DEVELOPMENT OF AN EXTRACTION METHOD FOR ESTIMATING PHYTOACCESSIBLE CONCENTRATIONS OF SOIL STERILANTS BROMACIL AND TEBUTHIURON

JACKIE MAXWELL, M.SC., P.AG.

SUPERVISOR(S)
SYLVIE QUIDEAU, PH.D.
MILES DYCK, PH.D.

Mitacs

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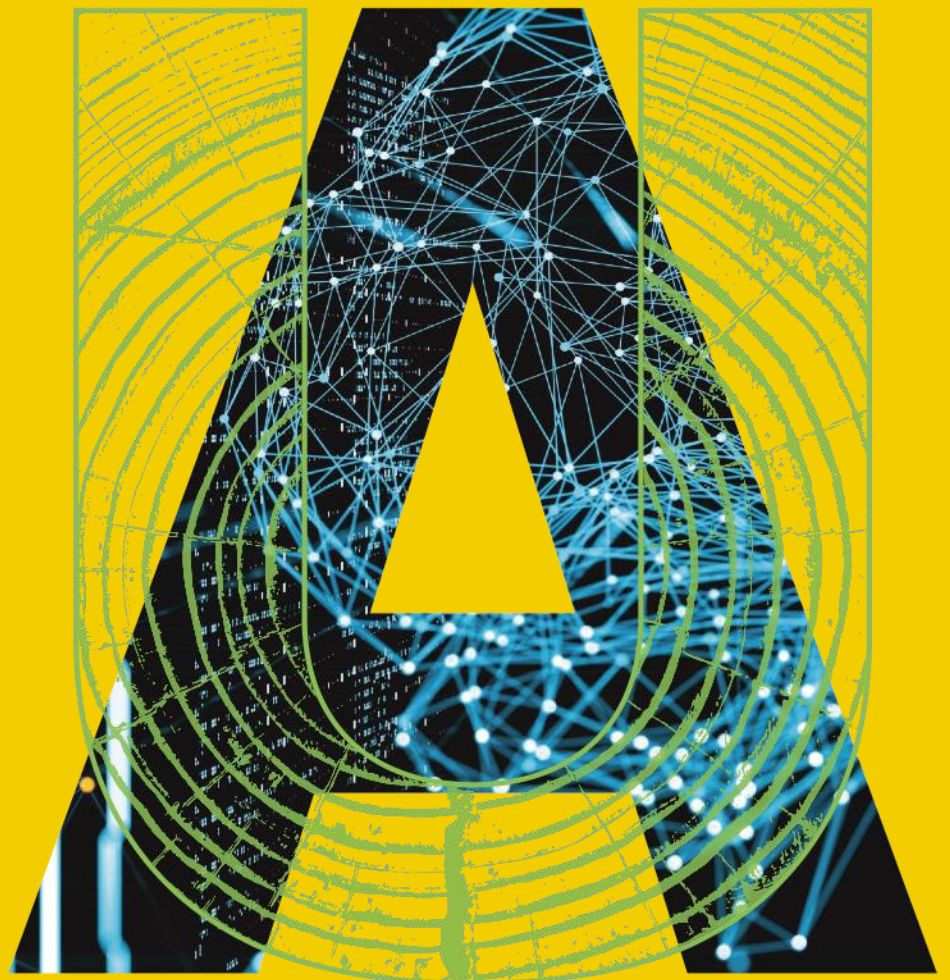
SSP
Soil Sterilants Program



Applied Science: Assessment of Contaminated Sites

ALBERTA TIER 1 GUIDELINE FOR TEBUTHIURON: **0.046 MG/KG** (DIRECT SOIL CONTACT – ECOLOGICAL)
SS19-6B: ESTIMATED **TOTAL** TEBUTHIURON: **0.148 MG/KG**
SS19-6B: ESTIMATED **PHYTOACCESSIBLE** TEBUTHIURON: **0.020 MG/KG**

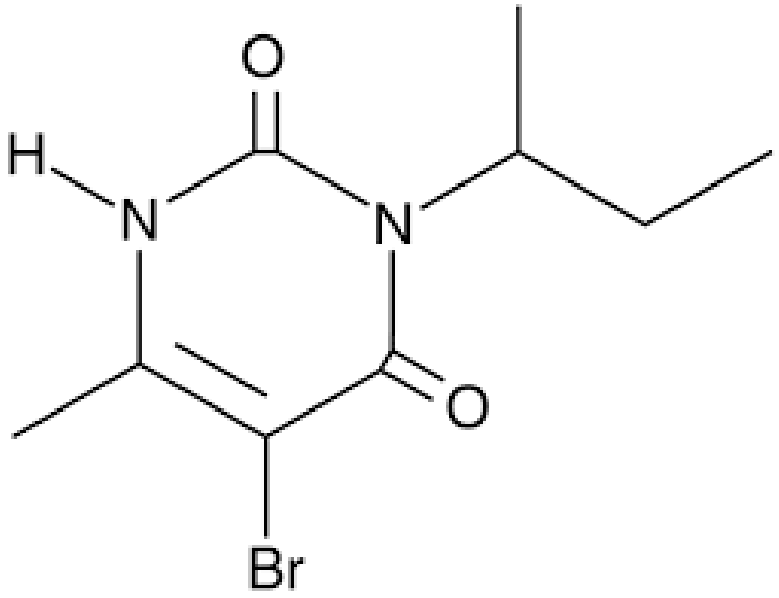
Looking west:
Background crop appears shorter, less developed

