

Proposal to Amend Remediation Standards N.J.A.C. 7:26D to add 2,3,7,8-Tetrachloro-dibenzo-*p*-dioxin

> External Stakeholder Meeting June 10, 2014

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Purpose

- To amend the 2008 Remediation Standards (N.J.A.C. 7:26D) by adding a soil remediation standard for dioxin
- Based on Feb. 2012 IRIS publication of an Oral Reference Dose (RfD), representing the first time a Tier I Toxicity value became available.





Agenda

- 2,3,7,8-TCDD (dioxin) and related dioxin-like compounds (DLC)
- Evaluation of dioxin through the World Health Organization (WHO) Toxic Equivalency (TEQ) Approach for mixtures of dioxins, furans and dioxin-like PCBs
- Primary sources of dioxins
- Dioxin investigations in NJ
- Historical dioxin remedial goals/action levels
- Proposed NJDEP soil remediation standard for dioxin
- Background conditions





What is "Dioxin"?

- The term dioxin is commonly used to refer to a mixture of chlorinated dioxin and furan congeners of similar structure and related toxicity.
- There are up to 75 congeners of chlorinated dioxins and 135 congeners of chlorinated furans, for a total of 210.
- 17 Tetra Octa chlorinated Dioxin/Furan congeners with chlorine attached at the 2,3,7 and 8 positions are the focus of environmental regulation due to related toxicity to 2,3,7,8-tetrachloro-dibenzo-p-dioxin (2,3,7,8-TCDD), the most toxic congener.
- 12 Dioxin-like PCBs



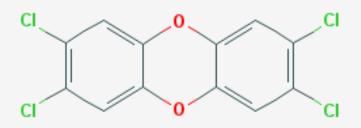


2,3,7,8-Tetrachlorodibenzo-p-dioxin

CAS # 1746-01-6

2,3,7,8-TCDD, dioxin

Poly-Halogenated, Poly-Aromatic Hydrocarbon

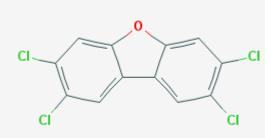


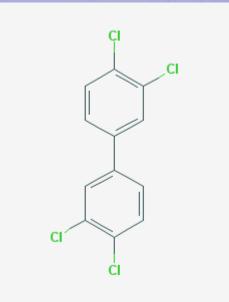




Chlorinated Dibenzo Furans and Dioxin-like PCBs

2,3,7,8-tetrachloro-dibenzo furan (2,3,7,8-TCDF) 3,3',4,4'-tetrachloro biphenyl (PCB 77)









Formation of Chlorinated Dioxins, Furans and Dioxin-like PCBs

- Byproduct of specialty chemical manufacturing, particularly processes involving chlorinated phenols, chlorinated benzenes, and the manufacture of chlorinated insecticides/herbicides and chlorine-based wood preservatives
- Combustion sources (particularly uncontrolled or incomplete combustion of chlorinated substances including PCBs and plastics)
- Pulp and Paper bleaching operations involving chlorine-containing chemicals (elemental chlorine, hypochlorite and others)
- Metal smelting

References: USEPA Dioxins, 1980; EPA 2000 Emergency Planning and Community Right to Know Act – Section 313; Pulp, Paper and Paperboard Mill Rule, 40 CFR Ch.1 (7-0103 Edition)



Characteristics of 2,3,7,8-TCDD

- Colorless, odorless, crystalline solid at room temperature
- Strongly Hydrophobic, e.g., Solubility in Water, 0.0000002 g/liter; versus *o*-dichlorobenzene, 1.4 g/liter
- Highly lipophilic, binds strongly to organic matter
- Highly bioaccumulative in food web
- Very stable and highly persistent in environment
- Recalcitrant to chemical and biological degradation processes





