Remediation Guidelines for Tebuthiuron and Bromacil

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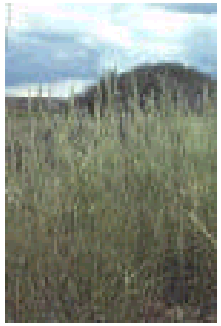
Outline

- Sterilants – Background
- Study Designs (to set Ecological Direct Soil Contact Pathway for site-specific projects/programs)
- Tebuthiuron Results
- Bromacil Results
- Summary



Sterilants - Background

- Sterilants are broad-spectrum (non-selective) herbicides; laboratories generally include six compounds in their target list: Diuron, Linuron, Simazine, Atrazine, Bromacil, and Tebuthiuron
- Sterilants are used to control weeds in non-crop areas, rangelands, right-of-ways (ROWs), and industrial sites
- Select sterilants were controlled by the federal government in the mid 1970s
- Sterilants are an issue for remediation and reclamation first identified in the 1980s when Alberta Environment (AENV)* and industry were reclaiming abandoned wells; Alberta Research Council (ARC) conducted research

* Renamed Alberta Environment and Sustainable Resource Development (AESRD)

Sterilants – Background (con't)

- These six compounds are different chemically and also have different vegetation control mechanisms, physical and chemical characteristics, and environmental fate and exposure
- Three of the compounds are very soluble and have contaminated groundwater aquifers in the US (Atrazine, Bromacil and Tebuthiuron)
- Laboratory detection limits in soils changed about 14 years ago (1998) from 0.01 mg/kg to 0.005 mg/kg in Alberta; plant bioassays were historically used to determine presence/absence

Sterilant Effects

- Areas applied with sterilants are generally bare of vegetation, although bare surfaces could also be caused by other things like poor growing medium
- If present, vegetation is often orange or rusty coloured

Sterilant Guidelines in Alberta

- "Alberta Tier 1 Soil and Groundwater Remediation Guidelines", August 2007 (updated 2010) included sterilants for the first time because Health Canada had introduced some "pesticide" values
  - AESRD guidelines for sterilants were established for some pathways to protect some receptors (incomplete) but did not necessarily consider the most limiting pathways
  - One of the critical exposure pathways for Agricultural and Natural Area land uses is the Direct Soil Contact pathway designed to protect ecological receptors (e.g. vegetation)
  - No guideline was established for this pathway; therefore, there is no soil benchmark for sterilants

Data Gaps

- An issue for upstream oil and gas remediation and reclamation is the lack of an Ecologicial Direct Contact pathway for the protection of the main receptors (e.g., vegetation)
- Also, the analytical method for some sterilants may not be sufficiently sensitive (e.g., the detection limit is too high) to adequately characterize soil and/or groundwater

Access Laboratory Detection Limits

Sterilant	Soil (mg/kg)	Water (ug/L)
Atrazine	0.005	0.1*
Bromacil	0.005 (0.002)	0.1
Diuron	0.005	0.1
Linuron	0.0003	0.1
Simazine	0.001	0.1
Tebuthiuron**	0.00016**	0.1

* Equivalent to 0.0001 mg/L or ppm (0.1 ppb)

** By special method using LC/MS

Tier 1 Agricultural Guidelines for Soil*

Sterilant	Coarse	Fine
Atrazine (and metabolites)	0.01	0.0088
Bromacil	0.009 (BDL**)	0.009 (BDL)
Diuron	3.5	1.9
Linuron	0.059 (BDL)	0.051 (BDL)
Simazine	0.038 (BDL)	0.033 (BDL)
Tebuthiuron	0.11 (BDL)	0.12 (BDL)

* Values in mg/kg; Natural Area guidelines are similar except for Tebuthiuron (coarse 3.7 mg/kg and fine 2.5 mg/kg)

