENOL¹

SAMPLE NO.	DESCRIPTION	WEIGHT	OCDD CONC (ng/g)
T16*	5% PCP/oil solution	10	5 100
T19*	pure PCP	10	220 000
N16*	5% PCP/oil solution	10	4 700
N19*	pure PCP	10	120 000

TABLE 16 OCDD IN WOOD

SAMPLE NO.	DESCRIPTION	WEIGHT	OCDD CONC (ng/g)
T13*	PCP treated wood	16	1 200
T14	PCP treated wood	19	1 500
N13	PCP treated wood	26	1 200
N14	PCP treated wood	27	2 500

TABLE 17 OCDD IN FINAL EFFLUENT

SAMPLE NO.	LOCATION	WEIGHT	OCDD CONC (µg/l)
T17	at discharge pipe	250	0.1
T18*	at discharge pipe	250	0.4
N17	at discharge pipe	250	0.02
N18	at discharge pipe	250	0.02

1 In this and subsequent tables all sample numbers starting with T refer to samples collected at the Truro plant and all sample numbers starting with N refer to samples collected at the Newcastle plant.

* Also analyzed by GC/MS.

TABLE 18 OCDD IN FILTERS

SAMPLE NO.	DESCRIPTION	WEIGHT	OCDD CONC (ng/g)
T12	carbon filter	25	36
T15	carbon filter	25	21
N12	polyurethane filter	20	1 800
N15*	polyurethane filter	25	5 500

TABLE 19 OCDD IN SOIL

SAMPLE NO.	LOCATION	WEIGHT	OCDD CONC (ng/g)
T4	Salmon R. riverbank	102	ND
T11	within plant	25	570
N7*	plant entrance	100	16
N10	excavation site	50	280
N11	within plant	25	1 500

TABLE 20 OCDD IN SEDIMENT

SAMPLE NO.	LOCATION	WEIGHT	OCDD CONC (ng/g)
T1	Salmon River	102	9.0
T2	Salmon River	102	0.1
T3	Salmon River	100	ND
T5	Salmon River	100	3.1
T6*	discharge stream	100	7.8
T7	discharge stream	100	51.
T8	discharge stream	100	30.
T9	discharge stream	100	4.2
T10	discharge stream	100	35.
N1	brook	100	7.9
N2	brook	100	19.
N3	brook	100	ND
N4	brook	100	6.9
N5	brook	100	6.6
N6	brook	100	7.6
N8*	brook	90	89.
N9	brook	50	13.

* Also analyzed by GC/MS.

Similar spiking experiments with soil and sediment samples collected in this survey gave highly variable results. This is attributed to the presence of a co-extractable material which altered the separation characteristics of the alumina and silica gel/celite/sodium sulfate chromatography columns and resulted in inconsistent recoveries. For this reason, no correction factors have been applied to reported concentrations. Creosote is the suspected source of co-contamination since it is also used extensively at both of the surveyed wood preserving operations.

5.3 Gas Chromatographic/Mass Spectrometric Analysis

Ten sample extracts (identified in Tables 15-20 with an asterisk) were re-analyzed by combined gas chromatography/mass spectrometry (GC/MS) in the selected ion monitoring (SIM) mode. Ions characteristic of OCDD, HCDD and TCDD were selected for scanning. The presence of OCDD was confirmed in all extracts, and in a few instances trace levels (unquantitated) of a heptachlorinated dioxin were indicated. Unfortunately, the creosote interferences noted previously also limited the usefulness of the GC/MS analyses. The particular constituents co-eluting with the TCDD and HxCDD have not been identified. The selectivity of the GC/MS system is restricted by the fact that, in most cases, the creosote content of the extracts is 2-3 orders of magnitude in excess of the total dioxin content. Several different gas chromatographic column packings were employed but none afforded acceptable resolution at the HxCDD and TCDD retention times. In addition, significant column deterioration was observed with repeated injections of highly contaminated samples.