Toxicity Information on 2,3,7,8-TCDD

- A potent toxicant to both wildlife and humans through a common biochemical mechanism, known as the Aryl hydrocarbon Receptor (AhR) producing both cancer and non-cancer effects.
- Shown to pose hazards in areas of development, reproduction, immune system functions, endocrine system functions and cancer.
- Characterized by EPA as "carcinogenic to humans" and other dioxin-like congeners are considered "likely to be carcinogenic to humans".
- Chronic and acute exposures in humans may result in chloracne, a severe and persistent skin rash

Reference: http://www.epa.gov/ncea/pdfs/dioxin/nas-review





Dioxin, Furan and Dioxin-like PCB Congeners of Concern

Compound	WHO 2005 TEF	Compound	WHO 2005 TEF
chlorinated dibenzo-p-dio,	xins	non-ortho substituted PCE	35
2,3,7,8-TCDD	1	PCB 77	0.0001
1,2,3,7,8-PeCDD	1	PCB 81	0.0003
1,2,3,4,7,8-HxCDD	0.1	PCB 126	0.1
1,2,3,6,7,8-HxCDD	0.1	PCB 169	0.03
1,2,3,7,8,9-HxCDD	0.1	mono-ortho substituted PCBs	
1,2,3,4,6,7,8-HpCDD	0.01	105	0.00003
OCDD	0.0003	114	0.00003
		118	0.00003
chlorinated dibenzofurans		123	0.00003
2,3,7,8-TCDF	0.1	156	0.00003
1,2,3,7,8-PeCDF	0.03	157	0.00003
2,3,4,7,8-PeCDF	0.3	167	0.00003
1,2,3,4,7,8-HxCDF	0.1	189	0.00003
1,2,3,6,7,8-HxCDF	0.1	105	0.00005
1,2,3,7,8,9-HxCDF	0.1	Reference: Van den Be	ra et al 2006
2,3,4,6,7,8-HxCDF	0.1		Organization Re-evaluation
1,2,3,4,6,7,8-HpCDF	0.01	of Human and Mammal	
1,2,3,4,7,8,9-HpCDF	0.01		d Dioxin-like Compounds
OCDF	0.0003		
	010005		

ToxSci Advance Access, 7 July 2006



Calculation of TCDD TEQ

$$TEQ = \sum_{i=1}^{n} (C_i \times TEF_i)$$

- *C_i* Individual TCDD or DLC concentration in environmental media.
- *TEF_i* Toxicity Equivalence Factor assigned for TCDD or the DLC.
- TEQ TCDD toxicity equivalence.

Reference:

http://www.epa.gov/superfund/health/contaminants/dioxin/pdfs/Use of Dioxin TEFs in Calculating Dioxin TEQs at CERCLA and RCRA Sites.pdf, May 2013





Example TCDD TEQ Calculation

Sample calculation:

Using the 2005 WHO TEFs (Van den Berg et. al. 2006), the TEQ for each DLC is estimated by multiplying the measured DLC concentration by the TEF corresponding to the DLC. The TEQ for the media sample is determined by summing the individual TEQ for TCDD with DLCs in the mixture. For example:

Individual concentration of TCDD as	nd DLCs in an environmental sample:
2,3,7,8 TCDD	
2,3,4,7,8- PeCDF	30 ppt
PCB 126	

TEFs:

2,3,7,8 TCDD	1
2,3,4,7,8- PeCDF	0.5
PCB 126	0.1

Individual TEQ:

2,3,7,8 TCDD	$\dots 10 \text{ ppt} \times 1 = 10 \text{ ppt} \text{ TEQ}$
PCB 126	

Total TEQ 10 ppt + 15 ppt + 2 ppt = 27 ppt TEQ



TEQ Approach continued

- Early dioxin assessments were for single congener - > 2,3,7,8-TCDD
- 1987 USEPA introduces use of the Toxic Equivalent Quotient (TEQ) Approach to address mixtures of chlorinated dioxins and furans
- Updated over the years, most recently, "Recommended Toxicity Equivalence Factors (TEFs) for Human Health Risk Assessments of 2,3,7,8-Tetrachlorodebenzo-p-dioxin and Dioxin-Like Compounds", USEPA, December 2010

http://www.epa.gov/raf/files/tefs-for-dioxin-epa-00-r-10-005-final.pdf

• Specific Superfund Guidance: "Use of Dioxin TEFs in Calculating Dioxin TEQs at CERCLA and RCRA sites", May 2013

http://www.epa.gov/superfund/health/contaminants/dioxin/pdfs/Use_of_Dioxin_TEFs_in_Calculating_Dioxin_TEQs_at_CERCLA_and_RCRA_Sites.pdf



What brought this concern to New Jersey?