** BDL = below detection limit of 0.005 mg/kg; groundwater assessment is necessary

Exposure Pathways

Sterilant	Human			Ecological							
	Direct Contact	Vapour Inh.	Pot. Water	Direct Contact	Nutr. Cycling	Livest. Inges.	Wildlife Inges.	Freshw. Aquatic	Livest. Water	Wildlife Water	Irrig. Water
Atrazine	X		X					X	X		X
Bromacil	X		X					X	X		BDL
Diuron	X		X								
Linuron	X		X					X			BDL
Simazine	X		X					X	X		BDL
Tebuthiuron	X		X					BDL	X		BDL

- "Overall" guidelines for Agricultural Land Use based on Human Direct Contact and usually Potable Water and Ecological, Freshwater Aquatic Life, Livestock Water and Irrigation Water
- No Ecological Direct Contact Exposure Pathway Value for Soil

Bromacil Tier 1 Soil Guidelines*

Pathway	Tier 1 (mg/kg)
Human – Direct Soil Contact	2,000
Human – Domestic Use Aquifer	10
Human – Vapour Inhalation	--
Eco – Direct Soil Contact	--
Eco – Freshwater Aquatic Life	0.009
Eco – Livestock Water	2.0
Eco – Irrigation Water	BDL*
Overall Guideline	0.009 (BDL)

* *For Agricultural Land Use, coarse textured soil (not all pathways calculated)*

** *BDL = below detection limit (groundwater assessment and comparison to groundwater remediation guidelines is necessary)*

Tebuthiuron Tier 1 Soil Guidelines*

Pathway	Tier 1 (mg/kg)
Human – Direct Soil Contact	1,600
Human – Domestic Use Aquifer	3.7
Human – Vapour Inhalation	--
Eco – Direct Soil Contact	--
Eco – Freshwater Aquatic Life	BDL**
Eco – Livestock Water	0.11
Eco – Irrigation Water	BDL
Overall Guideline	0.11 (BDL)

* *For Agricultural Land Use, coarse textured soil (not all pathways calculated)*

** *BDL = below detection limit (groundwater assessment and comparison to groundwater remediation guidelines is necessary)*

EBA Literature Review in 2007

(for Ecological Direct Soil Contact Information)

- Manufacturers know active ingredient rates that affect weeds or crops ("herbicide carry-over")
- Not many measured concentrations in soil reported
- Not much toxicity data for native prairie or boreal forest species and limited data for invertebrates

CONCLUSION

- Guidelines are lacking for the soil contact exposure pathway and the toxicity data were not adequate for deriving guidelines, interim guidelines, or soil quality criteria using Canadian Council of the Minister of the Environment (CCME) or Environment Canada (EC) procedures

Effect Levels on Crops and Weeds

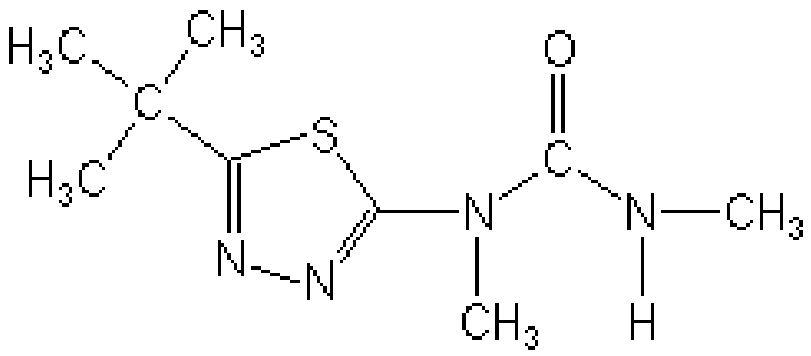
Sterilant	Effect Levels**	Confidence
Atrazine (0.01*)	0.01 – 0.02	Low
Bromacil	0.094 – 0.00585	Moderate
Diuron (3.5)	0.1 – 2.0	Low
Linuron (0.059)	0.25	Low
Simazine (0.038)	0.5	Low
Tebuthiuron (0.11)	0.015 – 0.0402	Moderate

* *Number in Brackets is the overall guideline for Agricultural Land Use coarse textured soil*

