Simplistic Modeling Methods for Nitrate in Groundwater: Case Study Obtaining Regulatory Closure

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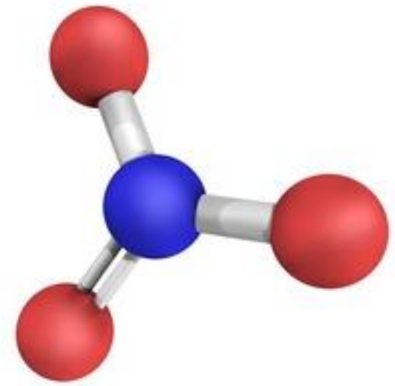
Outline

1. Background Information
2. Nitrate Model #1 – Dilution Factors
3. Nitrate Model #2 – ATRANS
4. Nitrate Model #3 – SST
5. Conclusions



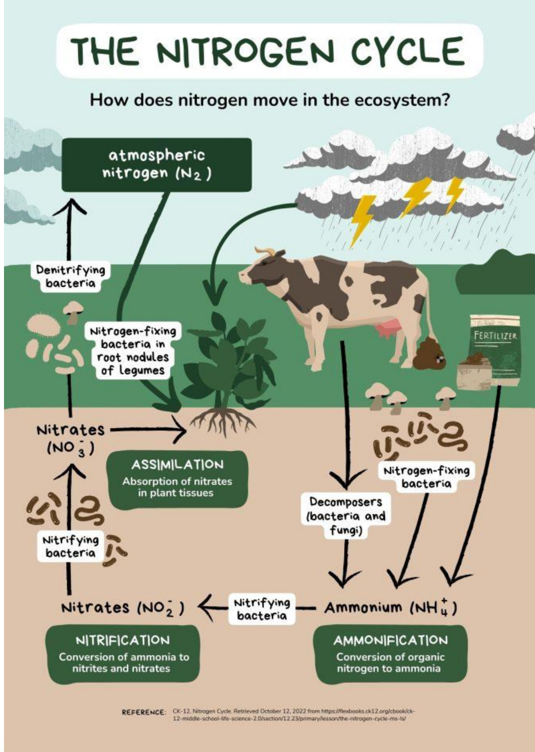
1. Background Information

- In Alberta, nitrate concentrations in groundwater at contaminated agricultural sites often exceed Tier 1 Guidelines.
    - Freshwater aquatic life – 3.0 mg/L
    - Potable water – 10 mg/L
- When seeking regulatory closure for a contaminated site, unaccounted for elevated nitrate concentrations in groundwater can result in a reclamation certificate application being rejected.

1. Background Information

Nitrate Sources

- Anthropogenic
  - Nitrogen fertilizers, manure, biosolids, irrigation water
  - Remediation activities
    (stimulate microbial activity)
- Natural
  - Soil nitrogen, ammonium-bearing clays,
    decaying plant material

