

Dioxin Degradation and Metals Biovolatilization at a Former Wood Treating Site

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Presentation



Site History Dioxins and PCP

Background

Results

Metals

Biovolatilization





Wood Preservers

Operated from 1961-73

Site used Chromated Copper Arsenate (CCA)

>1961-1967

Switched to Pentachlorophenol (PCP) in Diesel

> 1967-1970

Managed waste chlorophenol sludge by burning

Fire destroyed the plant in 1970

Site was bulldozed

Sawing operations continued on Site until 1973

Site History



First Environmental Investigations 1989-1993

> 20 years after closing

Minor Excavation of Source in 1993

Data for Arsenic and PCP is reliable

- > Consistent with current analytical methods
- Provides baseline for comparison to recent data

Dioxins first analyzed in 1995 Additional dioxin analyses from 2003 to 2015

PCP and Dioxins







Pentachlorophenol (PCP)

Octachlorodibenzodioxin (OCDD)

Site has unusually high dioxin concentrations due to burning of the chlorophenol sludge

Air deposition of smoke particulate, and bulldozing after fire in 1970 spread the dioxins around

Dioxins and TEQ



There are 75 different 'dioxins' and 135 different 'furans'

210 Compounds evaluated compared to most toxic dioxin
 2,3,7,8-TCDD

Toxicity Equivalence Factor (TEF)

Compound	2005 TEF
Polychlorinated dibenzo-p-dioxins (PCDDs)	
2,3,7,8-Tetrachloro-dibenzo-p-dioxin (TCDD)	1
1,2,3,7,8-Pentachloro dibenzo-p-dioxin (PeCDD)	1
1,2,3,4,7,8-Hexachloro- dibenzo-p-dioxin (HxCDD)	0.1
1,2,3,6,7,8-Hexachloro- dibenzo-p-dioxin (HxCDD)	0.1
1,2,3,7,8,9-Hexachloro- dibenzo-p-dioxin (HxCDD)	0.1
1,2,3,4,7,8,9-Heptachloro- dibenzo-p-dioxin (HpCDD)	0.01
Octachloro-dibenzo-p-dioxin (OCDD)	0.0003

Dioxin Mass and TEQ Contribution Highest Result on Site (137,700 pg/g Dioxin TEQ)







Dioxins can be created during manufacture of chlorinated organics

- Pentachlorophenol (PCP) and Pesticides 2,4-D and 2,4,5-T
- > From 1950-1973 Lysol used a chlorinated solvent contaminated with dioxins
- > Manufacturing process alterations to prevent formation and/or to remove dioxins
- Pesticides such as 2,4-D are still widely used
 - Not protected by patent
 - Low cost manufacturers in India and China
 - Tend not to include final steps to remove dioxins

Dioxins are also created whenever something containing chlorine is burned at low temperature

Pulp and paper mills in BC are not allowed to burn wood that has been in saltwater



Burning of PCP sludge creating dioxins

Air deposition from smoke and particulates
 Site operations and materials handling
 Fire at Site in 1970
 Bulldozing of soil after fire
 Tracking off site by equipment

Dioxin sampling focused on shallow soil within disturbed area (airphotos)

2015 Investigation Delineate Extent of Contamination



16 hectares (40 acres)

≻650 m by 250 m

Geophysics Survey for Electrical Anomalies Three Rounds of Sampling

Soil, Groundwater, Sediment and Surface Water

Primary Contaminants of Concern

Dioxins, Metals, Chlorophenols and Hydrocarbons

Essentially all samples analyzed for all contaminants

Site Conditions





Soil Sampling Direct Push Technique





Soil Sample Locations 299 Samples for Dioxins





Dioxins – Results > 4 pg/g Alberta Tier 1 Standard – 205 Samples





Dioxin Results > 250 pg/g Alberta Tier 1 Natural Area – 41 Samples





Dioxin Results > 1,000 pg/g – 27 Samples US EPA Draft Industrial Guideline is 950 pg/g







Minimal Groundwater Contamination

- Impacts are limited to source area
- > PCP, Dioxins and Metals
- Secondary contaminants related to biological activity

Primarily a shallow soil issue

PCP Degradation in Soil Half-Life of 2 years over 22 year interval





Highest PCP in 2015 at ground surface

Consistent with Anaerobic Biodegradation

Dioxin-TEQ Approximately 10 Year Interval



223 Analyses by EPA Method1613B (HRGC-GCMS)

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and

146 Analyses EPA Method 4435 (Calux Bioassay)

Total Dioxin Mass Decreased and Shifted to Less Chlorinated Dioxins





Total dioxin results are indicative of Reductive Dechlorination Supports interpretation of degradation based on TEQ data



CCA was only metals based preservative used

Never Arsenic by itself

Chromated Copper Arsenate has fixed molar ratio

As: Cr: Cu 1:2.0:0.7 Molar Ratio 1:1.4:0.6 Mass Ratio

Chromium and Copper concentrations are much lower than expected compared to 1993 Arsenic maximum



Metals Concentrations



20 years after Site closed, most of Chromium and Copper was already gone

At 50 years, Chromium and Copper are now near background concentrations

Arsenic $t_{1/2} = 8$ years



Not due to changing analytical methods

Method used in early work was similar to current method

Groundwater Transport

- Also does not explain lower concentrations
- High initial metals mass in soil
- >Not enough metals mass can be removed in groundwater
 - 10 m/year groundwater flow velocity
 - 50 years since contamination
 - Calculations based on 200 m³ soil volume

Mass Balance Calculations for Metals





Mass Balance Calculations for Metals







Arsenic was used as a pigment for wallpaper

- 1893 Italian physician 'Gosio gas'
 - Trimethylarsine and other forms

Recent work shows importance of Arsenic biovolatilization
e.g. Mestrot, 2013 and Wang, 2014
Being evaluated for remediation of Arsenic contaminated soils

Arsenic biovolatilization in DDT contaminated soils > Edvantoro, 2004



Conclusions

Wood treating site closed for 50 years

Dioxins

Pentachlorophenol (PCP)

➢ Metals (As, Cr, Cu)

Chlorinated organics biodegrading

Reductive Dechlorination

- Highest PCP results at ground surface

Dioxin-TEQ and total dioxin mass are decreasing
 Metals biovolatilization

Known process for Arsenic for over 120 years

Apparently faster for Chromium and Copper