5.4 High Resolution Mass Spectrometric Results

The analytical results obtained by the Laboratory Services Division (LSD) of Agriculture Canada for OCDD, HpCDD and HxCDD in six of the extracts analyzed by Wellington Science are listed in Table 21. LSD noted the following:

1. In those samples with appreciable levels of OCDD, measurable levels of the two heptachlorodioxin isomers were also found. The ratio of these 2 HpCDD isomers was approximately 1:2.
2. In samples N12 and T14 low levels of hexachlorodioxins were found. In the case of T14 (wood sample) the ratio of the 3 HxCDDs observed was 1:3:5. In N12 only one HxCDD isomer was detected.
3. Good comparability of OCDD results was only obtained between Wellington Science and Laboratory Services Division when the level of OCDD was low (<100 ppb). In those samples with OCDD levels above 1 ppm (Wellington results) the LSD results were appreciably higher. This may reflect solubility problems. Wellington Science used isooctane to dissolve PCDDs for EC/GC determinations and diethyl ether for GC/MS analysis. It was their contention that both solvents had a limited solubility for creosote and consequently the PCDD/creosote ratio in injected solutions was enhanced. LSD experience indicates that only benzene, toluene or xylene adequately solubilize OCDD. This may account for higher LSD results in "concentrated" solutions.

TABLE 21 DIOXINS (ng/g) IN SIX SAMPLES COLLECTED IN THE VICINITY OF THE TRURO AND NEWCASTLE WOOD PRESERVING PLANTS¹

SAMPLE NO.	TYPE	WEIGHT (g)	OCDD	HpCDD	HxCDD
T12	Carbon	25	31.2	7.8	ND
T14	Wood	19	2 500	580	36
T18	Effluent	250	0.32	ND	ND
N8	Sediment	90	84	120	ND
N12	Polyurethane	20	7 800	1 500	70
N14	Wood	27	3 400	1 100	ND

¹ Analysis performed by Laboratory Services Division, Agriculture Canada, Ottawa.

4. The ratio of the HxCDD isomers found in the T14 wood sample (i.e. 1:3:5) approximates that found in technical PCP. Also the 1:16:69 ratio of HxCDD:HpCDD:OCDD corresponds approximately to the technical PCP ratio. However, results for the polyurethane foam filter sample indicate that some preferential concentration of OCDD/HpCDD was occurring (also only one HxCDD isomer was observed in this sample).

6 DISCUSSION

6.1 Accuracy of Reported Values

In evaluating the significance of reported dioxin concentrations it is important to note that the average percent recovery realized by Wellington Science for OCDD in spiked sediments was only 37%. Therefore, a more accurate picture of actual dioxin levels may be obtained by doubling or even tripling the values reported. Laboratory Services Division (LSD) did not work-up the original samples, but rather were provided with dried extracts and therefore are unable to report percent recoveries.

Levels of the hexa- and hepta-isomers in the technical grade PCP used at the two plants has been predicted relative to the measured concentration of OCDD. The approximation is based on the relative content of OCDD, HpCDD and HxCDD in various PCP formulations previously reported and presented in Table 4 (Cochrane, 1981). The total heptachlorinated content is approximately the same order of magnitude as the octachlorinated isomer while the hexachlorinated materials are one order of magnitude less.

In a similar manner the HxCDD and HpCDD content has also been estimated* relative to OCDD levels for other matrices on the assumption that the hexa/hepta/octa ratio remains approximately unchanged.

6.2 Dioxins in Technical Grade Pentachlorophenol

The levels of OCDD measured in the technical grade PCP employed at the Truro and Newcastle wood preserving plants were 220 000 and 120 000 ng/g respectively. HpCDD and HxCDD levels were not reported but are estimated to be 100 000 and 10 000 ng/g respectively. The concentrations of dioxin impurities are significant but typical for PCP formulations of this type.

The Truro plant uses approximately 1 500 000 litres of 5% PCP solution per year with a potential dioxin throughput of 19 000 g OCDD, 9 000 g HpCDD and 600 g HxCDD. Using approximately 1 100 000 litres of 5% PCP solution per year the potential dioxin throughput per year at the Newcastle plant is 14 000 g OCDD, 7 000 g HpCDD and 500 g HxCDD.