** *Values in mg/kg*

Tebuthiuron

- Trade Names "Spike, Herbec, Brush, Bullet, Bushwacker, EL-103, Graslan, Herbic, Perflan, Reclaim, Tebusan, Sprakil, and Scrubmaster"
- Molecular Formula: $C_9H_{16}N_4OS$



1-(5-tert-butyl-1,3,4-thiadiazol-2yl)-1,3-dimethylurea

- Has very high to low mobility in soils (K_{oc} 4 to 517), has potential to leach (water solubility 2,500 mg/L @ 25°C)
- Sorption to soils increases with clay and organic matter content
- Mode of action is inhibition of photosynthesis

Tebuthiuron Background – Effects

- EBA literature review found data only for crops and weeds; no native prairie species and no invertebrates
- Wheat, the most sensitive of ten cereal crop species studied, had “no observed adverse effect level” (NOAEL) at **0.0201** mg/kg and “lowest observed adverse effect level” (LOAEL) at **0.0402** mg/kg (Waldrep 1988)
- Weeds are controlled at concentrations as low as **0.015** mg/kg (USEPA 2003)

Tebuthiuron Project

- Site was an Upstream Oil and Gas Battery from 1968, located in southeastern Alberta, with detectable concentrations of tebuthiuron in soil
- Land use was predominantly Native Prairie vegetation and soils were coarse-textured
- The site was in remediation stages, starting in 2006 when the first draft of the AESRD Tier 1 guidelines was issued
- Met with AESRD and ASRD to discuss approach, after the literature review revealed that the amount of information was insufficient to establish Tier 2 soil benchmarks for the Ecological Direct Contact Pathway

Tebuthiuron Project

- Bulk soil samples of site subsoil, control subsoil and control topsoil were collected
- Stantec Ecotoxicity Laboratory in Guelph, Ontario conducted a soil ecotoxicity assessment in order to generate the data required to establish site-specific Tier 2 Guidelines

Ecotoxicity Study

- **Environment Canada Biological Test Methods**
  - Tests for Toxicity of Contaminated Soil to Earthworms. EPS 1/RM/32 (2004)
  - Test Measuring Emergence and Growth of Terrestrial Plants Exposed to Contaminants in Soil. EPS 1/RM/45 (2005)
  - Guidance Document on Statistical Methods for Environmental Toxicity Tests. EPS 1/RM/46 (2005)
  - Test for Measuring Survival and Reproduction of Springtails Exposed to Contaminants in Soil. EPS 1/RM/47 (2007)
- **Canadian Council of Ministers of the Environment (CCME) Procedures used for Guideline Derivation**
  - A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines. PN1332 (2006)

Soil Ecotoxicity Testing

Testing followed Environment Canada Procedures

- Soil Invertebrates: springtail (*Folsomia candida*) and earthworm (*Eisenia andrei*)
- Plants:
  - blue grama grass (*Bouteloua gracilis*)
  - western wheatgrass (*Pascopyrum smithii*)
  - silver sage (*Artemis cana*)
  - Durum Wheat (*Triticum durum*)

