FATE OF MUSTARD IN SOIL

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OUTLINE

- Program
- Recovery in soil
- Hydrolysis
- Ionizing radiation
- Conclusions
- Future work

MOTIVATION

- Significant stocks of CWA (principally HD) held in Canada
- HD used in defence research
- Stocks destroyed
- Residual contamination due to past activities
- Possibility of future terrorist/criminal use

PROGRAM

- Study remediation of environmental contamination by CWAs
- Current focus is transport and fate of vesicants (HD and L) in soil
- Initial investigation of using ionizing radiation for remediation

TRANSPORT AND FATE OF HD

- Surrogate or analog chosen to represent prairie soil (highest levels of CWA contamination in Canada)
- Particle size ranges
  - sand: 2mm to 50 μm,
  - silt: 50 μm - 2 μm,
  - clay <2 μm

ANALOG SOIL

Material	Weight Proportion (%)
Quartz sand (#00)	55.2
F-20 Feldspar	18.4
Bentonite powder	11.0
Redart clay	7.4
Limestone	5.0
Black earth powder	3.0

HD IN ENVIRONMENT

- Rapid hydrolysis on dissolution in H_2O ($t_{1/2}$ = 4-8 min)
- Low solubility in H_2O (~ 900 mg/L)
- Little movement in soil
- HD in soil that does not vaporize remains relatively stable

HALF MUSTARD

- Chloro ethyl ethyl sulphide
- $CH_3CH_2SCH_2CH_2Cl$
- Investigated as a surrogate (commercially available – not controlled)
- Too volatile