6.3 Dioxins in Wood Products

Analysis of samples T14 and N14 from the surfaces of treated wood products by Wellington Science showed OCDD levels at 1 500 and 2 500 ng/g respectively.

* Estimates of HpCDD and HxCDD are based on LSD values reported in Table 4. They are crude approximations based on the assumption that dioxin ratios measured in the technical PCP are unchanged on environmental exposure. There will undoubtedly be some change but the extent is unknown.

The same samples were reanalyzed by LSD and found to contain HxCDD and HpCDD in addition to OCDD. Levels measured in sample T14 were 2 500 ng/g OCDD, 580 ng/g HpCDD and 36 ng/g HCDD. Levels of OCDD and HpCDD in sample N14 were 3 400 and 1 100 ng/g respectively. No HxCDD was detected in this latter sample. Although the the OCDD levels in the wood are relatively innocuous, HxCDD and HpCDD isomers are present at significantly high concentrations.

The dioxin contaminated wood can pose an environmental problem. Contamination of soil in areas where it is stored awaiting delivery is possible. In addition, soil at the base of PCP treated utility poles or other similar products may become contaminated.

However, once the treated wood is exposed to sunlight the OCDD is expected to degrade quite rapidly (Arsenault, 1976), and the hexa and hepta isomers should photolyze at an even more accelerated rate.

6.4 Dioxins in Effluents

Two final effluent samples were taken at the discharge pipes at both plants. The final effluent at Truro contained an average of 0.25 µg/l OCDD. This number was confirmed by LSD which reported a similar result for OCDD; neither the hexa or hepta isomers were detected. Both final effluent samples at Newcastle contained 0.02 µg/l OCDD.

The effluent at Truro is discharged to a stream which empties into the Salmon River. Effluent at Newcastle empties into a brook which eventually enters the Miramichi River.

While the dioxin levels in these effluents do not appear to be toxicologically significant they are contributing to PCDD buildup in the underlying sediments of the discharge streams and rivers. Consequently it is desirable to reduce or eliminate the quantities of dioxins entering the environment in this manner.

Although total effluent volumes are available for both operations the volumes attributable solely to PCP processing are not known for either plant. Therefore, an estimate of dioxin release to the environment via effluent discharge is not possible.

6.5 Dioxins in Treatment Systems

Both the Truro and Newcastle plants employ some type of filtration procedure in their effluent treatment systems. Four columns of activated carbon are used at Truro while Newcastle employs polyurethane foam filters. Both types of filters were sampled and analyzed for dioxin content.

The activated carbon samples (T12 and T15) from Truro contained 36 and 21 ng/g OCDD respectively. LSD reported 31 ng/g OCDD in sample T12 as well as 7.8 ng/g HpCDD.

The levels of dioxins in these filters are not sufficiently high to pose a disposal problem. However, other filters may be more contaminated depending on their service history. Disposal of the spent carbon should be conducted with due consideration of potential environmental problems.

Presently a considerable quantity of spent carbon, sealed in 45 gallon steel drums, is being stored awaiting disposal.

The levels of OCDD in the polyurethane foam filters employed at Newcastle (samples N12 and N15) reported by Wellington Science are 1 800 and 5 500 ng/g respectively. Sample N12 was reanalyzed by LSD and found to contain 7 800 ng/g OCDD.

These results are two orders of magnitude above the Truro levels and disposal obviously requires special precautions.

6.6 Dioxins in Soils

Soil samples were collected from a number of locations in the vicinity of both plants. At Truro, two soil samples were taken, one within the plant and one from the Salmon River riverbank. No OCDD was detected in the riverbank soil while soil within the plant contained 567 ng/g OCDD and an estimated 100 ng/g HpCDD and 10 ng/g HxCDD.

At Newcastle, surface soil samples were taken at the plant entrance, within the plant and at an excavation site outside the plant property. Levels of OCDD were measured at 16, 1 500 and 280 ng/g respectively. Estimates of HpCDD and HxCDD content at the most contaminated site are 1 000 and 100 ng/g respectively.

