# Dioxins – An Overview of Challenges and Current Regulations

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## Introduction

- Dioxins – the what and where
- Toxicity – bioaccumulation,
  carcinogens, and risk based criteria
- Analytical challenges
- Soil and Puget Sound sediment background levels
- Upland and In-water guidance
- Literally the million $ question: How do we address human health risk, background levels, and keep projects moving forward?

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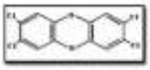
# Dioxins 101



2,3,7,8-tetrachlorodi-benzodioxin
(2,3,7,8-TCDD)

- "Dioxins" are a mixture of polychlorinated dioxins and furans
- 210 congeners – most not toxic, 17 regulated/tested
- Dioxin/furans are toxic and carcinogenic
- Toxicity associated with structure
- Bioacummulative in benthic critters and humans
- Cumulative toxicity of related compounds evaluated using the Toxicity Equivalency Quotient (TEQs)
- There is scientific controversy regarding effects at low doses (NAS 2006)

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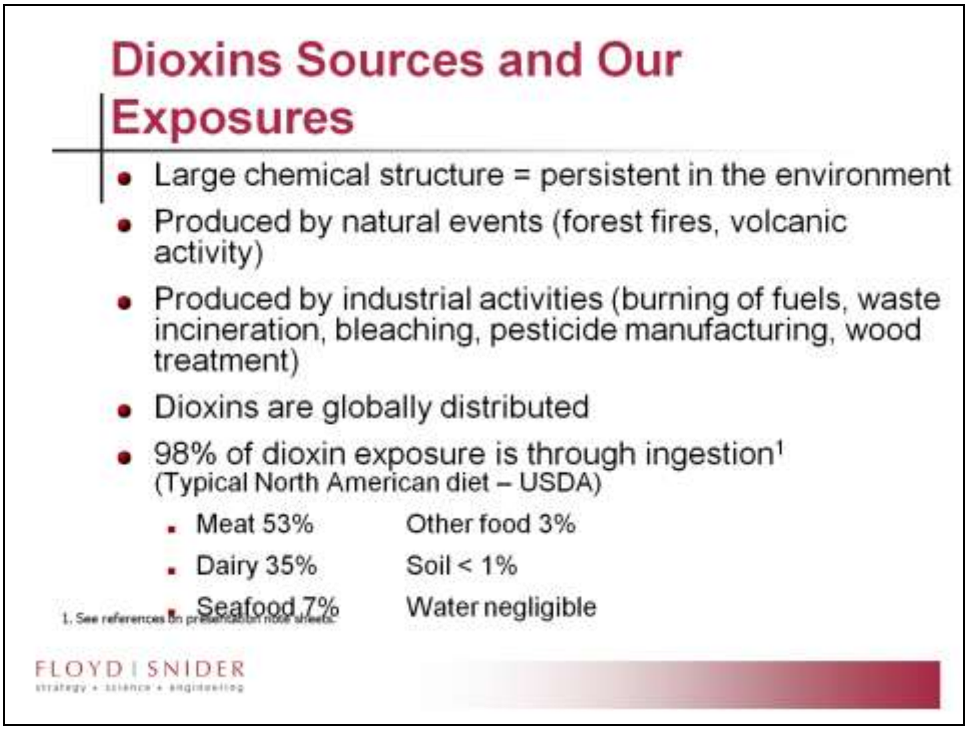


References for dioxin ingestion and exposure

US Department of Agriculture. Various dates. http://www.cfsan.fda.gov/~lrd/dioxinqa.html#r2 ; http://www.cfsan.fda.gov/~comm/tds-toc.html

US EPA, 2003. Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-*p*-Dioxin (TCDD) and Related Compounds National Academy Sciences (NAS) Review Draft. http://www.epa.gov/NCEA/pdfs/dioxin/nas-review/


**Puget Sound Dioxin References**


EIMS data reports from:
Padilla Bay, 1999
South Puget Sound Fish and Shellfish Verification of 303(d) listings, 2006
Washington State Toxics Monitoring Program: Exploratory Monitoring, 2005

Pirmie, M. 2005. *Agency Review Draft Remedial Investigation for the Marine Environment near the Former Rayonier Mill Site*. Port Angeles, Washington. April.

SAIC. 2006. *Data Report* for *2006 Full Monitoring at the Port Gardner Non-dispersive Unconfined Open-water Dredged Material Disposal Site.* 30 November.


**Global Dioxin References**


Scobie, S; Buckland, SJ; Ellis HK; Salter RT. 1999. Organochlorines in New Zealand: Ambient concentrations of selected organochlorines in estuaries. Published by Ministry for the Environment, PO Box 10-362, Wellington, ISBN 0 478 09036 6.

Mosse PRL; Haynes, D. 1993. Dioxin and Furan concentrations in Uncontaminated Waters, Sediments and Biota of the Ninety Mile Beach, Bass Strait Australia. Marine Pollution Bulletin. 26(8): 465-468.