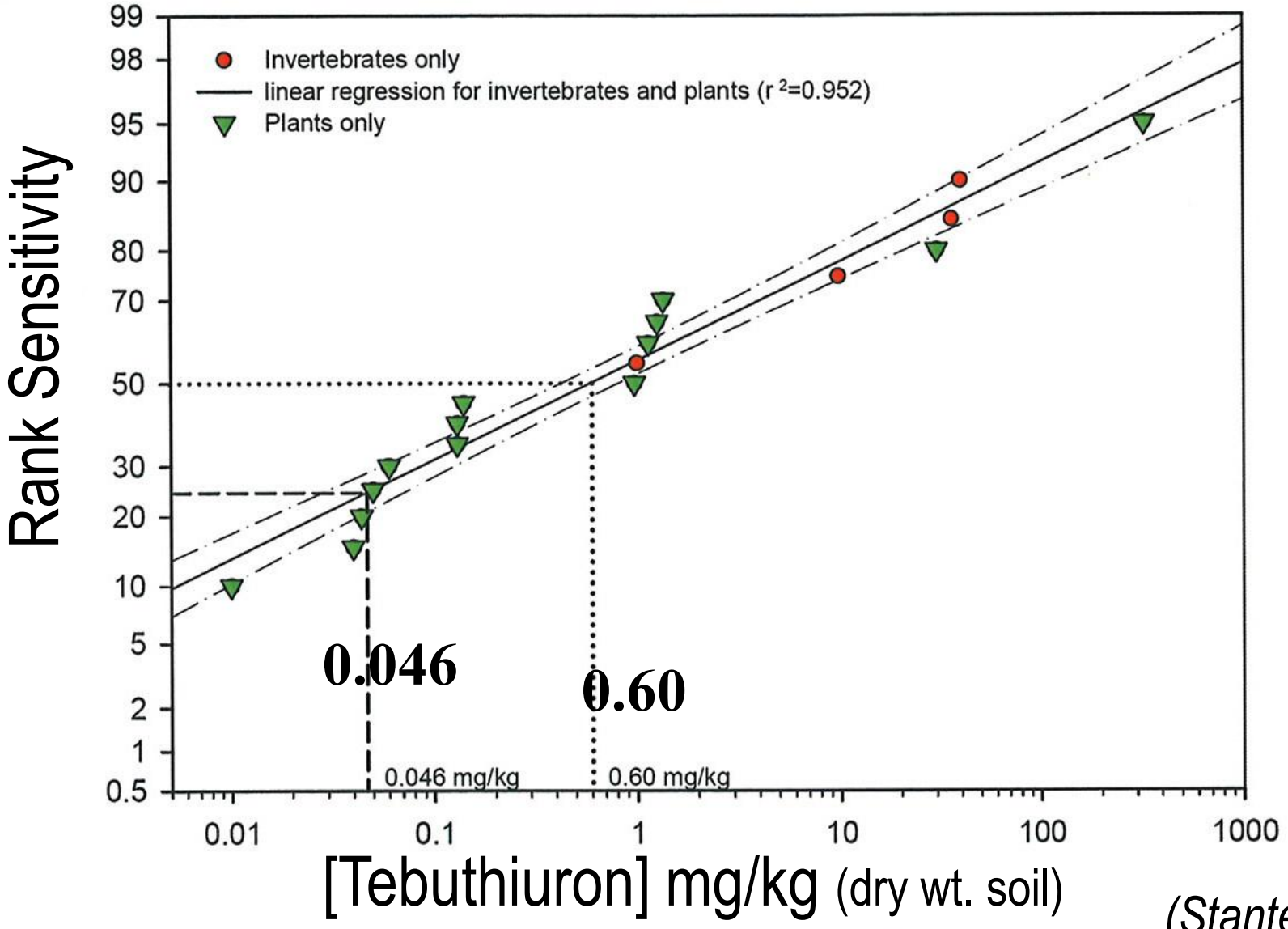
In addition, two native prairie grass species were confirmed as not suitable for ecotoxicity testing: June grass (*Koeleria macrantha*) and needle and thread grass (*Hesperostipa comata*)

Soil Ecotoxicity Testing

- Access Labs provided a special low level detection method of analysis (LC/MS)
  - method detection limits of 0.00016 mg/kg in soil
- Range finding tests for invertebrates and plants
  - soils spiked with varying Tebuthiuron concentrations
- Chronic (invertebrates) and definitive (plants) screening tests were conducted
- Invertebrates and Durum Wheat were the least sensitive species tested

Soil Ecotoxicity Test Results

(Combined Plant and Invertebrates IC25)



(Stantec 2008)

