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PCDDs/PCDFs in Soils at a Former Tannery Site-- Profiles as Evidence of PCP Contamination

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PART VI: Site Assessment

Chapter 12

PCDDS/PCDFS IN SOILS AT A FORMER TANNERY SITE - PROFILES AS EVIDENCE OF PCP CONTAMINATION

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ABSTRACT

PCDDs/PCDFs contamination in soils at a former tannery site in Eastern Massachusetts was found to be widespread. PCDDs/PCDFs concentrations (the sum as (Cl_4 – Cl_8); tetra-octachloro totals) in the majority of the soil samples (17/32) far exceeded concentrations (10-1000 times) typically found in soils in industrial/urban settings worldwide (1-10 ppb). The distribution pattern of PCDDs/PCDFs in site soils in combination with highly elevated concentrations did not indicate significant influences from off-site sources (e.g. aerial distribution pattern). Widespread chromium contamination in soils often collocated with elevated concentrations of OCDD suggested that both contaminants could be attributed to a common industrial source: the former tannery operations. (total chromium concentrations in the soil samples ranged from 22.2 – 3,457 mg/kg).

Elevated PCDDs/PCDFs concentrations predominated by OCDD were most likely attributable to the historical use of pentachlorophenol (PCP) and/or products containing PCP. PCP was likely used as a fungicide/biocide in tannery processes that took place at the site. PCP origins were established through comparison of PCDDs/PCDFs profiles found in soils to those characteristic of PCP products as reported in the open literature (PCDDs/PCDFs profiles found in PCP products are predominated by hexa, hepta and octa congeners). Elevated OCDD concentrations present in site soils may not be solely attributable to historical use of PCP. OCDD, which is the most common PCDDs/PCDFs

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congener present as a contaminant (artifact of PCP production chemistry) in PCP may also be formed photochemically. The latter reaction takes place over time in surface soils with PCP serving as the precursor compound. The extent to which this reaction has contributed to OCDD levels found in soils has been estimated by comparison of profiles found in site soils to those characteristic of commercial PCP products.

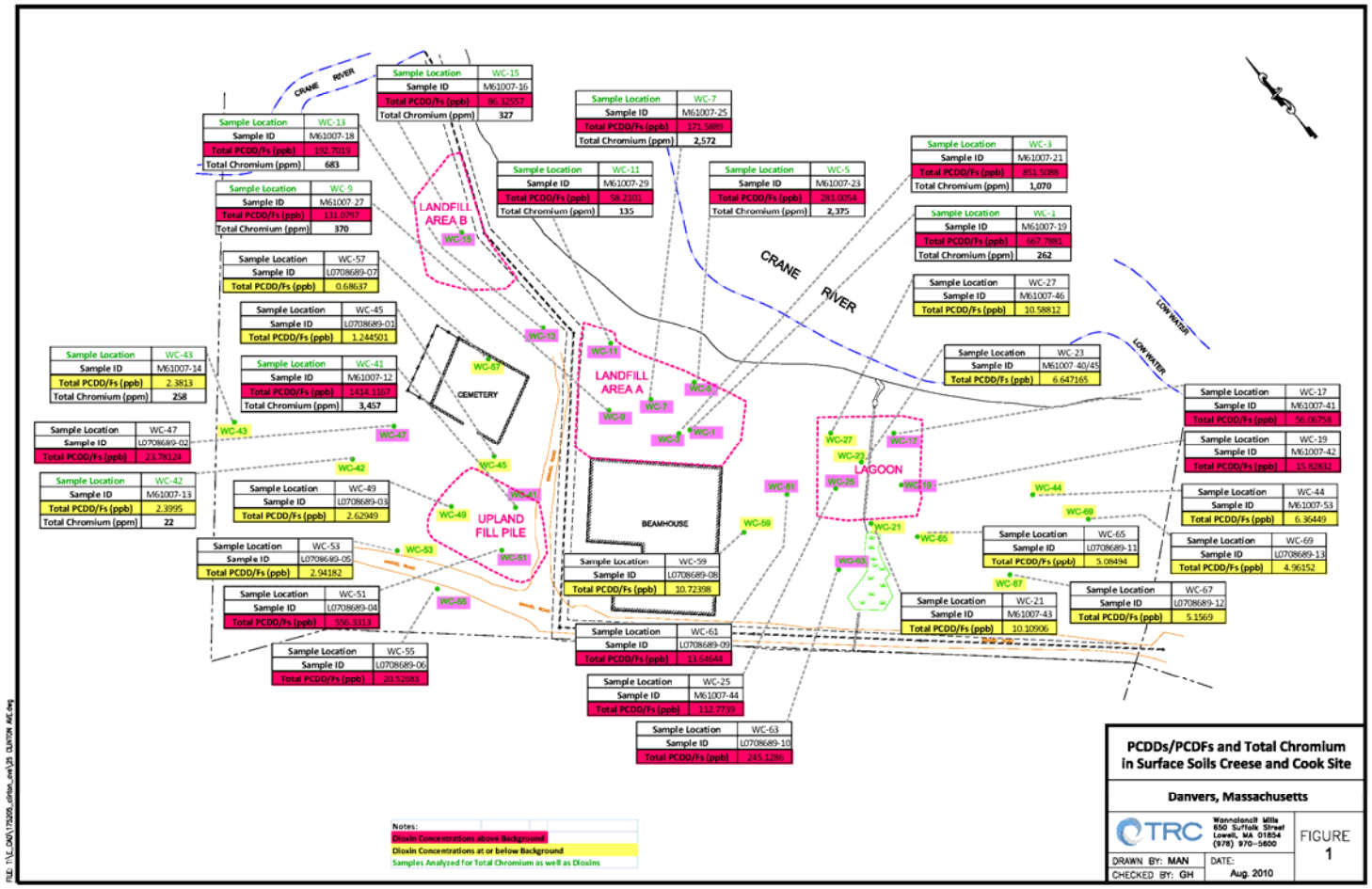
Keywords: PCDDs, PCDFs, tannery site, soil