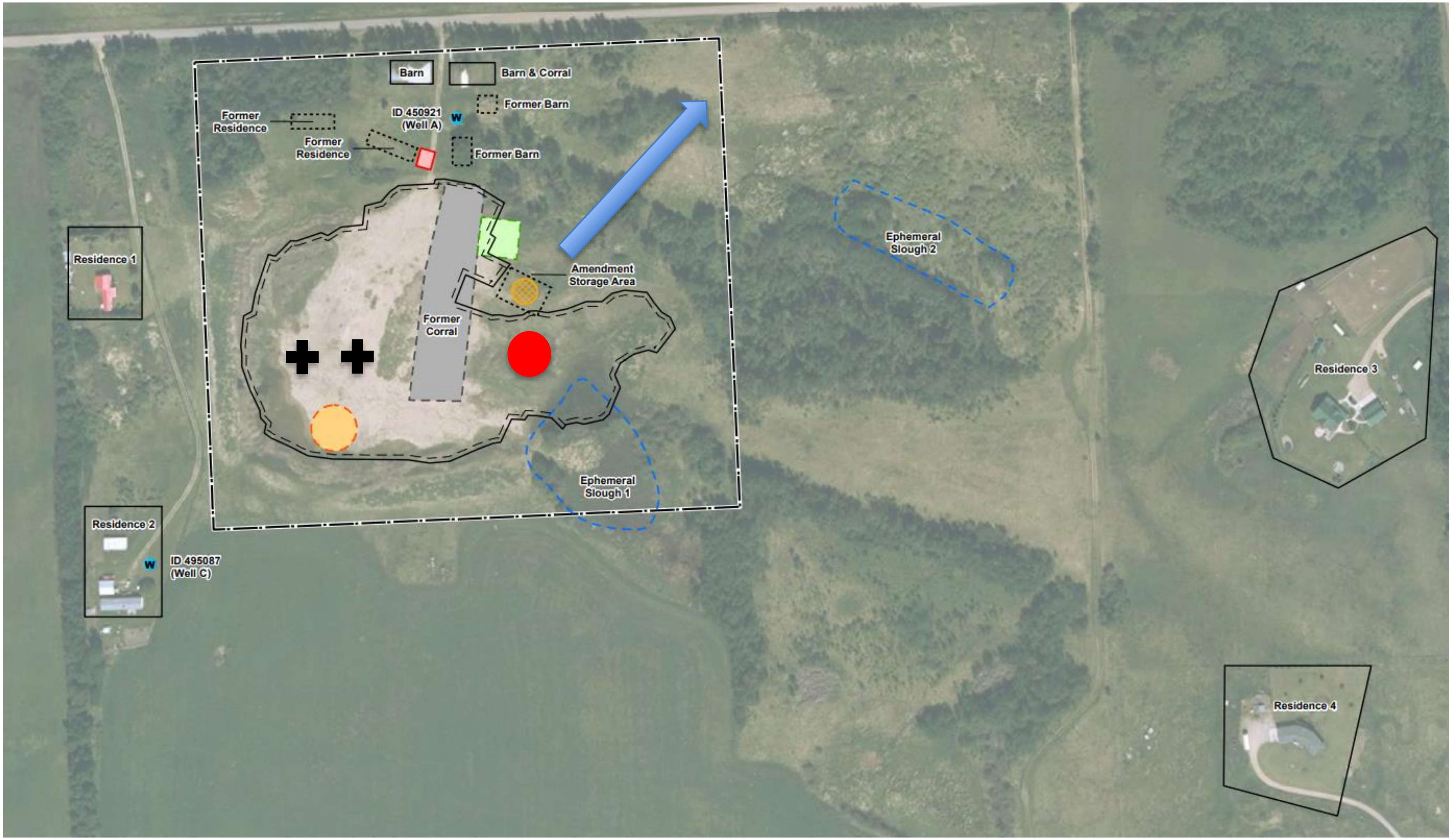


1. Background Information

Site Information

- Site is a former wellsite. Currently fully decommissioned.
- Infrastructure included two pumpjacks and a production flare pit.
- Site is surrounded by agricultural land and uncultivated low-lying and treed areas.
- A number of nearby residences 50 to 400 m distance.
- Approx. distance to nearest downgradient surface water feature is 218 m.
- Nine registered water wells within 1.0 km of site:
  - 7 domestic use, 1 stock and domestic use, 1 stock use
  - 2 nearest domestic wells completed at 24.4 and 61.0 mbgs
  - Well at 24.4 mbgs now decommissioned