Tebuthiuron Summary by Land Use*

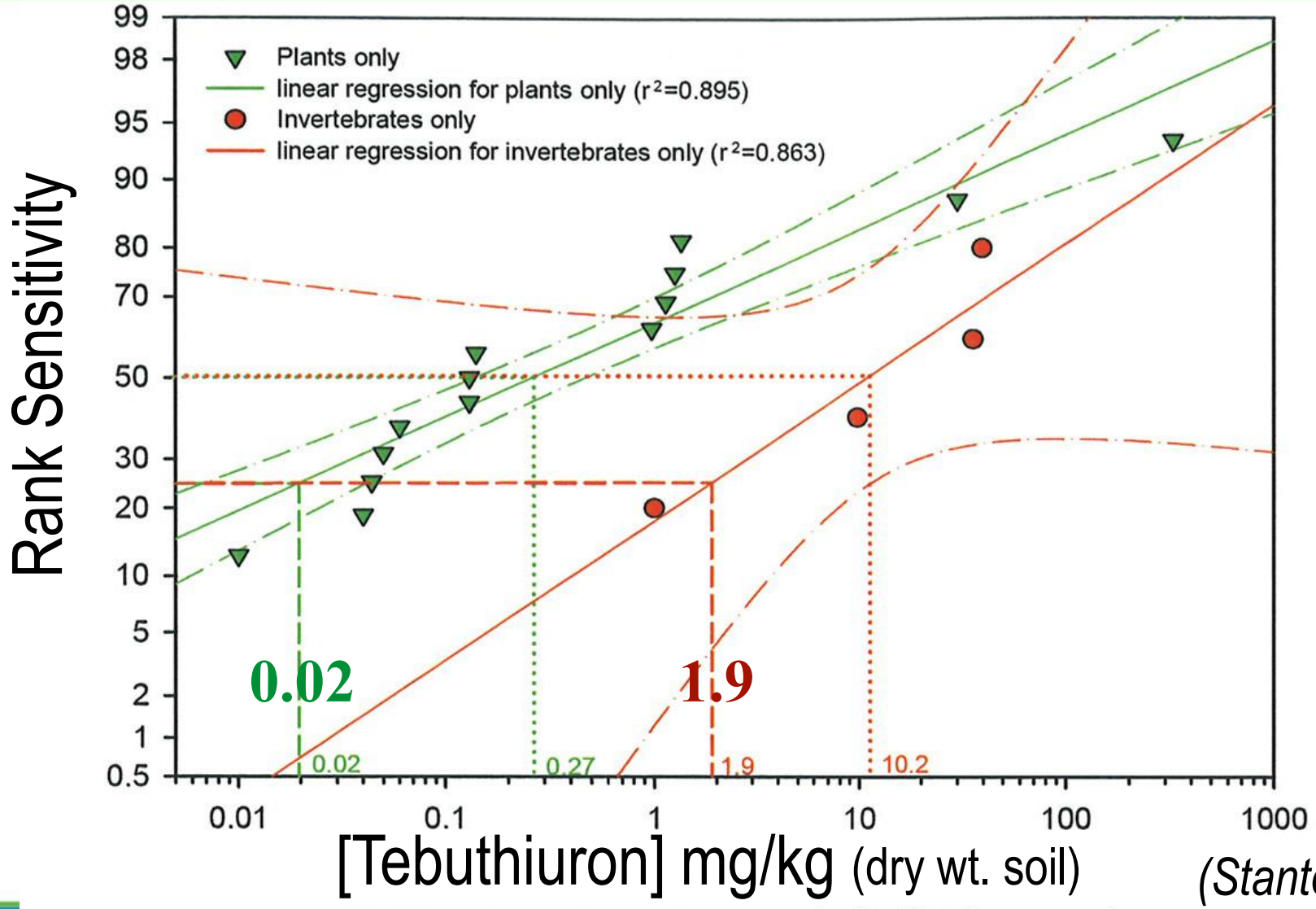
(Plant and Invertebrates Using IC25)

Soil Texture	Agric./Resid.	Com./Indus.
Coarse	0.046	0.60

- *Values in mg/kg*

Soil Ecotoxicity Test Results

(Plants and Invertebrates Data Separately - IC25s)



(Stantec 2008)