- Discovery of significant levels of 2,3,7,8-TCDD (dioxin) in fish and crab tissue in coastal waters of NJ (1980 - 1985)
- Subsequent discovery of high levels of 2,3,7,8-TCDD in soil at several sites in NJ through Federal and State Phase I and II Dioxin Investigations
- Former Diamond Shamrock (aka: Diamond Alkali facility) at 80 Lister Avenue in Newark, NJ - - > produced large quantities of the defoliant Agent Orange, a 50:50 mixture of 2,4,5-Trichlorophenoxy acetic acid (2,4,5-T) and 2,4,-Dichlorophenoxyacetic acid (2,4-D). A key precursor compound was 2,4,5-Trichlorophenol (2,4,5-TCP), known to be contaminated with high levels of dioxin.
- Discovery of 2,3,7,8-TCDD in high levels in Passaic River sediments





Dioxin Site Investigations

- Tested for only when suspected, based on site history
- Special analysis (not listed on PP+40 or TCL lists)
- <u>Analytical Methods</u>: High Resolution Gas Chromatography and High Resolution Mass Spectrometry (HRGC/HRMS) using either USEPA 1613b or SW-846 8290; both target the 17 WHO dioxin/furan congeners, achieving detection limits (DL) of less than 1 pg/g (ng/kg or ppt)

http://www.epa.gov/superfund/programs/clp/download/dlm/dlm22a-c.pdf

• <u>Primary media of concern</u>: soil and sediment. Rarely found in groundwater, unless in presence of chlorinated "source" solvents (chlorinated phenols and/or benzenes). May be found in surface water as suspended solids or dissolved phase.





Historical Soil Remedial Goals

 1984, in response to dioxin contamination at the Times Beach, Missouri, Superfund Site, a landmark risk assessment was conducted by Dr. Renate Kimbrough et. al., resulting in Center for Disease Control (CDC) recommendations for 2,3,7,8-TCDD:

> 1 ug/kg (ppb) - residential sites 5 - 20 ug/kg - non-residential sites

- April 1991 USEPA initiates the Dioxin Reassessment Project
- April 1998 USEPA formalized earlier soil action levels (listed above) through USEPA - OSWER Directive 9200.4-26, "Approach for Addressing Dioxin in Soil at CERCLA and RCRA Sites", April 1998 - -> TEQ Approach formally endorsed by USEPA for assessing site data using "TCDD -TEQ" value
- 1998 and again in 2008 ATSDR recommend use of 50 ng/kg, (pg/g or ppt) as an Environmental Media Evaluation Guide (EMEG), above which further investigation is encouraged.



USEPA Interim Draft Preliminary Remediation Goals

2009 – USEPA issue draft, interim, preliminary remediation goals (PRGs) using newer information from the Dioxin Reassessment Program, based on non-cancer hazards:

- 72 ppt for residential use sites
- 950 ppt for non-residential use sites

Oral RfD: 1 pg/kg-day





Soil Standard Development

- February 2012 A final Oral RfD published in IRIS of 7.0E-10 mg/kg-day or 0.7 pg/kg-day, a Tier I Toxicity value
- Spring 2012, EPA retracts the 2009 PRGs and the 1998 action levels
- Spring 2012, NJDEP derives preliminary soil criteria for dioxin in residential and non-residential settings using the new RfD and the ingestion-dermal exposure pathway