Brochu, C; Moore, S; Pelletier, E. Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans in Sediments and Biota of the Saguenay Fjord and the St Lawrence Estuary. Marine Pollution Bulletin. 30(8):515-523.

Sakurai, T, et al. 2000. Polychlorinated dibenzo-p-dioxins and dibenzofurans in sediment, soil, fish, shellfish and crab samples from Tokyo Bay area, Japan. Chemosphere/ 40:627-640.

Desphpande, AD, et al. 2000. Contaminant Levels in Muscle of Four Species of Recreational Fish from the New York Bight Apex. NOAA Technical Memorandum NMFS-NE-157.

Fiedler, H; Cooper, KR; Bergek, S; Hjelt, M; Rappe, C. 1997. Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans (PCDD/PCDF) in Food Samples Collected in Southern Mississippi, USA. Chemosphere. 34 (4-5):1141-1419.

Lindstrom, G; Smastuen Haug, L; Nicolaysen, T; Dybing, E. 2002. Comparability of world-wide analytical data of PCDDs, PCDFs and non-ortho PCBs in samples of chicken, butter and salmon. Chemosphere. 47:139-146.

Schecter, A; Cramer, P; Boggess, K; Stanley, J; Olson, JR. 1997. Levels of dioxins, dibenzofurans, PCB, and DDE congeners in pooled food damples collected in 1995 at supermarkets across the United States. Chemosphere. 34(5-7):1427-1447.

# Dioxin Analytical Challenges

- Human health risk based clean up levels are often below background and analytical detection limits
- Analysis is at trace levels – part per trillion (ng/kg)
- Cross contamination – "hot sample" and getting back to background
- Risk of false positives – polychlorinated compounds (e.g., diphenyl ethers) co-eluting within the dioxin/furan retention times

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# Dioxin Analytical Challenges

- Standard reference material – often not applicable to detection limits trying to achieve
- Presence of pentachlorophenol and use of acetone during certain extraction steps can generate dioxins[1]
- TEQ criteria so low that in some cases handling non-detects with substitution of ND = ½ DL can result in TEQ exceedances

1. Identified by Analytical Perspectives , tested and confirmed by ARI.
2. February, 2007 EPA update.

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SRMs often not applicable to dioxin detection limits due to dioxin level in SRMs being an order of magnitude above the detection limits

# Dioxin Analytical Considerations

- Two primary methods for dioxins: USEPA 8290 & USEPA 1613
  - 1613 has a holding time of 1 year – allow for composite analysis, archival of discrete samples
  - SW846 Chapter 4 - NO HOLDING TIME for PCBs and dioxin/furans[2]
- Not all labs calculate detection limits the same way – EDL, MDL, RL
- Costly analysis – approximately $1,000 per sample (price decreasing with more lab competition)

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# Higher Data Validation Needed

- Because of:
  - Cross contamination risks,
  - False positive risks,
  - Potential dioxin generation during extraction,
  - Differing detection limit calculations
- Higher level data validation (Full, Level IV) is needed

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# Dioxin Background - Soils

- WA State natural background average: 5.2 ng/kg (2010, updated TEF values from previous average of 2.2 ng/kg)[1,2]
- WA State urban background: 0.133 to 19.5 ng/kg (average of 7.7 ng/kg)[2]
- Western WA soil dioxin concentrations
  - open areas (0.32 to 4.15 ng/kg),
  - forested areas (2.05 to 5.61 ng/kg), and
  - urban areas (0.13 to 19.9 ng/kg) [3]

1. Technical Memorandum. Natural Background for dioxins/furans in Washington soils. April 28, 1010. Washington State Department of Ecology.
2. Concise Explanatory Statement and Responsiveness Summary for the Amendment of Chapter 173-340 WAC, Model Toxics Control Act Cleanup Regulation (CES; WSDOE 2007).
3. Screening Survey for Metals and Dioxins in Fertilizer Products and Soils in Washington State. Washington State Department of Ecology. Publication Number 99-309. April 1999.