1. Background Information

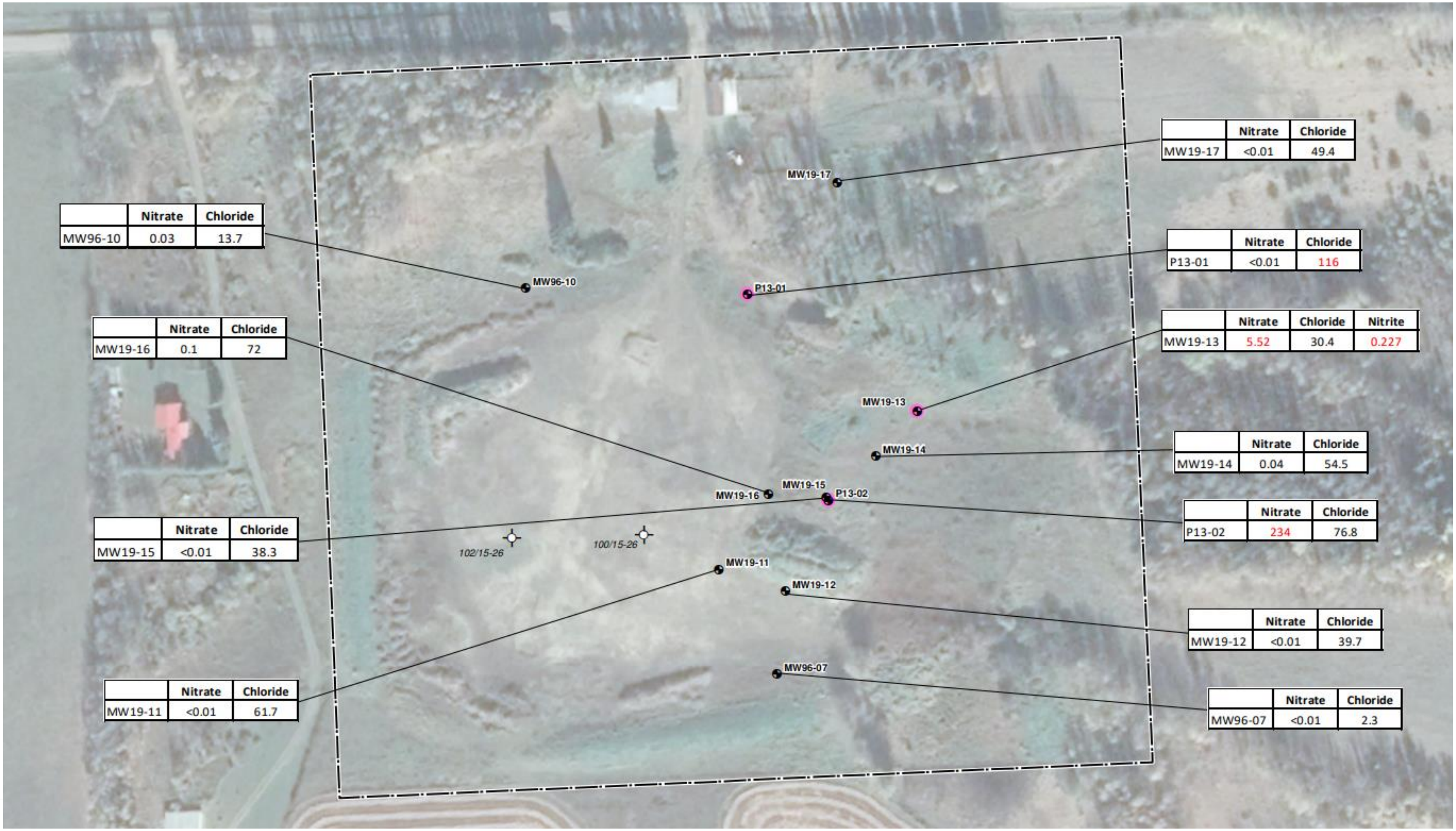


1. Background Information

Site Assessment and Remediation

- Long history dating back to 1996.
- Included numerous ESAs, excavations (flare pit and others), in-situ and ex-site biopiles, and interceptor trench.
- Initially, PHCs (including BTEX) were the main contaminants of concern.
- By 2021, contaminant issue was elevated nitrate and nitrite in groundwater.
- Nitrate/nitrite potentially attributed to:
  - Bioremediation amendment storage (nitrogen amendment)
  - Animal waste storage within former corral/sewage lagoon area