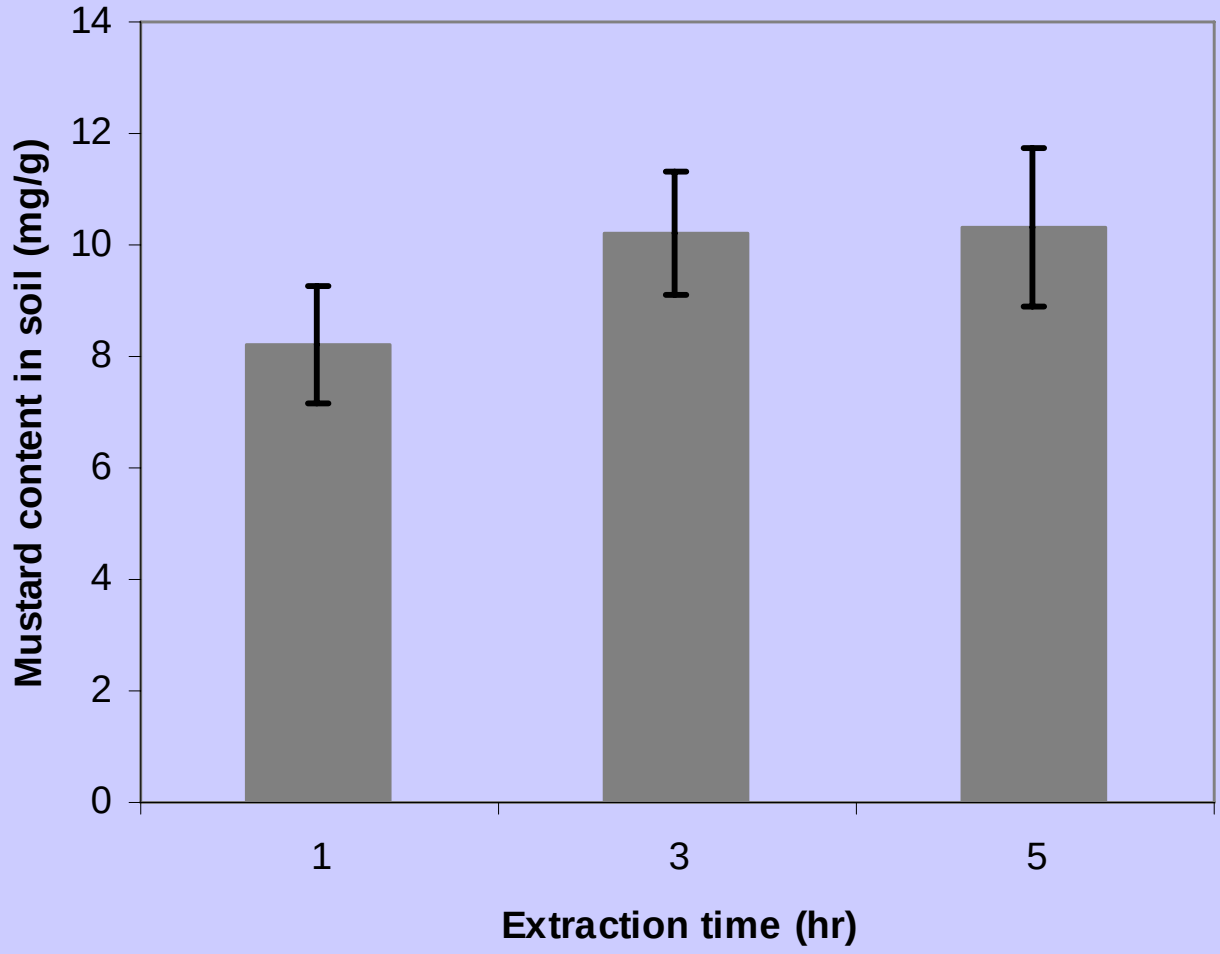
AGENT RECOVERY FROM SOIL

Agent	Recovery (%)
Half Mustard	85
Mustard	100

AGENT RECOVERY FROM SOIL

- 0.5-1 g HD dissolved in 20 mL $CHCl_2$ and added to soil
- 48 h to evaporate solvent
- Sample capped and shaken to mix HD with soil
- HD extracted using $CHCl_2$