Looking South:
Viewed from the seeding direction, no visual difference

Up Close:
Weeds are dying from selective herbicide application, crop is alive

Even Closer:
Obvious weeds are chlorotic, crop is not

Soil Sterilants Bromacil & Tebuthiuron

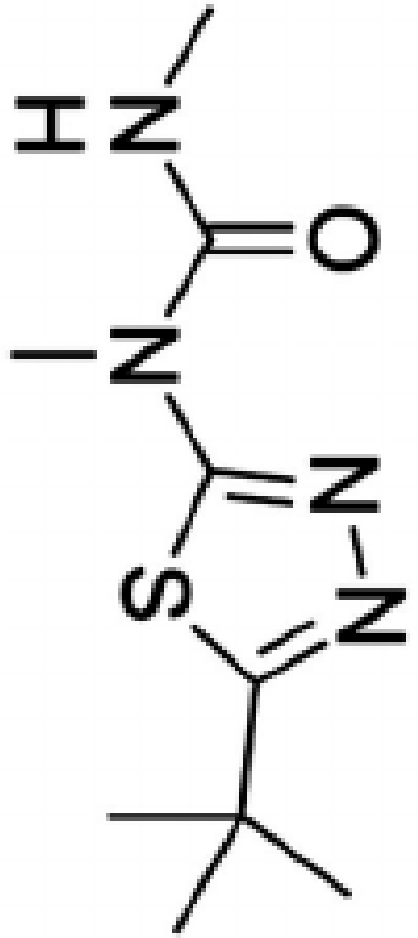


Bromacil

- Solubility in water 815 mg/L
- Solubility in methanol 14,000 mg/L
- Linear K_{oc} 32 mg/L

Tebuthiuron

- Solubility in water 2,500 mg/L
- Solubility in methanol 170,000 mg/L
- Linear K_{oc} 80 mg/L



Drozdowski, B., Powter, C., & Levy, S. (2018). Management of Sterilant Impacted Lands: Literature Synthesis; Pesticide Properties Database. (2021). *Tebuthiuron (Ref: EL 103);* Pesticide Properties Database. (2021). *Bromacil (Ref: DPX N0976)*

OBJECTIVES & HYPOTHESIS

1) $Phytoacessible\ Sterilant \neq Total\ Sterilant, as$

$Adsorbed\ Sterilant \gg 0$

2) $Adsorption = \beta_0 + \beta_1(Organic\ Matter) + \beta_2(Clay)$

$+\beta_1\beta_2$

Hypothesis: Adsorption to soil organic matter and/or soil particles reduces what remains soluble or phytoaccessible of bromacil or tebuthiuron concentrations; this soluble or phytoaccessible portion is less than the bromacil or tebuthiuron concentration estimated by 99 percent methanol extraction conducted at commercial laboratories.

01

How can the soluble / phytoaccessible portion of bromacil and tebuthiuron be estimated?

Total, Bioavailable, Bio/Phyto-Accessible Concentrations of Soil Sterilants

	Total	Bioavailable	Bioaccessible	Phytoaccessible
Definition	ALL possible sterilant, adsorbed and solubilized	Solubilized sterilant in contact with cell membrane	Bioavailable, plus that which may become available	Desorbed and solubilized at one point in time
Method	99% MeOH, shake, concentrate, filter, HPLC/MSD	Individual measurements of processes leading to cell membrane contact	Individual measurements of processes	Wait for it!