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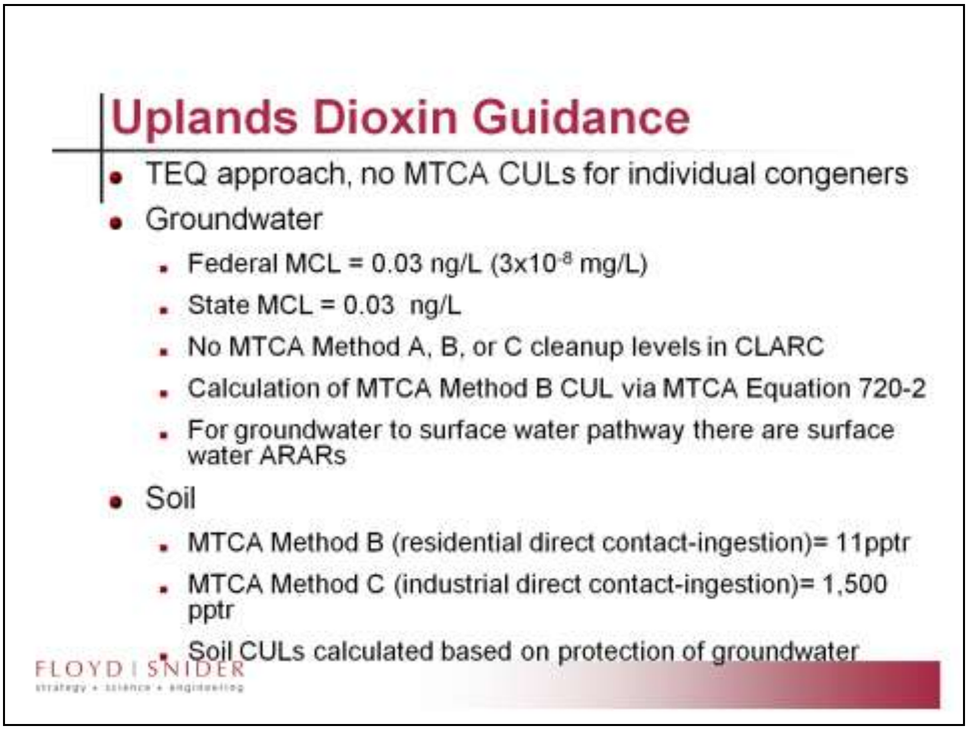
# Dioxin Background Puget Sound Sediments

- OSV Bold 2008 Main Basin Survey [1] & Existing Sediment data
  - 2008 Main Basin TEQs ranged from 0.012 to 0.245 ng/kg [1]
  - 90% UCLfor the $90^{th}$ percentile of the distribution of the background Puget Sound Main Basin dataset, rounded up to the nearest whole digit = 4 ng/kg

1. USEPA. 2008. OSV Bold Survey Report. Puget Sound Sediment PCB and Dioxin 2008 Survey. September 11.




As shown in previous slide soil and groundwater are not where we are getting our exposures, but this is where dioxins are primarily entering the food chain.

# MTCA Ecological Dioxin Guidance

- Simplified Terrestrial Ecological Evaluation Procedure (Table 749-2)
  - Unrestricted land use soil concentrations
    - Dixons: 5 ng/kg; Furans: 3 ng/kg
  - Industrial or commercial site soil concentrations
    - Dixons: 5 ng/kg; Furans: 3 ng/kg
- Ecological Indicator Soil Concentrations – Protection of Terrestrial Plants and Animals (Table 749-3)
  - Wildlife soil concentrations
    - Dixons: 2 ng/kg; Furans: 2 ng/kg

*Currently under revision & may decrease

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Simplified TEE for use where a site-specific TEE is not required.

## Sediments Guidance - MTCA/SMS Cleanup

- Marine Sediment Management Standards (SMS)
  - No dioxin standards at this time
- Draft SMS Freshwater Sediment Standards
  - No dioxin standards at this time
- Dioxin is regulated in SMS via a narrative for bioaccumulative risk
- Sediment cleanup sites – development of site-specific clean up levels based on exposures, risk, background, and sources

**No SMS standards because dioxins aren't toxic to benthic aquatic species*

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## Sediments Guidance – Dredge Material Disposal

- Dredge Material Management Program (DMMP) 2010 Proposed Interim Guidelines
  - Dispersive disposal sites suitability guideline
    - Max DMMU dioxin concentration < 4 pptr TEQ
  - Non-dispersive disposal sites suitability guideline
    - Max DMMU dioxin concentration < 10 pptr TEQ
    - Volume-weighted average concentration of all DMMUs < 4 pptr TEQ

**SMARM 2010 Proposed Dioxin Guidelines (Available the Seattle USACE DMMO Website)**

Dispersive disposal sites suitability guideline:

Maximum dioxin concentration in any single dredge unit (DMMU) is 4 pptr TEQ – site management objective for dispersive sites.

Other dioxin concentrations can be approved on a case-by-case basis

Non-dispersive disposal sites

Maximum dioxin concentration in any single dredge unit (DMMU) is 10 pptr TEQ as long as the volume-weighted average concentration in materials from the entire project is less than 4 pptr TEQ (dispersive site management objective)

Case-by-case determinations can be made with respect to bioaccumulation testing, BMPs, other bioaccumulatives chemicals, and frequency of disposal site use. Small business consideration as well.

## Overall Challenges with Dioxins

- Risk based levels are often below background and at or below what is analytically achievable and meaningful
- Are we focusing on dioxin risk possibilities or probabilities? Protecting real, if not actual exposures?
- Regulatory agencies what guidance that is protective and clear, Business's what guidance that is predictive and fair - question is how do we get there?
- How do we protect human health while keeping cleanup and dredging programs programmatic and realistic?
- Can we really make decisions about how clean is clean enough WITHOUT understanding the trade-offs?

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# Thank you

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