1. INTRODUCTION

PCDDs/PCDFs contamination in soils at a former tannery site in Eastern Massachusetts was found to be widespread. PCDDs/PCDFs concentrations in the majority of the soil samples far exceeded concentrations typically found in soils in industrial/urban settings worldwide. Widespread chromium contamination in these same soils collocated with elevated concentrations of OCDD suggested that both contaminants could be attributed to the former tannery operations. PCP was likely used as a fungicide/biocide in tannery processes that took place at the site. Historically, pentachlorophenol was often used to prevent growth of bacteria on the animal skin prior to mineral tanning, using chromium sulfate. PCDDs profiles in these highly contaminated soils were compared to profiles characteristic of commercial pentachlorophenol (PCP) and PCP containing products. Results of these analyses provide evidence for the presence of PCP in soils on site. OCDD formation via photochemical reactions from precursor PCP is also suggested.

2. MATERIALS AND PROCEDURE

Surficial soils were sampled across the property of the former tannery site. Refer to Figure 1 for the actual locations of sampling sites. Analyses were performed using high-resolution gas chromatography in combination with high resolution mass spectrometry. Details of the sample collection and laboratory analyses are described in Orchard Farm Trust (2007). PCDDs/PCDFs profiles were examined in soil samples with elevated concentrations of both chromium and PCDDs/PCDFs. These profiles were compared to PCDDs/PCDFs profiles found in a number of PCP products as reported in the open literature.


CRANE RIVER
LANDFILL AREA B
LANDFILL AREA A
CEMETERY
BEAMHOUSE
LAGOON
UPLAND FILL PILE
LOW WATER
PCDDs/PCDFs and Total Chromium in Surface Soils Creese and Cook Site
Danvers, Massachusetts
TRC
Wannalancit Mills 650 Suffolk Street Lowell, MA 01854 (978) 970-5600
FIGURE 1
DRAWN BY: MAN
CHECKED BY: GH
DATE: Aug. 2010
Notes:
Dioxin Concentrations above Background
Dioxin Concentrations at or below Background
Samples Analyzed for Total Chromium as well as Dioxins

3. DATA AND ANALYSIS

Results for the thirty-two soil samples expressed as total PCDDs/PCDFs (the sum of Cl_4 – Cl_8) in units of ppb are shown in Figure 1. The majority of the soil samples (17/32) far exceeded concentrations (10-1000 times) typically found in soils in industrial/urban settings worldwide (1-10 ppb) (Jones and Duarte-Davidson, 1997, Im et al, 2002, Birmingham, 1990, Creaser et al, 1990, Pearson et al, 1990). The distribution pattern of PCDDs/PCDFs in site soils in combination with highly elevated concentrations did not indicate significant influences from off-site sources (e.g. aerial distribution pattern). Twelve (12) of the seventeen (17) soil samples showing the highest dioxin levels were concentrated in areas identified as the locations of former tannery operations (see Figure 1). Widespread chromium contamination in these same soils often collocated with elevated concentrations of OCDD suggested that both contaminants could be attributed to the former tannery operations. Total chromium concentrations in the soil samples as shown in Figure 1 ranged from 22.2 – 3,457 mg/kg. Results for the most highly contaminated soil samples are shown in Table 1 on a congener sum specific basis (Cl_4-Cl_8PCDDs/PCDFs). The profiles shown are dominated by heptaCDDs and OCDD. Profiles for seven (7) of these soils samples expressed on a % basis (% contribution of concentration of each congener to the total concentration of Cl_6-Cl_8PCDDs) are shown in Figure 2.