Methods to Estimate Phytoaccessibility

Nutrients

- ‘Classical’ extractants specific to macro-or-micronutrient(s)
- These do not destroy soil structure or change pH
- e.g., 0.073 sodium acetate, **0.01 M calcium chloride**

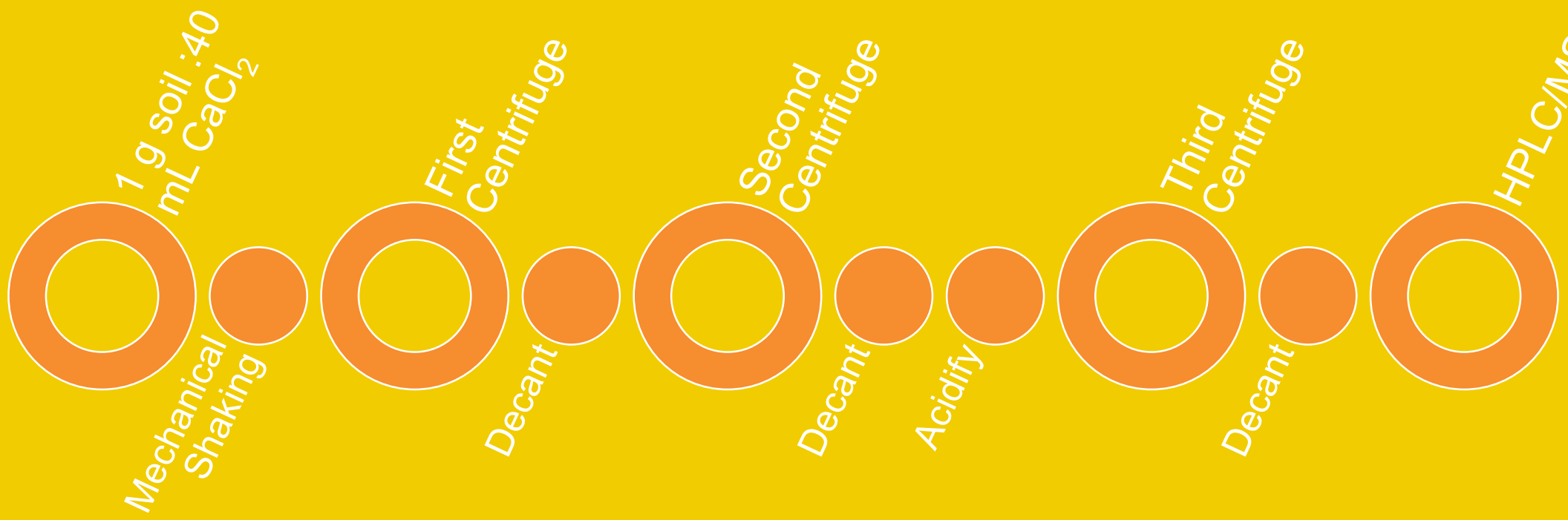
Application Rates

- Rates tested by bioassays
- Different soils tested
- Extract spiked soil with **0.01 N or 0.01 M calcium chloride**
- Soil or extract concentration measured

Contaminants

- Adsorption/desorption studies using **different ionic strengths of calcium chloride**
- Bioassay experiments and measure concentration in tissues