1. Background Information



	Nitrate	Chloride
MW19-17	<0.01	49.4

	Nitrate	Chloride
MW96-10	0.03	13.7

	Nitrate	Chloride
P13-01	<0.01	116

	Nitrate	Chloride
MW19-16	0.1	72

	Nitrate	Chloride	Nitrite
MW19-13	5.52	30.4	0.227

	Nitrate	Chloride
MW19-14	0.04	54.5

	Nitrate	Chloride
MW19-15	<0.01	38.3

	Nitrate	Chloride
P13-02	234	76.8

	Nitrate	Chloride
MW19-12	<0.01	39.7

	Nitrate	Chloride
MW19-11	<0.01	61.7

	Nitrate	Chloride
MW96-07	<0.01	2.3

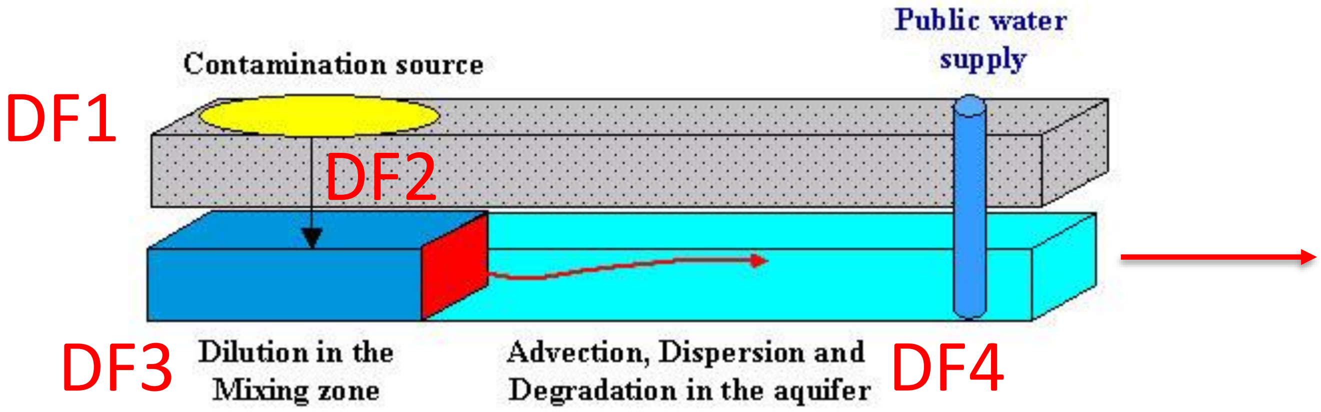
2. Nitrate Modeling #1

Dilution Factors

1. Dilution factors are used to develop guidelines protective of groundwater pathways, including FAL and potable water.

$$SRG_{GR} = SWQG_{FL} \times DF$$

- D1 - partitioning of the substance from soil to pore water (leachate);
- D2 - transport of leachate from the base of contamination to the GW table;
- D3 - mixing of leachate w/ groundwater;
- D4 - transport of the substance in GW down-gradient to a discharge point.



2. Nitrate Modeling #1

Dilution Factors

1. Freshwater aquatic life was evaluated by calculating a DF4 value and multiplying this value by the surface water quality guideline for nitrate.

$$GWRG_{GR} = SWQG_{FL} \times DF4$$

2. DUA was evaluated by using a modified version of the DF4 equation to represent DF2. Simulating saturated vertical transport of nitrate through sandy clay/clay till soils at the site. Major changes to DF4 model were:

   - defining the distance traveled by a contaminant using the thickness of the saturated zone below the source as opposed to the lateral distance between source and receptor, and
   - using an infiltration rate as opposed to Darcy velocity in determining the contaminant velocity

2. Nitrate Modeling #1

DF4 Model Results for FAL Receptor

Alberta Tier 2 Soil Remediation Guidelines Protective of Groundwater Pathways - Calculator V2.54

Form Date: 2021-01-27

Site-specific Parameters - User Defined			Denotes value changed from default	
		Units		AEP Defaults
Z	5.2	m	depth to bottom of contaminated soil	3
d	1.59	m	depth from surface to groundwater surface	3
X	10	m	length of contaminated soil parallel to groundwater flow	10
Y	10	m	source width perpendicular to groundwater flow	10
x	218	m	lateral distance between source and receptor	10
y	0	m	distance to receptor perpendicular to groundwater flow	0
t	500	years	transport time	500
Unsaturated Zone (values used for DF1 and DF2)				Coarse
I	0.06	m/y	infiltration rate	0.06
Θ_w	0.119	-	water filled porosity	0.119
Θ_a	0.241	-	air filled porosity of the contaminated soil	0.241
ρ_b	1.7	g/cm^3	dry soil bulk density of the contaminated soil	1.7
f_{oc}	0.005	g/g	fraction organic carbon of the contaminated soil	0.005
M_w	0.07	-	soil water content of the contaminated soil	0.07
Saturated Zone (values used for DF3 and DF4)				Coarse
I	0.06	m/y	infiltration rate	0.06
Θ_t	0.36	-	total soil porosity in the aquifer	0.36
ρ_b	1.7	g/cm^3	dry soil bulk density in the aquifer	1.7
K	13.9	m/year	aquifer hydraulic conductivity	320
i	0.008	m/m	lateral hydraulic gradient in aquifer	0.028
d_a	5	m	unconfined aquifer thickness	5
f_{oc}	0.005	g/g	fraction organic carbon in the aquifer	0.005

Site-specific Parameters - Calculated			
		Units	
b	0	m	thickness of unsaturated zone below the source
∂_u	0	m	dispersivity in the unsaturated zone
V	0.1112	m/y	Darcy velocity in groundwater
Z_d	4.62333	m	average thickness of mixing zone (2 when considering DUA)
r	0.1	m	mixing depth due to dispersion
s	4.52333	m	mixing depth due to infiltration rate
D_x	21.8	m	dispersivity in the direction of groundwater flow
D_y	2.18	m	dispersivity perpendicular to the direction of groundwater flow
C	0.11468	-	dimensionless group C
D	-0.1147	-	dimensionless group D
DF3	1.85686	-	dilution factor 3
$DF3_{(DUA)}$	1.37067	-	dilution factor 3 in DUA (Z_d = 2)

