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Bromacil residues in soil and groundwater at contaminated sites - Do they matter?

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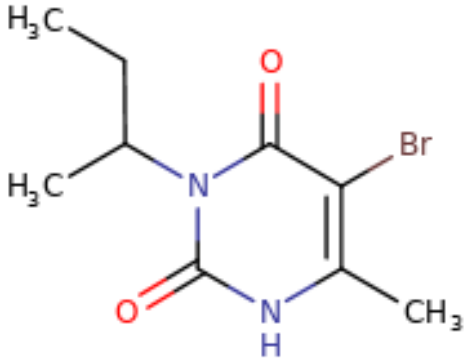
Outline

- History and use
- Environmental fate and partitioning
- Environmental quality guidelines
- Case Study
- Risk Characterization
  - Toxicity
  - Environmental degradation
  - Groundwater modelling
- Conclusions

$C_9H_{13}BrN_2O_2$



Bromacil

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History and Use

- Broad-spectrum herbicide
- Part of uracil herbicide family
- Inhibits plant growth through the inhibition of photosynthesis
- Registered as pesticide in the U.S. in 1961

Bromacil is a broad spectrum herbicide used to control weeds in the agricultural food crops citrus and pineapple. In addition, both bromacil and its lithium salt are used to control weeds and brush in nonagricultural areas including utility right-of-ways, railroads, electrical switching stations, and industrial yards (US EPA 1996).

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Environmental Fate and Partitioning

Property	*Value*	*Reference*
Molecular weight	261.12 g/mol	SRC 2013
Henry's law constant	0.0117 atm-m^3/mol	SRC 2013
Vapour pressure	1.1E-07 mmHg	SRC 2013
Water solubility	324 mg/L	SRC 2013
Half-life in soil	275 days	US EPA 2012
Half-life in groundwater	???	US EPA 2012

Not Volatile

Soluble

Persistent

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Environmental Fate and Partitioning

- Fugacity modeling (US EPA 2012)

Environmental Media	***Air (%)***	***Water (%)***	***Soil (%)***	***Sediment (%)***
Released to soil	<1%	6.9	93	<1
Released to water	<1%	99	<1%	<1%

Environmental Quality Guidelines

Media[(1)]	Human Contact	Potable Water	Eco-Contact	Freshwater Aquatic Life	Irrigation	Livestock Watering
Soil [mg/kg]	2,000	7	0.2	0.009	NGA	2
Ground Water [mg/L]	NGA	0.95	0.44	0.005	0.0002	1.1
Surface Water [mg/L]	NGA	0.95	NGA	0.005	0.0002	1.1

(1) Assumed agricultural land use and fine grained soils (AEP 2016).