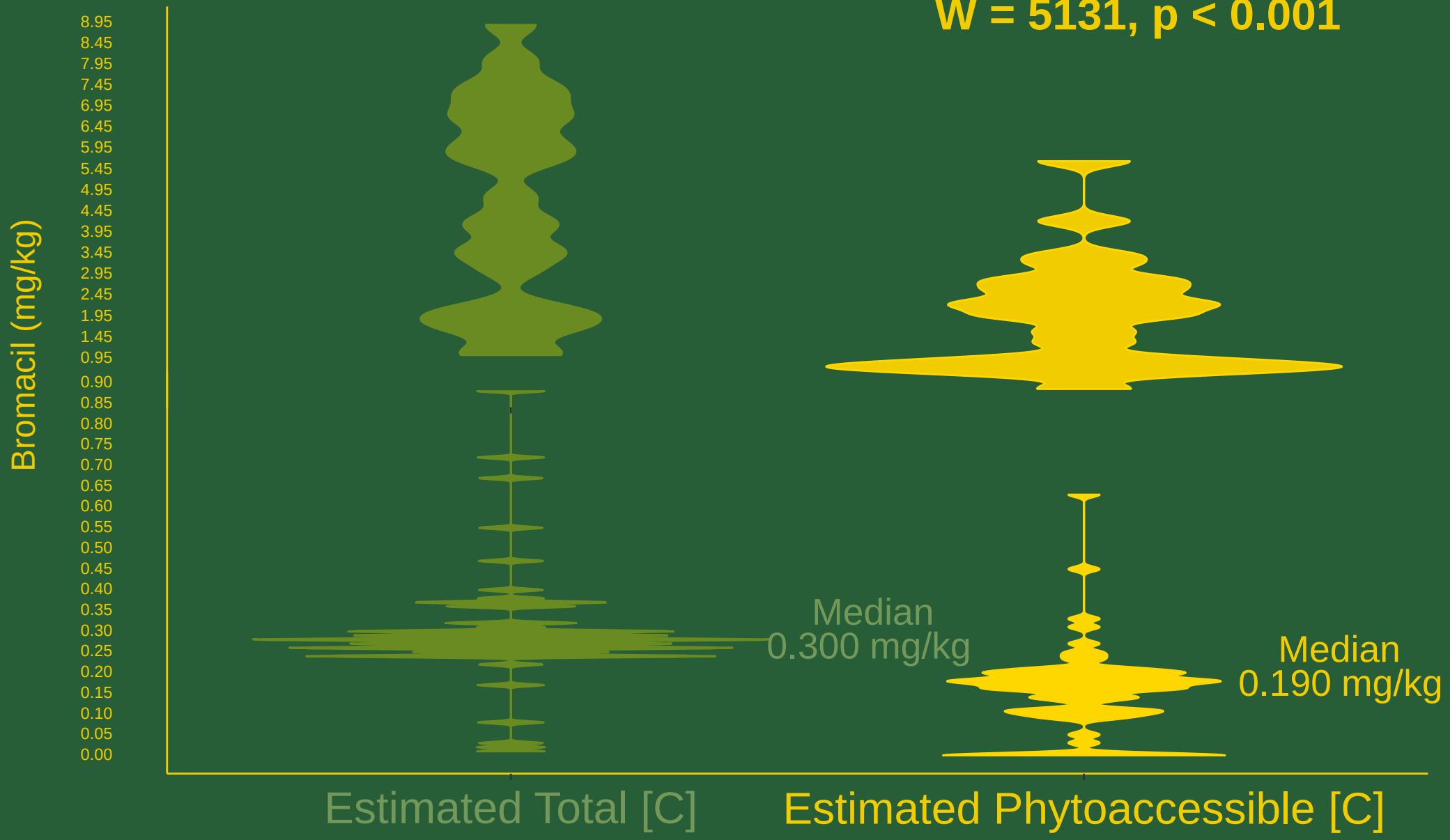
Q01: Method



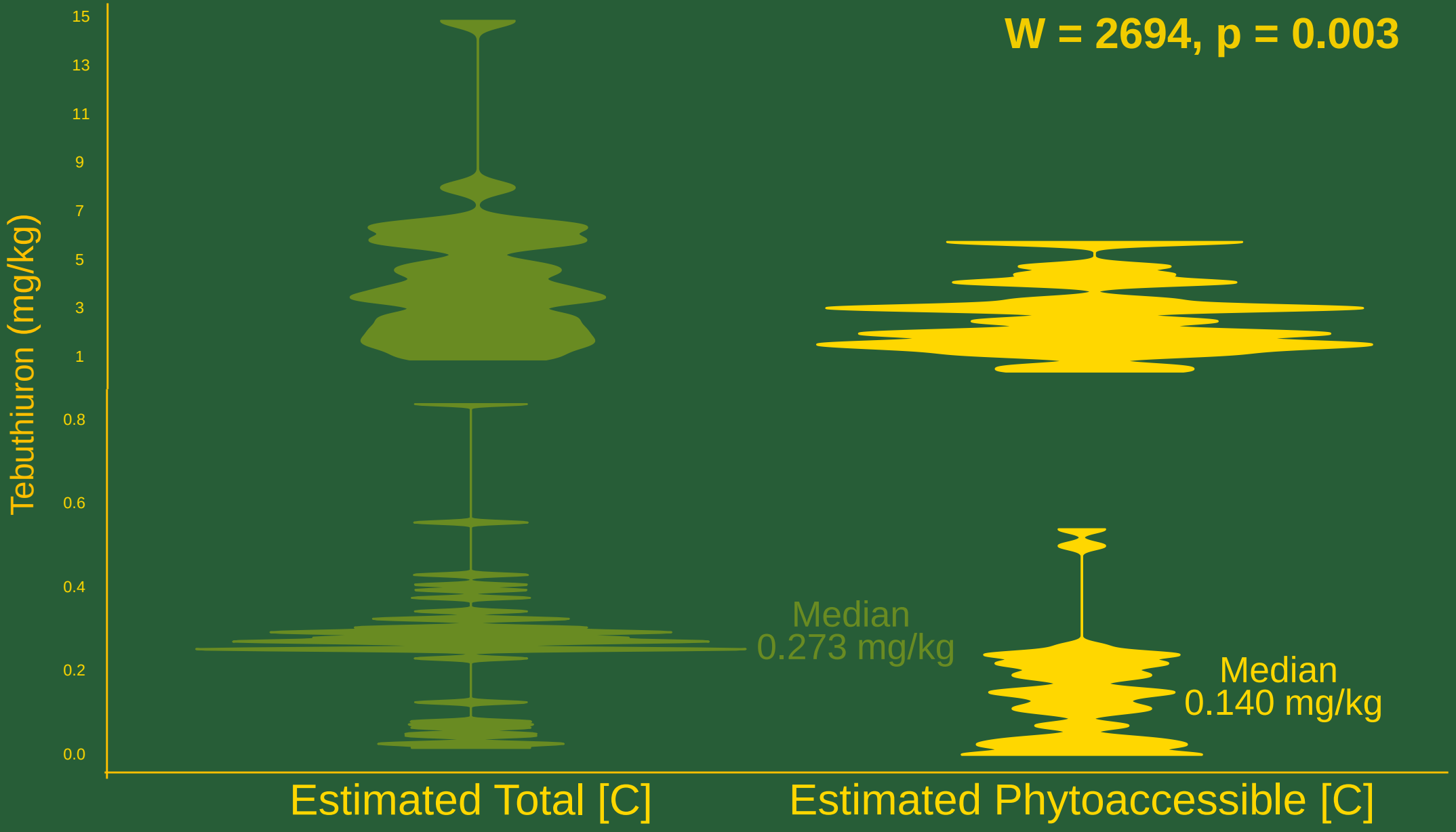
Garrett, R. G., Hall, G. E. M., Vaive, J. E., & Pelchat, P. (2009). A water-leach procedure for estimating bioaccessibility of elements in soils from transects across the United States and Canada. Applied Geochemistry, 24, 1438–1453.; Houba, V. J. G., Temminghoff, E. J. M., Gaikhorst, G. A., & van Vark, W. (2000). Soil analysis procedures using 0.01 M calcium chloride as extraction reagent. Communications in Soil Science and Plant Analysis, 31(9–10), 1299–1396.; Alva, A. K., & Singh, M. (1991). Sorption-desorption of herbicides in soil as influenced by electrolyte cations and ionic strength. Journal of Environmental Science and Health, 26(2), 147–163.; McKenzie, R. H. (2016). Determining Plant Available Phosphorus. Top Crop Manager West, 40, 41, 59…etc!