Substance-specific Parameters - User Defined (AEP 2019 defaults unless highlighted)			
	Nitrate	Units	
K_{oc}	0	L/kg	organic carbon-water partition coefficient
H'	0	-	dimensionless Henry's Law constant
$t_{1/2US}$	-	years	chemical half-life in unsaturated zone
$t_{1/2s}$	7	years	chemical half-life in saturated zone

Substance-specific Parameters - Calculated			
L_{us}	0	1/year	decay constant for chemical in unsaturated zone
L_s	0.088585141	1/year	decay constant for chemical in saturated zone
V_u	0.504201681	m/y	average linear leachate velocity
R_u	1	-	retardation factor in unsaturated zone
R_s	1	-	retardation factor in saturated zone
v	0.308888889	m/year	velocity of the contaminant
A	-20.49891009	-	dimensionless group A
B	-4.90852213	-	dimensionless group B
DF1	0.07	L/kg	dilution factor 1
DF2	1	-	dilution factor 2
DF4	6201910156	-	dilution factor 4

Soil Remediation Guideline (mg/kg)	
	Nitrate
FAL	>1,000,000
Lowest:	>1,000,000

GW Remediation Guideline (mg/L)	
	Nitrate
FAL	>1,000,000
Lowest:	>1,000,000

*Guideline values round to 2 significant digits consistent with CCME 2006

References

AEP 2019. Alberta Tier 2 Soil and Groundwater Remediation Guidelines.

CCME 2006. A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines.

2. Nitrate Modeling #1

DF2 for saturated vertical transport (modified DF4) - V1.1

Form Date: 2021-01-27

Site-specific Parameters - User Defined			Denotes value changed from default	
		Units		**AEP Defaults**
Z	5.2	m	depth to bottom of contaminated soil	3
d	10.5	m	depth to DUA	3
Y	10	m	source width perpendicular to groundwater flow	10
y	0	m	distance to water well perpendicular to groundwater flow	0
t	500	years	transport time	500
Saturated Zone (values used for $DF2_{(saturated)}$ - all versions)				Fine
Θ_t	0.47	-	total soil porosity in the saturated unit	0.47
ρ_b	1.4	g/cm^3	dry soil bulk density in the saturated unit	1.4
K	1.39	m/year	aquifer hydraulic conductivity	32
i	0.016	m/m	vertical hydraulic gradient in saturated unit	-
f_{oc}	0.005	g/g	fraction organic carbon in the saturated unit	0.005

References

AEP 2019. Alberta Tier 2 Soil and Groundwater Remediation Guidelines.
CCME 2006. A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines.
Equilibrium Environmental Inc. (2020). Subsoil Salinity Tool Version 3.0 User Manual.

Substance-specific Parameters (all versions)			
	Nitrate	Units	
K_{oc}	0	L/kg	organic carbon-water partition coefficient
$t_{1/2s}$	7	years	chemical half-life in saturated zone
L_s	0.088585141	1/year	decay constant for chemical in saturated zone
R_s	1	-	retardation factor in saturated zone

Site-specific Parameters - (model-specific)			
Version 1			
$I_{(as\ V)}$	0.012	m/y	drainage rate (AT1 infiltration rate; AEP 2019)
Version 2			
$I_{(as\ V)}$	0.006	m/y	drainage rate (default values; Equilibrium 2020)
Slightly dry / semi-arid			Climate Moisture Index (obtained from SST 3.0)
Version 3			
$I_{(as\ V)}$	0.02224	m/y	drainage rate (as K * i; assumes K is purely in the vertical direction)

Substance-specific Parameters (model-specific)			
v	0.025531915	m/year	velocity of the contaminant
A	-9.45295781	-	dimensionless group A
B	-6.074471798	-	dimensionless group B
$DF2_{(Saturated)}$	12745.80925	-	dilution factor 2 for saturated transport
v	0.012765958	m/year	velocity of the contaminant
A	-14.81857653	-	dimensionless group A
B	-5.436972187	-	dimensionless group B
$DF2_{(Saturated)}$	2726628.798	-	dilution factor 2 for saturated transport
v	0.047319149	m/year	velocity of the contaminant
A	-6.14540884	-	dimensionless group A
B	-6.698310645	-	dimensionless group B
$DF2_{(Saturated)}$	466.5703625	-	dilution factor 2 for saturated transport

Site-specific Parameters - Calculated (all versions)			
		Units	
$b_{(as\ x)}$	5.3	m	thickness of saturated zone below the source
D_x	0.53	m	dispersivity in the direction of groundwater flow
D_y	0.053	m	dispersivity perpendicular to the direction of groundwater flow
C	4.71698	-	dimensionless group C
D	-4.717	-	dimensionless group D

If saturated zone thickness (b) < 1; DF2 calculated to be 1.