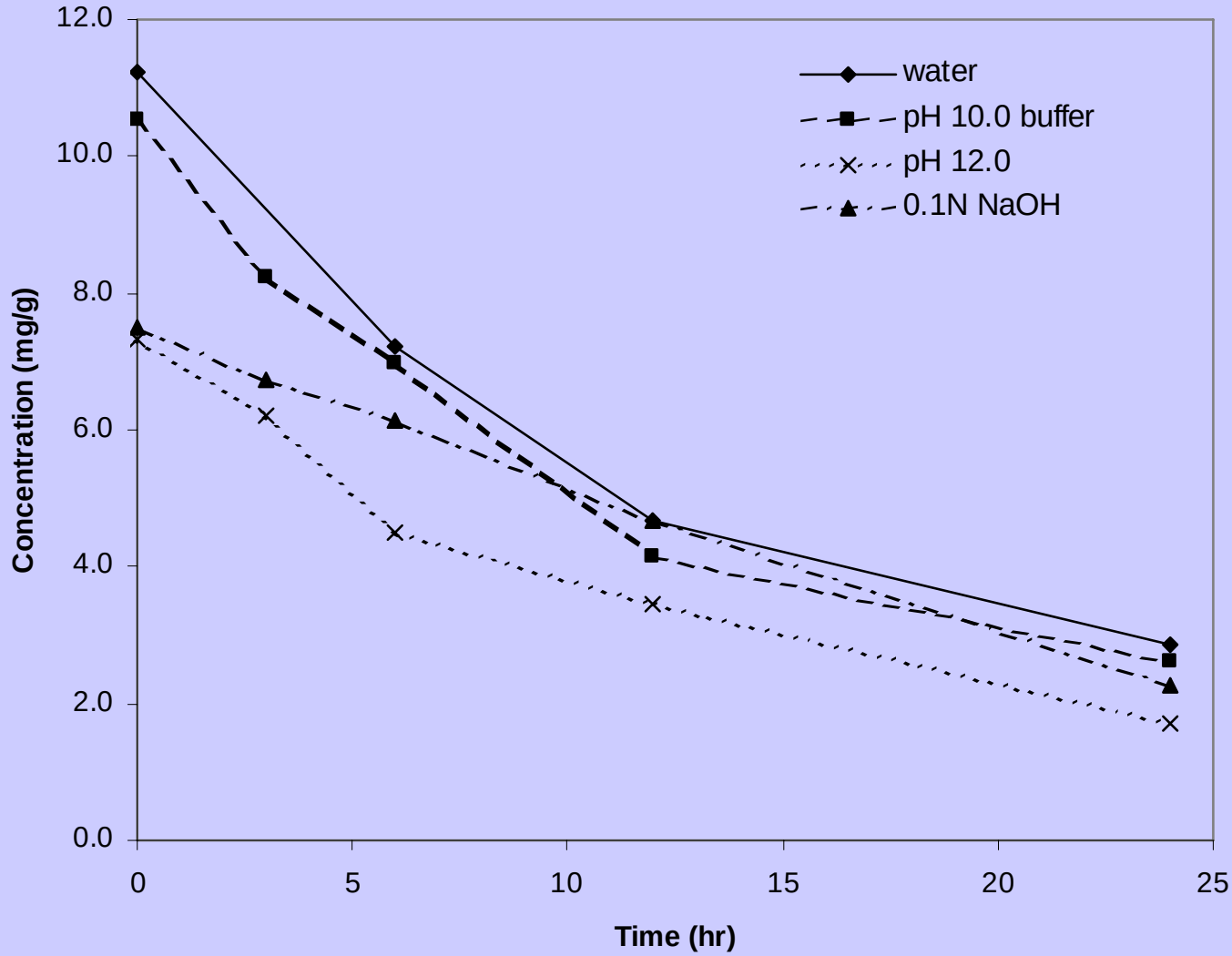
HD EXTRACTION FROM SOIL



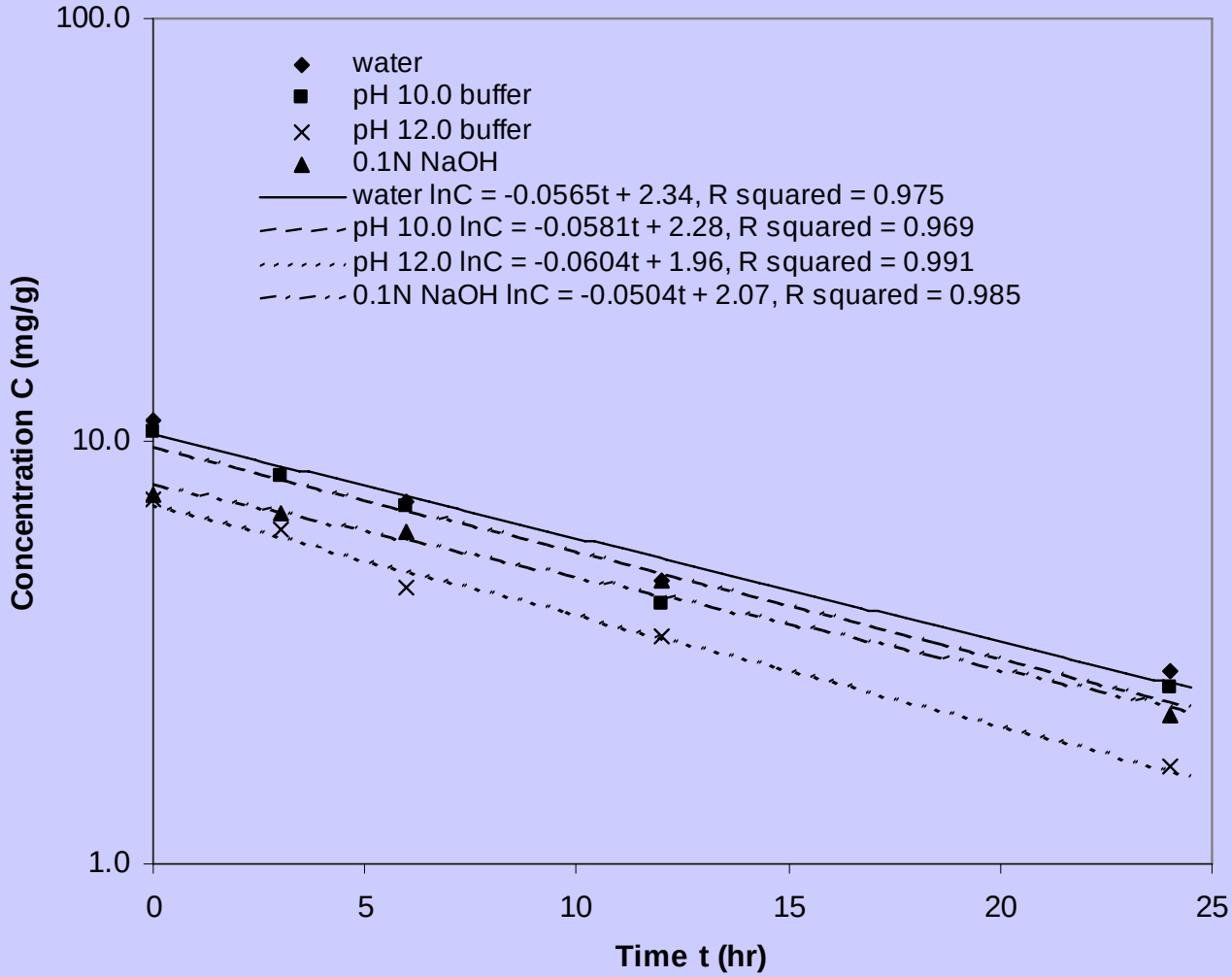
HYDROLYSIS

- Natural degradation up to 12 months in soil
- Hydrolysis study to examine effect of pH on degradation of HD in moist soil
- Reaction treated as single phase or pseudo homogeneous

HYDROLYSIS


12.0
10.0
8.0
6.0
4.0
2.0
0.0
Concentration (mg/g)
0
5
10
15
20
25
Time (hr)
water
pH 10.0 buffer
pH 12.0
0.1N NaOH

HYDROLYSIS


100.0
10.0
1.0
Concentration C (mg/g)
0
5
10
15
20
25
Time t (hr)
water
pH 10.0 buffer
pH 12.0 buffer
0.1N NaOH
water lnC = -0.0565t + 2.34, R squared = 0.975
pH 10.0 lnC = -0.0581t + 2.28, R squared = 0.969
pH 12.0 lnC = -0.0604t + 1.96, R squared = 0.991
0.1N NaOH lnC = -0.0504t + 2.07, R squared = 0.985

HYDROLYSIS

- Increasing pH expected to increase rate of hydrolysis
- Effect weak
- 0.1 N NaOH lower rate constant than H_2O
  - higher viscosity?
  - perhaps not enough OH^- to act as buffer

HYDROLYSIS

Medium	Rate constant ($\times 10^2$ h^{-1})	Half-life (h)
Water	5.65	12.3
pH 10.0 buffer	5.81	11.9
pH 12.0 buffer	6.04	11.5
0.1 N NaOH	5.04	13.7

IONIZING RADIATION

- Environmentally benign short-lived isotopes
- ^{24}Na
  - $t_{1/2}$ = 14.97 h
  - 2 hard γ (1368, 2754 keV)
- 1000 ppm Na solution irradiated for 24 h at $5x10^{11}$ n/cm^2s
- Na_2CO_3 powder irradiated for 48 h

IONIZING RADIATION

Medium	HD Irradiation Time (h)	Dose (cGy)	HD Recovered (%)
Na solution	24	3.7	106
Na solution	48	5.7	113
Na_2CO_3	100	1100	94

CONCLUSIONS

- Hydrolysis rate only modestly enhanced by increasing pH
- Rate constants determined for pseudo first order reaction
- Larger doses of ionizing radiation destroy HD

FUTURE WORK

- Transport and remediation studies to be extended to L and GB (and perhaps VX)
- Possible international collaboration