Q01 Results: Estimated Phytoaccessible Bromacil

W = 5131, p < 0.001



Q01 Results: Estimated Phytoaccessible Tebuthiuron

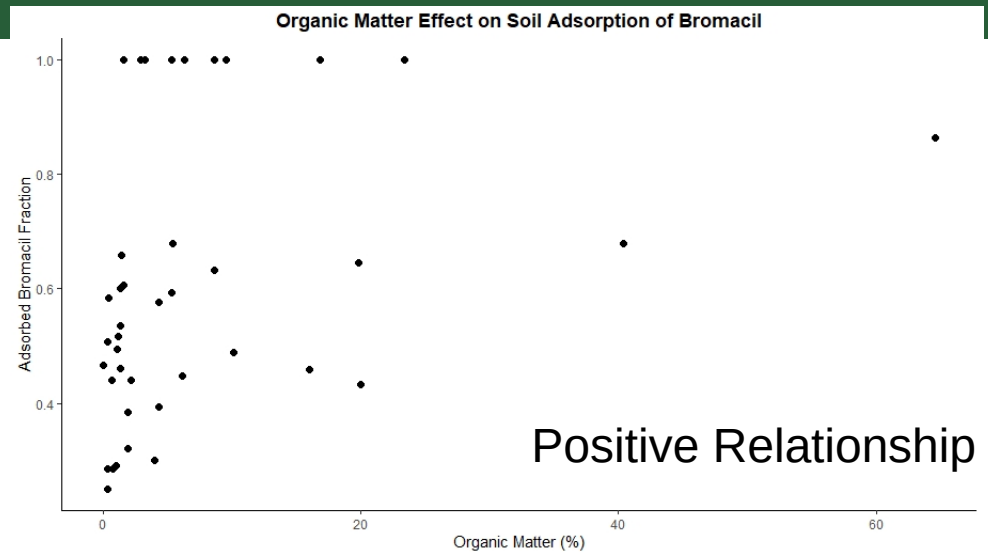


02

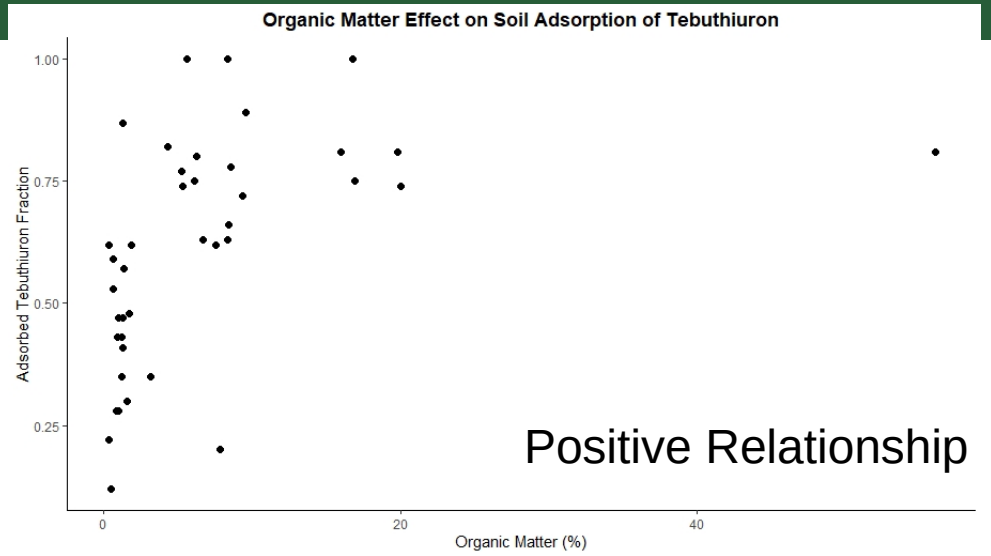
Do higher percentages of clay and organic matter significantly increase adsorption of bromacil or tebuthiuron?