Site Specific Guideline for Tebuthiuron

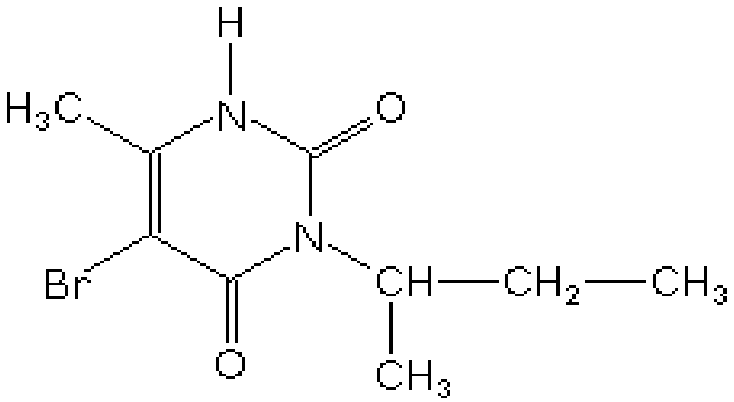
- Canadian Council of the Ministers of the Environment (CCME) procedures were used to determine the threshold effect concentration (TEC) for agricultural land use
- This method uses species sensitivity distributions of inhibiting concentration for a 25 percent effect (IC25) considering all of the endpoints (invertebrates and plants)
- TEC for invertebrates and plants was **0.046** mg/kg
- TEC for just plant species was **0.020** mg/kg

Proposed Site-Specific Guideline for Native Prairie, coarse textured soils is 0.020 mg/kg

Compares to Literature Review effect level 0.015 mg/kg (NOAEL) to 0.042 (LOAEL)

Bromacil

- Trade Name: "Hyvar X/XL"; also combined with other products (i.e with Diuron is "Krovar I", with 2,4-D is Calmix and Hybor-D)
- Molecular Formula: $C_9H_{13}BrN_2O_2$



5-bromo-6-methyl-3-(1-methylpropyl)-2,4(1H,3H)-pyrimidinedione

- Has very high to low mobility in soils (K_{oc} 2.3 to 289), has potential to leach (water solubility 815 mg/L @ 25°C)
- Sorption to soils increases with clay and organic matter content