Residential Equations

Noncancer:		
SRS = THQ * BW *	AT * 365 d / yr	
$SRS = \frac{1}{(EF * ED * 10^{-6} kg/mg)[(\frac{1}{RfD_o} * II)]}$	$(\frac{1}{RfD_{ABS}} * AF * A$	IBS _d * EV * SA
SRS = Health-Based Soil Remediation Criterion (ingestion/dermal)	Chemical-specific	mg/kg
THQ = Target Hazard Quotient	1	unitless
BW = Body Weight	15	kg
AT = Averaging Time	6	years
EF = Exposure Frequency	350	days/year
ED = Exposure Duration	6	years
RfD _o = Oral Reference Dose	Chemical-specific	mg/kg-day
IR = Soil Ingestion Rate	200	mg/day
RfD _{ABS} = Dermally Adjusted Reference Dose	Chemical-specific	mg/kg-day
AF = Skin-soil Adherence Factor	0.2	mg/cm ² -event
ABS₄ = Dermal Absorption Fraction	Chemical-specific	unitless
SA = Skin Surface Exposed - child	2,800	cm ²
EV = Event Frequency	1	events/day

* http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/equations.htm



Non-Residential Equations

Noncancer:				
SRS = - THQ * BW * AT * 365d / yr				
$SRS = \frac{THQ * BW * AT * 365d / yr}{(EF * ED * 10^{-6} kg / mg)[(\frac{1}{RfD_o} * IR) + (\frac{1}{RfD_{ABS}} * AF * ABS_d * EV * SA)]}$				
SRS = Health-Based Soil Remediation Criterion (ingestion/dermal)	Chemical-specific	mg/kg		
THQ = Target Hazard Quotient	1	unitless		
BW = Body Weight	70	kg		
AT = Averaging Time	25	years		
EF = Exposure Frequency	225	days/year		
ED = Exposure Duration	25	years		
RfD ₀ = Oral Reference Dose	Chemical-specific	mg/kg-day		
IR = Soil Ingestion Rate	100	mg/day		
RfD _{ABS} = Dermally Adjusted Reference Dose	Chemical-specific	mg/kg-day		
AF = Skin-soil Adherence Factor	0.2	mg/cm ² -event		
ABS _d = Dermal Absorption Fraction	Chemical-specific	unitless		
SA = Skin Surface Exposed	3,300	cm ²		
EV = Event Frequency	1	events/day		

* http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/equations.htm



NJDEP Draft Proposed Soil Standard for 2,3,7,8-TCDD

A draft soil remediation standard will be derived using the IRIS RfD of 7E-10 mg/kg-day, along with the NJDEP standard non-cancer equations for combined ingestion and dermal exposures, and incorporating updated, default exposure parameters.

Residential:

~50 ppt

Non-Residential:

~700 ppt

As with other contaminants, alternate soil standards may be derived on a site-specific basis for alternate exposure scenarios (i.e., recreational)





What about Background?

- Average soil background conditions for TCDD TEQ has been observed to be in the realm of generally less than 10 ppt, often less than 5 ppt.
- This observation is based on case-specific projects in NJ, dioxin background studies performed by some States (Ohio, Michigan, Connecticut and others) and evaluations performed by the USEPA (2003, 2007 and 2011)

References:

USEPA 2000 and 2003, Draft Dioxin Reassessment documents USEPA 2007, Pilot Survey of Levels of PCDDs, PCDFs, PCBs and Hg in Rural Soils of the US 2011 SETAC Presentation by Matthew Lambert, USEPA Office of Superfund Remediation and Technology Innovation, Science Policy Branch





Next Steps

- Develop guidance on application of the 2,3,7,8-TCDD standard in New Jersey using the most updated dioxin investigation tools and best practices
- Await completion of USEPA Dioxin Reassessment Project for updated information on cancer toxicity of 2,3,7,8-TCDD and related dioxin-like compounds





Sources for Additional Information

- USEPA Dioxin Tool Box website: <u>http://www.epa.gov/superfund/health/contaminants/dioxin/dioxinToolbox.htm</u>
- USEPA Dioxin Science Plan website: <u>http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=209690</u>





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