Case Studies

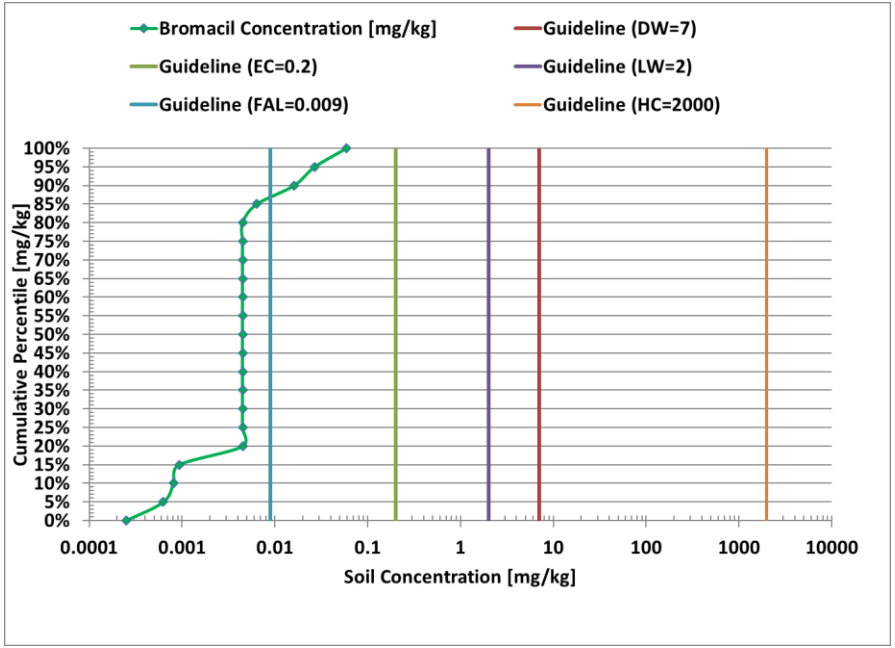
1. Power Station
2. Abandoned Well Site

Case Study #1 – Soil Concentration

Sample Depth	Mean	Min	Max	N	Agricultural Guideline (mg/kg)[2]
0 – 1.5 mbgs	0.0068	<0.005	0.059	70	2,000 (HC)
					7.0 (DW)
					0.2 (EC)
					0.009 (FAL)
					2 (LW)
>1.5 mbgs	0.027	<0.009	0.045	12	2,000 (HC)
					7.0 (DW)
					0.2 (EC)
					0.009 (FAL)
					2 (LW)

1) Average calculated assuming that non-detects were present at a concentration equivalent to the method detection limit (MDL).
2) Value obtained from AEP (2016).

Notes:
HC (Human Contact); DW (Drinking Water); EC (Eco-contact); FAL (Freshwater Aquatic Life); LW (Livestock Watering)
Shading indicates an exceedance of a specific guideline

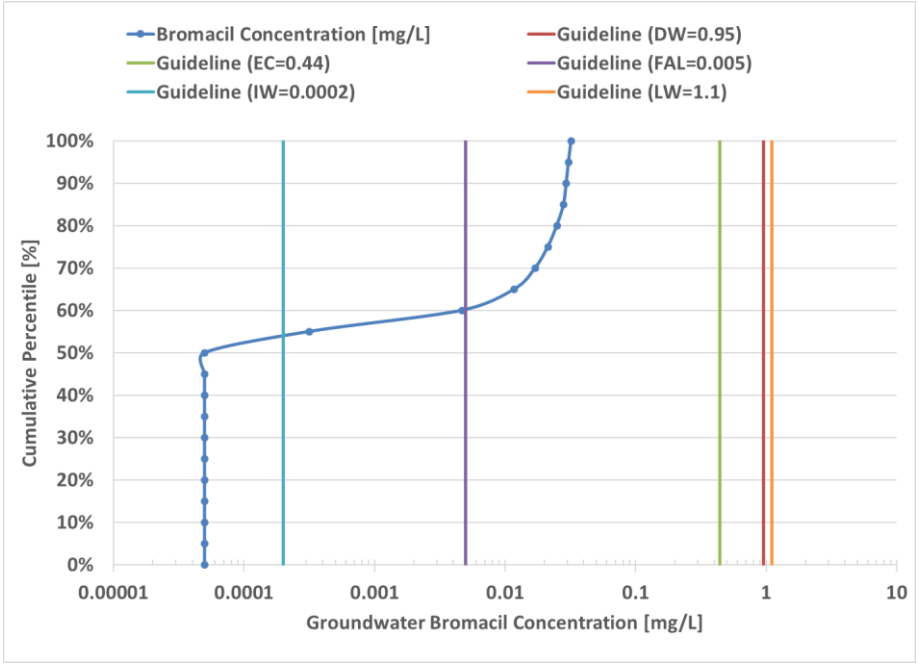


Case Study #1 – Groundwater Conc.

Mean	Min	Max	N	Agricultural Guideline[2]
0.0097	<0.0001	0.032	14	0.95 (DW)
				0.44 (EC)
				0.005 (FAL)
				0.0002 (IW)
				1.1 (LW)

1) Average calculated assuming that non-detects were present at a concentration equivalent to the method detection limit (MDL).
2) Value obtained from AEP (2016).