The OCDD concentrations at the most contaminated sites in Truro and Newcastle are elevated but on their own should not pose a concern. However, assuming the predicted quantities of HpCDD and HxCDD content

approximate the actual situation, these levels are sufficiently high to warrant concern. Direct environmental risks are limited as these sites are within the plant confines. The only biota expected to be exposed to such contaminated sites are various insect species. It should be noted that contaminated soil may enter receiving waters by way of rainwater runoff and wind erosion.

If the soil in the contaminated areas is particularly sandy, groundwater contamination could occur. However, very little vertical migration is expected and most of the dioxin should remain in the top six inches of soil.

Because dioxins are resistant to degradation the PCDD levels in the soil are expected to persist for several years risking potential biotic exposure and accumulation.

6.7 Dioxins in Sediments

The levels of OCDD in the Truro discharge stream sediments range from 36 ng/g at the base of the effluent pipe to 30 ng/g at the point of entry to the Salmon River. The OCDD levels in the river sediments range from 9.0 ng/g near the mouth of the discharge stream to 0.1 ng/g approximately 0.5 km downstream. OCDD was not detected approximately 1 km upstream from the discharge stream. The levels of HpCDD and HxCDD were not quantitatively determined but are estimated to be about 10 and 1 ng/g respectively in the discharge stream and 1 and 0.1 ng/g respectively in the Salmon River sediments.

The effluent at the Newcastle plant discharges into a brook which eventually enters the Miramichi River. All sediment samples were taken from the brook proper, none were collected from the Miramichi River.

Levels in the sediments ranged from 7.6 ng/g OCDD directly under the discharge pipe to 87 ng/g OCDD at one of the more distant sampling sites (Sample N8). With this latter exception all values were below 20 ng/g. The value for N8 was confirmed by LSD, which measured its OCDD content at 84 ng/g and its HpCDD content at 120 ng/g.

Dioxin levels in stream sediments at the two plants would not appear to represent an environmental hazard. There are no biota, except possibly a few aquatic worms, inhabiting the tested areas and consequently exposure is restricted.

The behaviour of dioxins in sediments is dependent on their own physical and chemical properties as well as the physical and chemical properties of the sediments. Because dioxins in sediments are very stable they are expected to persist in these areas. However, with continued improvement in waste management practices, the levels of dioxins leaving the plants are expected to decrease. As dioxins are practically insoluble in water and are relatively immobile in sediments, very little transport and relocation will occur. Migration will be mainly a function of movement of sediment particles on which they are adsorbed.

7

RECOMMENDATIONS

1. While dioxin contamination in sediments collected in the immediate vicinity of wood preserving plants at Truro, Nova Scotia, and Newcastle, New Brunswick, has been established, the sampling program was too limited to allow a zone of contamination/influence to be defined. In order to alleviate this information gap, it is recommended that:
 - (a) Dioxin levels in Salmon River water and sediment be determined.
 - (b) Dioxin levels be determined in the water and sediments of the Miramichi River in the vicinity of the point of entry of the drainage brook.
 - (c) Biota inhabiting dioxin contaminated portions of the Salmon and Miramichi Rivers be examined to determine dioxin content.
 - (d) Terrestrial and aquatic plants growing in contaminated areas be analyzed to evaluate dioxin uptake.
 - (e) Ground water in both areas be sampled to determine whether migration of dioxins from the contaminated soil has occurred.

2. On the basis of the analytical results reported in this survey, the analytical technique should be improved. Method development work should be instituted to modify and refine the procedure to increase the recovery efficiency and eliminate interferences, particularly those arising from creosote contamination.
3. Future dioxin investigations at these two operations and at a similar operation in Clarendville, Newfoundland should include studies on HpCDD and HxCDD isomers. OCDD values afford an indication of overall dioxin content but the compound itself is rather innocuous.
4. At both processing facilities additional effluent treatment is recommended to complement that already installed. This would not only limit the environmental release of dioxins but also control discharge of creosote, PCP and impurities associated with these wood treatment chemicals.
5. Consideration should be given to regulating a maximum acceptable level of dioxins in the technical grade pentachlorophenol used for wood preservation.
6. Studies on polynuclear aromatic hydrocarbon (PAH) contamination resulting from the creosoting operations at these plants should be conducted.

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