Exploratory Data Analysis

Organic Matter

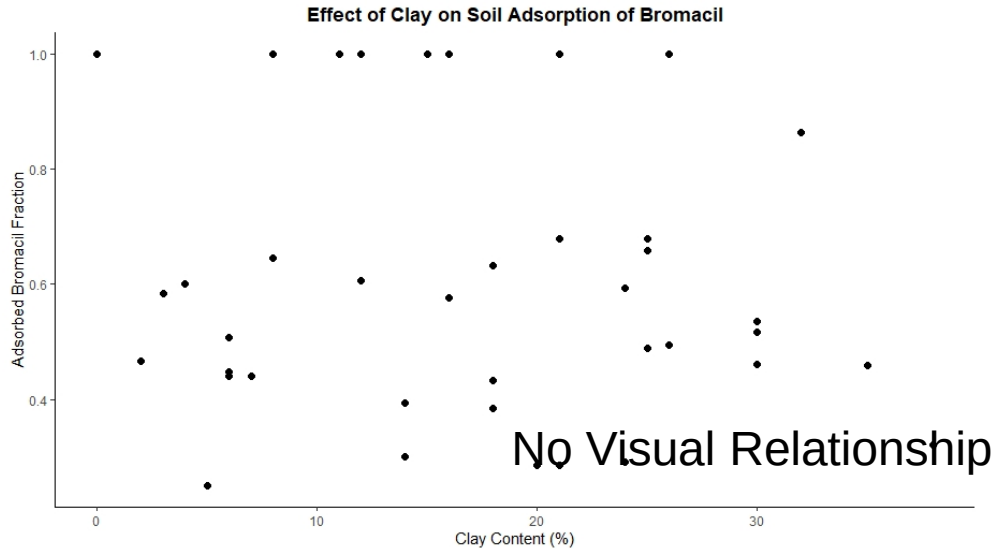


Positive Relationship

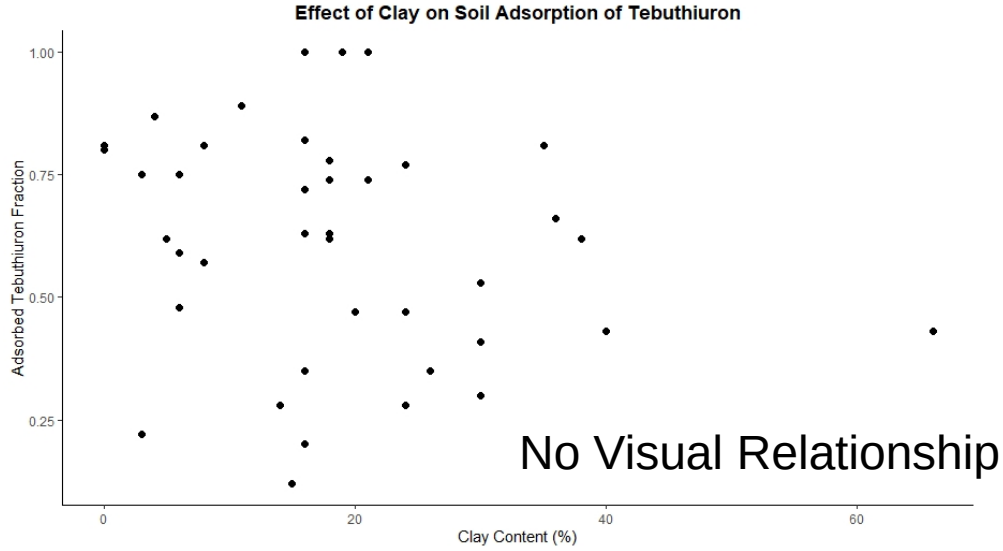


Positive Relationship

Clay



No Visual Relationship



No Visual Relationship

Q02: Method

$$Adsorbed\ Fraction = \frac{Total - Extract}{Total}$$

where:

Total = total sterilant concentration (mg/kg), estimated by 99 percent methanol extraction, or the spiked amount