Notes:
DW (Drinking Water); EC (Eco-contact); FAL (Freshwater Aquatic Life); Irrigation Water (IW); LW (Livestock Watering)
Shading indicates an exceedance of a specific guideline



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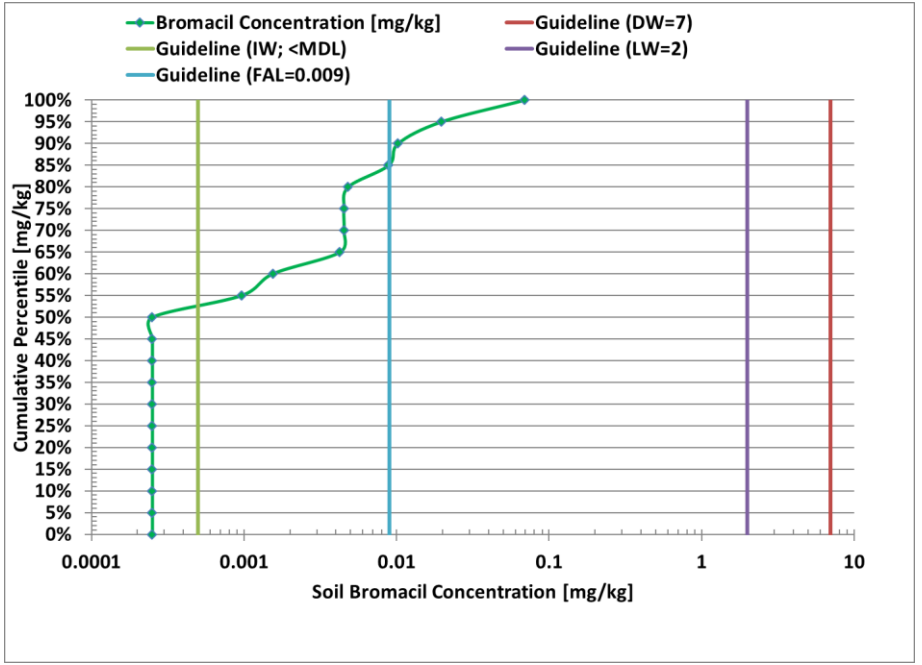
Case Study #2 – Soil Concentration

Sample Depth	Mean	Min	Max	N	Agricultural Guideline (mg/kg)[2]
0 – 1.5 mbgs	0.0041	0.0003	0.01	16	2,000 (HC)
					7.0 (DW)
					0.2 (EC)
					0.009 (FAL)
					2 (LW)
>1.5 mbgs	0.0054	0.0003	0.069	34	2,000 (HC)
					7.0 (DW)
					0.2 (EC)
					0.009 (FAL)
					2 (LW)

1) Average calculated assuming that non-detects were present at a concentration equivalent to the method detection limit (MDL).
2) Value obtained from AEP (2016).

Notes:
HC (Human Contact); DW (Drinking Water); EC (Eco-contact); FAL (Freshwater Aquatic Life); LW (Livestock Watering)
Shading indicates an exceedance of a specific guideline



