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Remediation Options and Treatment for Tebuthiuron at an Upstream Oil and Gas Site

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Outline



- Tebuthiuron Background
- Tebuthiuron Guidelines
- Remedial Options
- Remediation





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Tebuthiuron Background - Use

- Sterilants are strong herbicides that generally include six compounds: Diuron, Linuron, Simazine, Atrazine, Bromacil, and Tebuthiuron
- Tebuthiuron is a broad-spectrum herbicide used to control weeds in non-cropland areas, rangelands, right-of-way (ROW), and industrial sites.
- 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.



Tebuthiuron Background - Properties

- Trade Name is "Spike"
- Broad-spectrum herbicide (sterilant)
- Molecular Formula: C₉H₁₆N₄OS



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

- 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
- Commercial laboratory detection limits in Alberta decreased from 0.01 mg/kg about 10 years ago to 0.005 mg/kg

Tebuthiuron Background - Effects

- Areas applied with Tebuthiuron are generally bare of vegetation, but the bare surface could also be caused by other things like poor growing medium
- If present, vegetation is often orange or rusty coloured
- Maturity of vegetation might be affected (broken stalks)





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Tebuthiuron Background – Guidelines

- "Alberta Tier 1 Soil and Groundwater Remediation Guidelines" (August 2007) included sterilants for the first time because Heath Canada had introduced some "pesticide" values
 - AENV guidelines for sterilants were established for some pathways to protect some receptors (incomplete) and did not necessarily look at most limiting pathways
 - One of the critical exposure pathways for Agricultural and Natural Areas 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



Tebuthiuron Background – Tier 1 Soil Guidelines

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

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

• 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, had a "no observed adverse effect" at 0.0201 mg/kg and "lowest observed adverse effect" at 0.0402 mg/kg (Waldrep 1988).
- Weeds are controlled at concentrations as low as 0.015 mg/kg (USEPA 2003).

Tebuthiuron Background – Site-Specific Guidelines

 Canadian Council of the Ministers of the Environment (CCME) procedures were used to determine the threshold effect concentration (TEC) for agricultural land use

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- 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 is 0.020 mg/kg

Remedial Options – Literature Review

Sterilant	MNA	Adsorption	Phyto-	Biodeg-	Thermal	Chem.	Flushing	Photo-	Volatil-
			remed.	radation	Desorp.	Hydrol.		lysis	ization
Atrazine	х	?	Х	?	х		х		х
Bromacil		х		х	?		Х	х	
Diuron	х	Х		х	?		?	?	
Linuron	х	Х	х	х	?				
Simazine	х	Х		х	?	х		х	
Tebuthiuron		Х			х		х		

- MNA Monitored Natural Attention
- Adsorption with amendments, usually activated charcoal and/or organic matter
- Biodegradation in-situ or ex-situ, aerobic
- Photolysis includes photodegradation and UV Treatment
- Volatilization enhanced by steam injection, electrical resistance and Radio Frequency and/or with Vapour Extraction (in-situ)

Remedial Options – Comparison

- Adsorption by amending contaminated soil with activated charcoal; it requires mechanical mixing of charcoal into soil.
- Thermal desorption is a process by which contaminants are destroyed by heating wastes to moderate temperatures. These temperatures range from 200°F to 1,000°F depending on the contaminant.
- Soil flushing is a process where a solution is injected in the ground in order to dissolve soluble contaminants and then physically move the contaminants to an area where they may be extracted from the ground and treated or disposed of.



Remedial Options – Selection Rationale

- Adsorption The theory is the rate of release is slower than the rate of degradation. There is no literature showing long term effectiveness
- Thermal Desorption A pilot test was successful for treating soil with Tebuthiuron and Bromacil to below laboratory detection limits. A thermal desorption unit (TDU) was readily available at the time.
- Soil Flushing Requires a source of water, and a water recover and treatment system



Remediation – Background

- Site was an Upstream Oil and Gas Battery from 1968, located in southeastern Alberta, and was predominantly Native Prairie vegetation
- Tebuthiuron was above laboratory detection limits for the majority of surface soils to a depth of 4.0 m
- Site was in remediation stages, starting in 2006 when the first draft of the AENV Tier 1 guidelines was issued that included sterilants



Remediation – Assessment



Remediation – Thermal Desorption

- Nelson Environmental Remediation Ltd. (NER) thermal desorption unit was used
- A pilot test was successful at treating soil with tebuthiuron and bromacil.
- "Temperature ramping" was performed to determine optimum treatment temperature





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Remediation – Thermal Desorption

- A total of 15,136 tonnes of soil with tebuthiuron was treated
- Treated soil was used
 as backfill on-site



Provided by Nelson Environmental Remediation Ltd



Tebuthiuron Remediation – Dewatering

- Dewatering was necessary in one area of the site where excavation to recover hydrocarbons was necessary
- The water was monitored and treated by charcoal filters when required
- An additional 1,671 tonnes of soil with hydrocarbons was treated by thermal desorption





Tebuthiuron Remediation – Confirmatory Sampling

Confirmatory soil samples for tebuthiuron all meet the 0.020 mg/kg site-specific Tier 2 guideline in the root zone with the exception of 3 samples where further excavation could not be completed due to conflicts with third party pipelines





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Summary

• Tebuthiuron is broad spectrum herbicide that can be an issue during remediation and reclamation

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- In a literature review, options for remediating tebuthiuron include, charcoal adsorption, soil flushing, and thermal desorption
- Thermal desorption is an effective way to treat soil with tebuthiuron. Approximately, 15,136 tonnes of soil with tebuthiuron was treated





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