Extract = sterilant extracted by 0.01 M calcium chloride (mg/kg)

Q02: Selected Categories for Organic Matter & Clay

A 2x2 ANOVA tested 1) if higher %OM increases adsorption, 2) if higher %clay increased adsorption, and 3) if there is an interactive effect b/w %OM & %clay

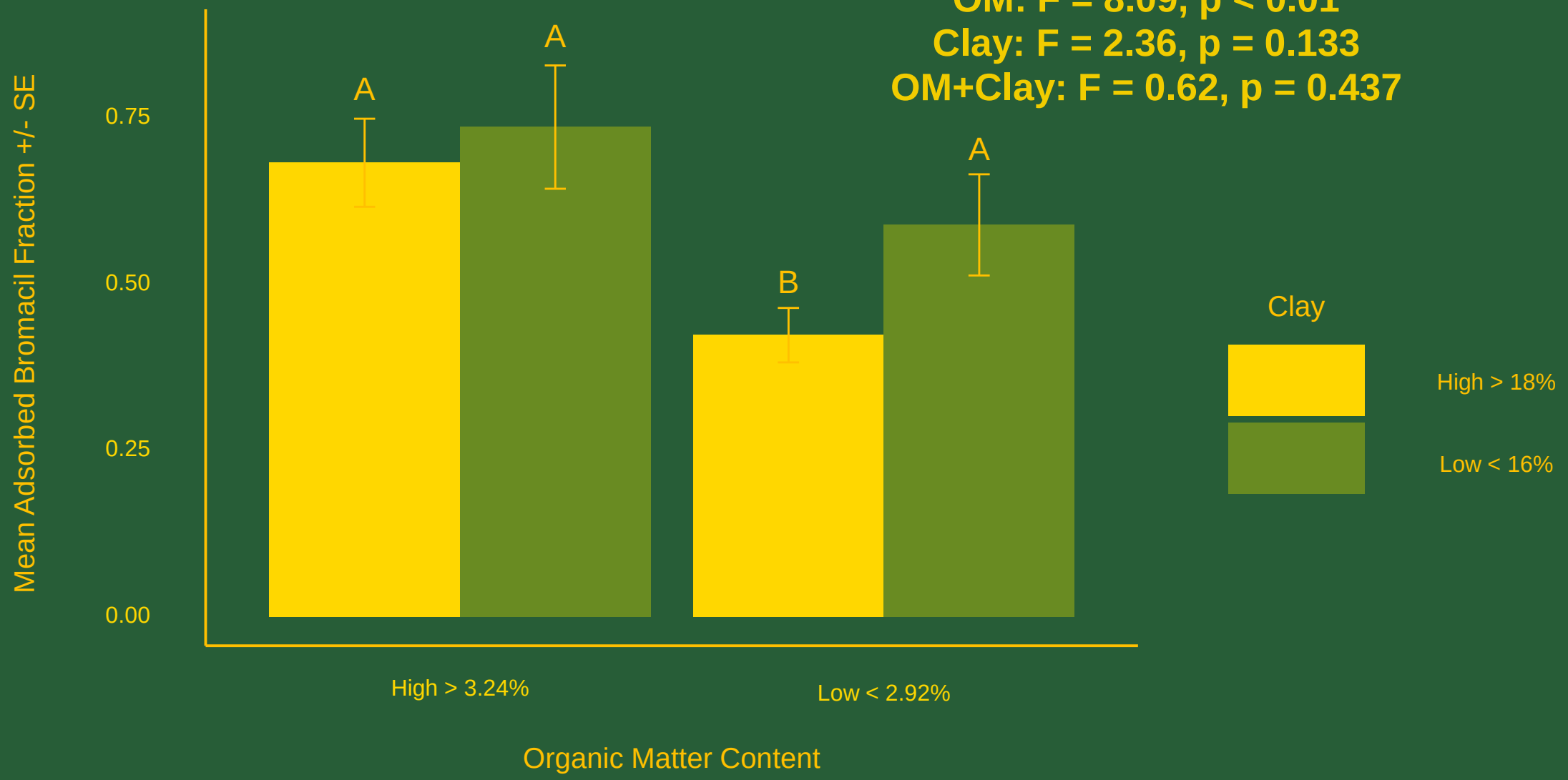
Bromacil	High Clay Content (18-38%)	Low Clay Content (0-16%)
High Organic Matter (3.24-64.6%)	10	10
Low Organic Matter (0.00-2.92%)	10	10

Tebuthiuron	High Clay Content (18-66%)	Low Clay Content (0-16%)
High Organic Matter (5.29-66%)	10	10
Low Organic Matter (0.28-4.34%)	10	10

RENR 581: Introduction to Exploratory Data Analysis, and RENR 582: Elementary Statistics in the Applied Sciences