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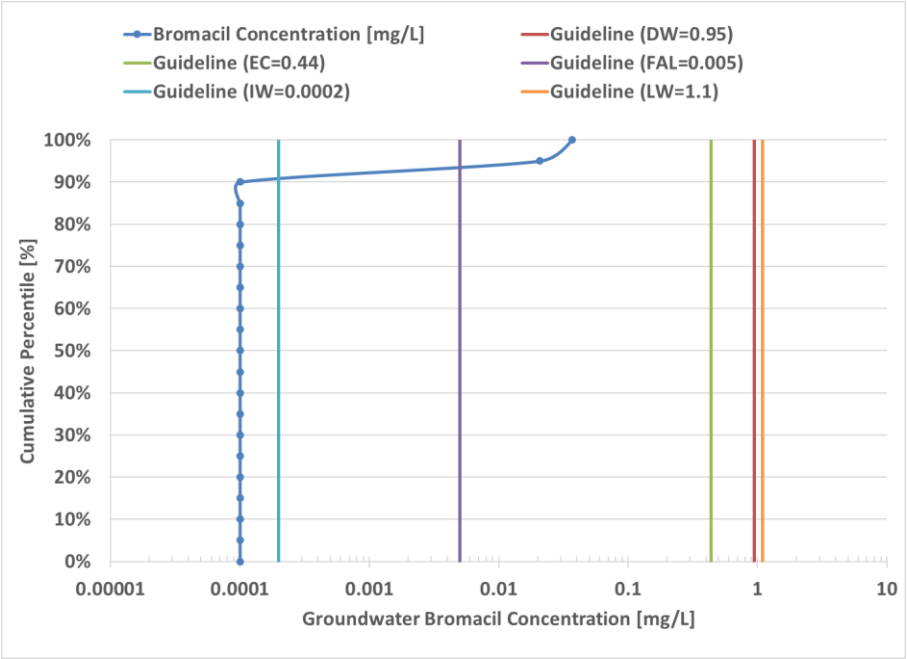
Case Study #2 – Groundwater Conc.

Mean	Min	Max	N	Agricultural Guideline[2]
0.0016 mg/kg	0.0001	0.037	164	0.95 (DW)
				0.44 (EC)
				0.005 (FAL)
				0.0002 (IW)
				1.1 (LW)

1) Average calculated assuming that non-detects were present at a concentration equivalent to the method detection limit (MDL).
2) Value obtained from AEP (2016).

Notes:
DW (Drinking Water); EC (Eco-contact); FAL (Freshwater Aquatic Life); Irrigation Water (IW); LW (Livestock Watering)
Shading indicates an exceedance of a specific guideline



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Case Study – Screening Results

- Bromacil concentrations exceeded guidelines for the protection of freshwater aquatic life and irrigation watering.
- All other pathways of concern (i.e., drinking water, human contact, eco-contact, livestock watering) were below guidelines.
- Major concern is off-site risks to surface water (i.e., freshwater aquatic life and irrigation crops).
- No waterbodies within 300m but bromacil persistent

Risk Characterization

- Groundwater greater relevance for protection aquatic life.
- Toxicological basis of aquatic life and irrigation guidelines
- Bromacil degradation and environmental fate
- Groundwater transport modelling
- Data gaps and uncertainties

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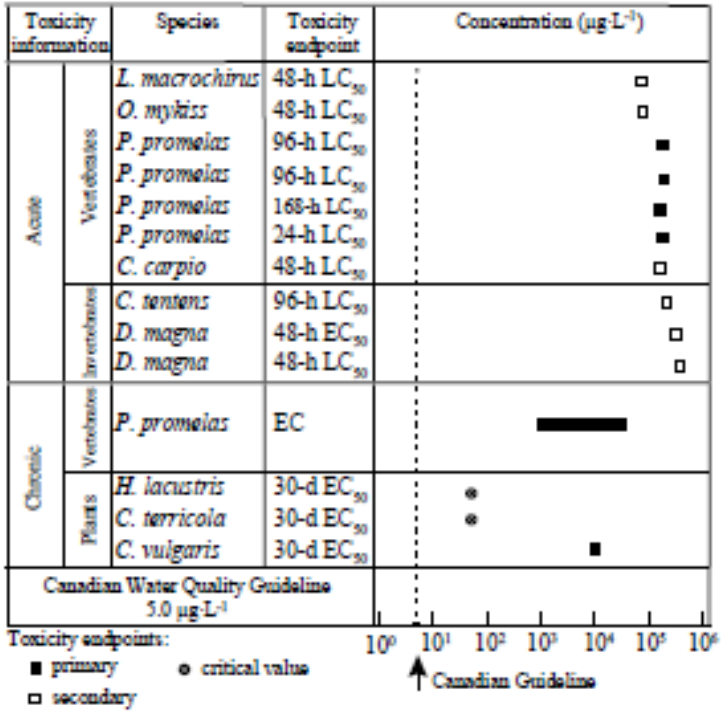
Risk Characterization – Toxicity