Bromacil – Effects Levels

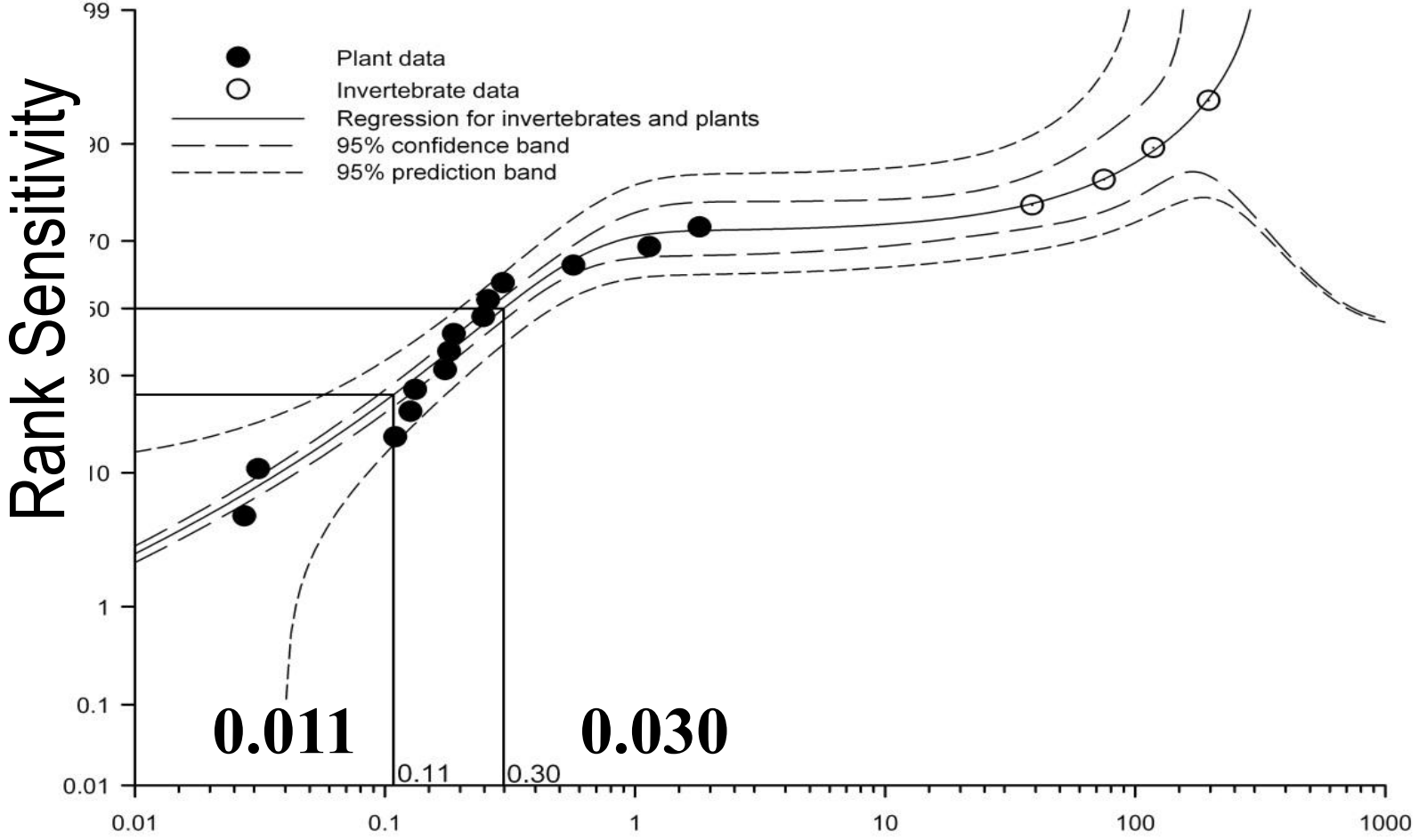
- EBA literature review found data only for crops and weeds; no native prairie species and no invertebrates.
- Wheat and Canola were most sensitive species
- USEPA (2003) reviewed 23 studies: NOAEL ranged from **0.00115** mg/kg **to 0.0585** mg/kg and one study was **0.094** mg/kg; LOAEL of **0.0077** mg/kg
- ARC (1989) reported concentrations of **0.8** mg/kg to **2.0** mg/kg had an effect on plant growth of oats, with more impact noted in sandy soils

Bromacil Study Design

- Soils used for the study included:
  - fine textured topsoil - same as that used for studies to set petroleum hydrocarbon guidelines (Delacour series - Orthic Black Chernozem on Till)
  - Coarse textured topsoil (Midnapore series – Orthic Black Chernozem on glaciofluvial sediments)
- Range-finding and chronic/definitive tests conducted
- Bromacil spiked into soils at different concentrations
- Soil Invertebrates: springtail (*Folsomia candida*) and earthworm (*Eisenia andrei*)
- Plants: three species used:
  - blue grama grass (*Bouteloua gracilis*)
  - Durum Wheat (*Triticum durum*)
  - alfalfa (*Medicago sativa*)

Bromacil Ecotoxicity Test Results

(Plant and Invertebrates Combined E/IC25)



(Stantec 2012)

Bromacil Summary by Land Use*

Plant and Invertebrates Combined E/IC25

Soil Texture	Agric./Resid.	Com./Indus.
Coarse	0.11	0.30
Fine	0.25	0.93

Plant Data Only E/IC25

Soil Texture	Agric./Resid.	Com./Indus.
Coarse	0.12	0.20
Fine	0.20	0.49

* Values in mg/kg

Summary

- Tebuthiuron site-specific remediation guidelines for the direct eco-contact pathway based only on plants species for a native pasture area on coarse textured soils was calculated as 0.020 mg/kg
- Bromacil direct eco-contact pathway for agricultural land use for a remediation program using plant and invertebrate data was calculated as 0.11 mg/kg for coarse textured soils and 0.25 mg/kg for fine textured soils

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Thank You!