All seven (7) of these soil samples also contained total chromium at concentrations > 260 ppm (mg/kg) and represent locations used for former tannery processes (Orchard Farm Trust, 2007). Profiles representing three (3) commercial PCP containing products expressed on a % basis (% contribution of concentration of each congener to the total concentration of Cl_6-Cl_8PCDDs) are shown in Figure 3. The profiles shown in Figure 3 represent actual results from analyses of thirty-four (34) individual batches of technical PCP produced by three (3) separate manufacturers (Singh et al, 1985).

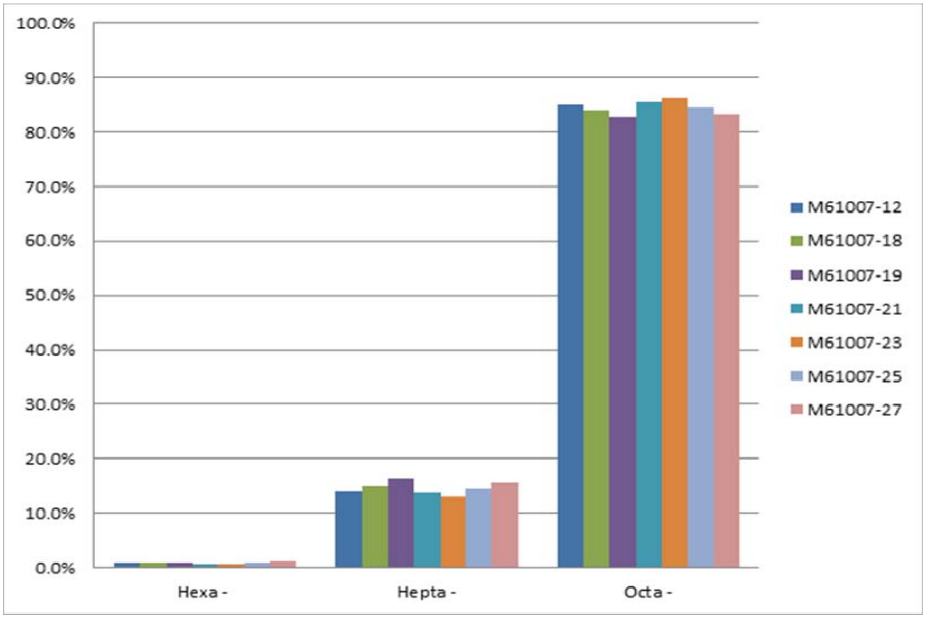


Figure 2: PCDD (Cl_6- Cl_8) Profile of Soil Samples with High Chromium (>260ppm)