- FAL guideline (0.005 mg/L) based on inhibition of photosynthesis in plants.
- This value is based on a 30-day EC50 of 0.05 mg/L in the most sensitive aquatic species (green algae) to which an uncertainty factor of 10 was applied (CCME 1999a).
- Clear difference between aquatic plants and invertebrates or vertebrates.
- US EPA (2018) has a similar limit of 0.0068 mg/L.

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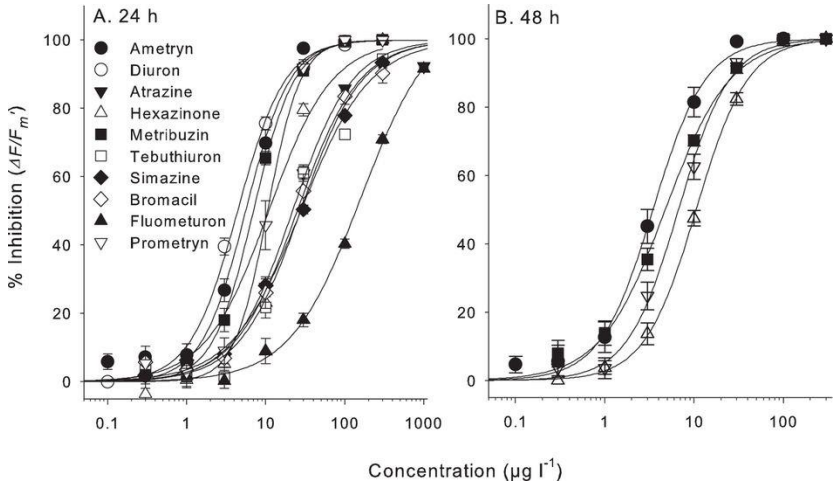
Risk Characterization - Toxicity

Adam et al. 2015



- Seagrass toxicity comparison to other photo-inhibitory herbicides.

Risk Characterization – Toxicity

- Irrigation guideline (0.0002 mg/L) based on inhibition of growth in plants (e.g., 30% reduction in biomass).
- This value is based on maximum allowable toxic concentration (MATC) of 0.02 mg/L in the most sensitive plant (cucumber) to which an uncertainty factor of 100 was applied (CCME 1999b).
- Guideline of 0.0006 mg/L also developed for cereals and pasture grasses.

Risk Characterization - Degradation

- Bromacil is mobile in soil, soluble in water and detected in groundwater when used as a herbicide in relation to agricultural use (Zhu and Liu 2002).
- More persistent and less mobile in soils with higher organic matter content.
- Degradation rates vary (2-8 months) with soil organic matter content with a conservative half-life of 275 days (US EPA 2012).

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Risk Characterization - Degradation

- No acceptable degradation rate of bromacil in aquatic systems.
- Based on the US EPA (2012) for risk assessment when single half-life value is available or limited:
  - Multiply by 3 (275 x 3 = 825 days) to estimate conservative value for soil; and
  - Multiple soil value by 2 to estimate groundwater half-life (825 x 2 = 1,650 days).
- Values used for risk assessment.