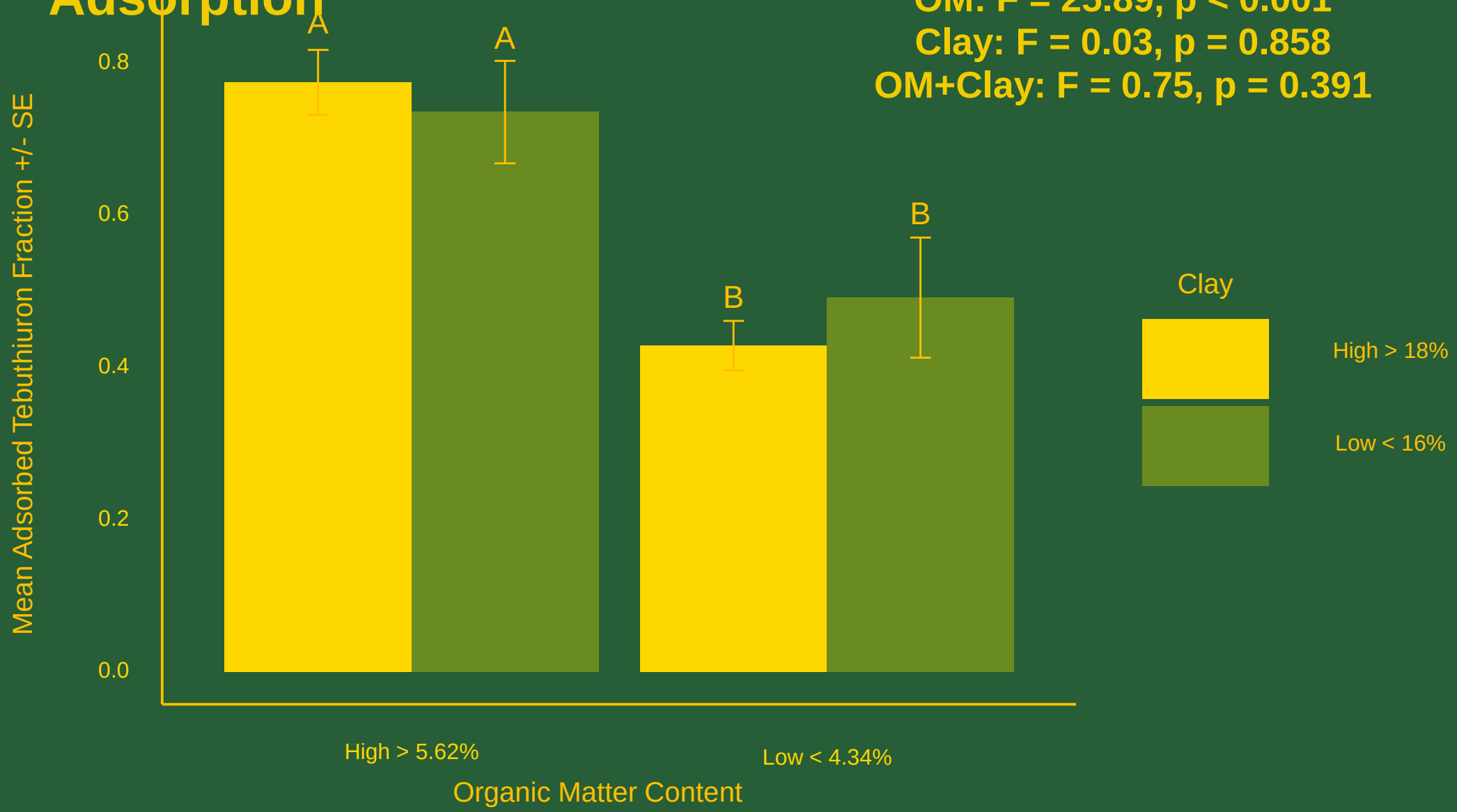
Q02 Results: OM & Clay Effect on Bromacil Adsorption

OM: F = 8.09, p < 0.01
Clay: F = 2.36, p = 0.133
OM+Clay: F = 0.62, p = 0.437



Q02 Results: OM & Clay Effect on Tebuthiuron Adsorption

OM: F = 25.89, p < 0.001
Clay: F = 0.03, p = 0.858
OM+Clay: F = 0.75, p = 0.391



Discussion

For large areas of marginal bromacil or tebuthiuron contamination, economical approaches are needed to reduce risk, meet regulatory requirements, and ***protect soil health****. Removal of soil which, marginally, does not meet the provincial guidelines could affect productivity of agricultural land more than potential risk posed by sterilant concentrations in soil.*

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FUTURE RESEARCH

- Refinement of total, bioavailable and bioaccessible definitions for organic contaminants
- Comparative extraction between 99 percent methanol and 0.01 M calcium chloride using developed method
- Examine micro-pore sequestration of sterilants

Jokes?

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