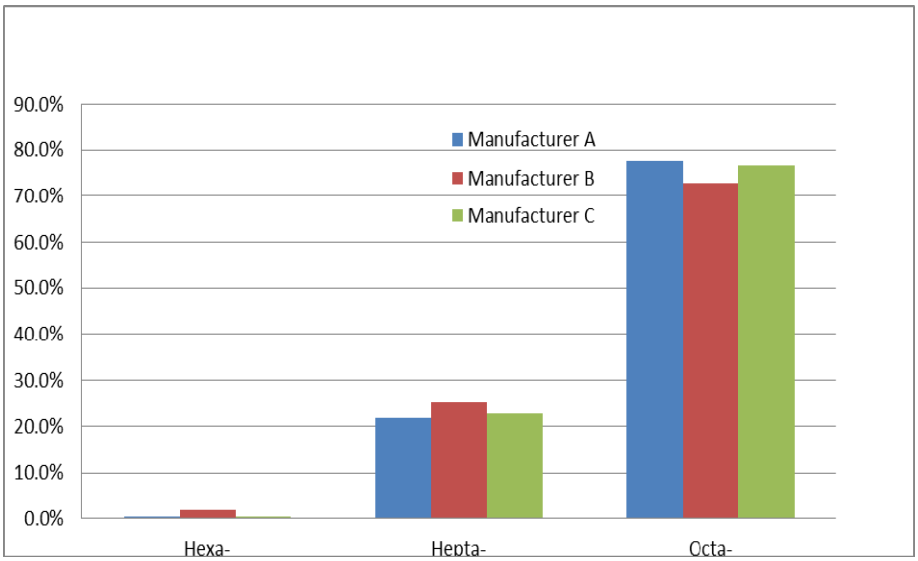


Figure 3. PCDD (Cl_6- Cl_8) Profile of Technical Grade PCP Products

Table 1: Summary of Results – Soil Samples

Concentrations ranging from 91 ppb to 300 ppb

Sample ID	L0708689-10	M61007-18	M61007-23	M61007-25	M61007-27	M61007-44	AVERAGE
Sample Collection Date	6/18/2007	11/21/2006	11/21/2006	11/21/2006	11/21/2006	11/22/2006	Concentration
Analyte							
OCDD	**182**	**158**	**218**	**136**	**98.9**	**94.4**	147.883
OCDF	**16.1**	**1.1**	**11.8**	**4.23**	**4.4**	**0.826**	6.409
Total TCDDs	**0.0278**	**0.0211**	**0.116**	**0.032**	**0.0524**	**0.0165**	0.044
Total PeCDDs	**0.14**	**0.115**	**0.12**	**0.128**	**0.168**	**0.119**	0.132
Total HxCDDs	**1.9**	**1.69**	**1.8**	**1.4**	**1.37**	**1.06**	1.537
Total HpCDDs	**29.2**	**28.5**	**32.9**	**23.3**	**18.5**	**13.9**	24.383
Total TCDFs	**0.0668**	**0.0118**	**0.0334**	**0.015**	**0.0273**	**0.0149**	0.028
Total PeCDFs	**0.194**	**0.04**	**0.126**	**0.0939**	**0.102**	**0.0305**	0.098
Total HxCDFs	**2.3**	**0.794**	**2.41**	**1.08**	**1.28**	**0.407**	1.379
Total HPCDFs	**13.2**	**2.43**	**13.7**	**5.31**	**6.28**	**2**	7.153
Total PCDDs	213.2678	188.3261	252.936	160.86	118.9904	109.4955	173.979
Total PCDFs	31.8608	4.3758	28.0694	10.7289	12.0893	3.2784	15.067
Total Dioxins and Furans	245.1286	192.7019	281.0054	171.5889	131.0797	112.7739	189.046

Concentrations greater than 500 ppb

Sample ID	L0708689-04	M61007-12	M61007-19	M61007-21	AVERAGE
Sample Collection Date	6/18/2007	11/22/2006	11/21/2006	11/21/2006	Concentration
Analyte					
OCDD	**458**	**1180**	**502**	**683**	705.750
OCDF	**3.13**	**9.89**	**30.4**	**24.3**	16.930
Total TCDDs	**0.0388**	**0.0956**	**1.08**	**0.747**	0.490
Total PeCDDs	**0.247**	**0.454**	**0.54**	**0.437**	0.420
Total HxCDDs	**6.48**	**12.5**	**6.24**	**5.8**	7.755
Total HpCDDs	**80.1**	**195**	**98.7**	**110**	120.950
Total TCDFs	**0.0255**	**0.0391**	**0.0871**	**0.0638**	0.054
Total PeCDFs	**0.18**	**0.288**	**0.301**	**0.261**	0.258
Total HxCDFs	**2.8**	**4.85**	**7.34**	**5.6**	5.148
Total HPCDFs	**5.33**	**11**	**21.1**	**21.3**	14.683
Total PCDDs	544.8658	1388.0496	608.56	799.984	835.365
Total PCDFs	11.4655	26.0671	59.2381	51.5248	37.074
Total Dioxins and Furans	556.3313	1414.1167	667.7981	851.5088	872.439

4. CONCLUSION

The most dominant congeners in all of the batch samples of PCP analyzed were Cl_6-Cl_8PCDDs. The predominance of these congeners in both PCP products and site soils in combination with the profiles shown in Figures 2 and 3 strongly suggests PCDD contamination in soils at the former tannery site is attributable to PCP containing products.

Elevated PCDDs/PCDFs concentrations were dominated by OCDD likely attributable to the historical use of pentachlorophenol (PCP) and/or products containing PCP. Elevated OCDD concentrations present in site soils are likely not solely attributable to historical use of PCP. OCDD, which is the most common PCDDs/PCDFs congener present as a contaminant (artifact of PCP production chemistry), in PCP may also be formed photochemically in soils , with PCP serving as the precursor compound (Holt et al, 2008, Liu et al, 2002, Lampariski et al, 1980).

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