Risk Characterization - Modelling

- Groundwater transport modelling (AEP 2016)
- Maximum soil at Site #1 was 0.059 mg/kg
- Soil leachate predicted to be 0.13 mg/L
- Groundwater concentration at site predicted to be 0.034 mg/L
- Maximum measured groundwater concentration at site was 0.032 mg/L

DF1 - Partitioning of the contaminant between soil, soil vapour and soil pore water (0.45);
DF2 - Leaching of the contaminant through the unsaturated zone to the groundwater table (1.0);
DF3 - Mixing and dilution of leachate into groundwater (3.86); and,
DF4 - Saturated zone transport of the contaminant to a down-gradient receptor (1.0).

$$GW[\frac{mg}{L}] = \frac{Soil[\frac{mg}{kg}]}{DF1 \times DF2 \times DF3 \times DF4}$$

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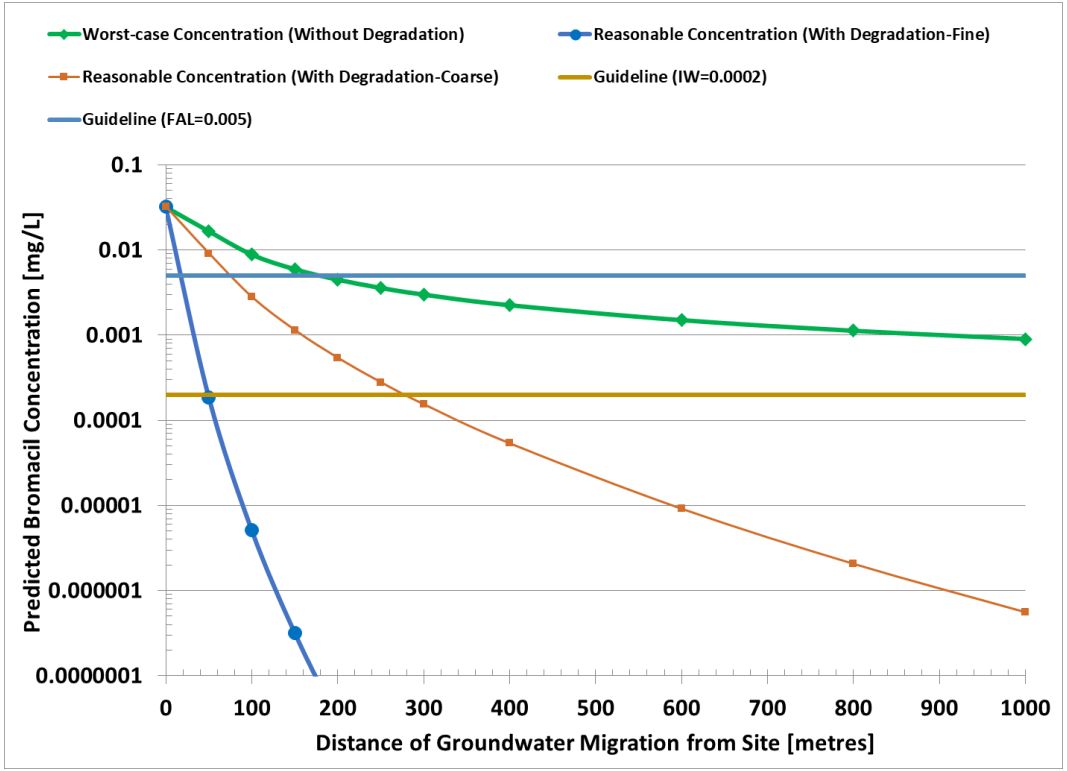
Risk Characterization – Modelling



- Predicts how concentrations of bromacil in groundwater decrease with increasing distance.
- Based on the Domenico and Robbins (1985) groundwater transport model from CCME (2006).
- Assumed $t_{1/2}$=1,650 days.

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Risk Characterization – Modelling

- The predicted concentration without degradation represents a worst-case and unrealistic concentration scenario as degradation is expected to be active to some extent in the saturated zone.
- Therefore, the predicted concentrations with degradation presents a reasonable scenario (i.e., saturated zone degradation half-life of 1,650 days was considered conservative).

Conclusions

- Risks to aquatic life are not expected as the Site is not near (i.e., within a 500 metres) an existing water body.
- Risks to aquatic life are not expected as predicted groundwater concentrations are expected to fall below FAL guidelines with 50 to 200m of the Site.
- Risks to crops via irrigation needs to be considered pathway operable near the Site.

Questions?

References

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