SRG_{DUA} (mg/kg)	
	Nitrate
Version 1	25000
Version 2	>1,000,000
Version 3	920
Lowest value	920

Shallow $GWRG_{DUA}$	**<5.2 mbgs**
	Nitrate
Version 1	130000
Version 2	>1,000,000
Version 3	4700
Lowest value	4700

3. Nitrate Modeling #2

ATRANS

- There are several analytical methods that could be used to approximate plume migration in a homogeneous, isotropic aquifer.
- These methods all use an approximation of the **Advection-Dispersion Equation** that is the basis for most fate and transport models.

$$\frac{\partial c}{\partial t} = -v'\frac{\partial c}{\partial x} + D_x'\frac{\partial^2 c}{\partial x^2} + D_y'\frac{\partial^2 c}{\partial y^2} + D_z'\frac{\partial^2 c}{\partial z^2} - \lambda c$$

where:

c	=	dissolved concentration [M solute/ L^3 water];
s	=	sorbed concentration [M solute/ M solids];
x,y,z	=	spatial coordinates [L]; and
t	=	time [T].
θ	=	saturated water content [L^3 water/ L^3 porous medium];
ρ_b	=	bulk density [M solids/ L^3 porous medium];
q	=	Darcy flux [L/ T];
D_x, D_y, D_z	=	dispersion coefficients [L^2/ T]; and
λ	=	first-order decay coefficients [T^{-1}].

3. Nitrate Modeling #2

ATRANS

- Selected ATRANS to simulate nitrate transport in shallow groundwater.
- A 3D analytical solution for transport from a patch boundary condition with time varying concentration.
- The solution considers the following transport processes: advection, dispersion, sorption, and first-order transformation reactions.
- The solution assumes the groundwater flow field is steady and uniform.
- ATRANS is public domain software provided by S.S. Papadopulos & Associates Inc.

https://www.sspa.com/software/atrans

3. Nitrate Modeling #2

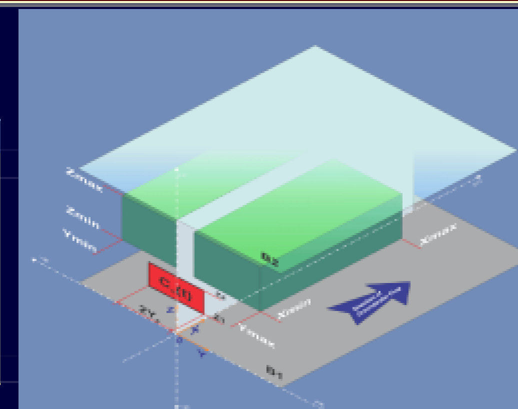
Why ATRANS?

- 3D capabilities, considers longitudinal, horizontal and vertical dispersion.
- Solutions to the ADE that implement higher order mathematical methods generally yield more accurate solutions.
- General ease of use. One input page, one output page.
- Functionality – constant, decaying, and other source types.

3. Nitrate Modeling #2

ATRANS
S.S. PAPADOPULOS & ASSOC.

Version 1.10 (Build on July 04, 2016)



INPUT PARAMETERS

Seepage Velocity	3.09E-01	V	[L/T]
Aquifer porosity	0.36	e	-
Aquifer Top Elevation	6.00	B2	[L]
Aquifer Bottom Elevation	1.00	B1	[L]
Longitudinal Dispersivity	21.800	α_L	[L]
Transverse Dispersivity	2.180	α_{TH}	[L]
Vertical Dispersivity	0.100	α_{TV}	[L]
Effective Diffusion Coeff.	0.000	D*	$[L^2T^{-1}]$
Retardation Factor	1.000	R	[-]
1st Order Decay Coeff.	0.099	λ	$[T^{-1}]$
Total source width along y-axis	20.000	$2Y_0$	[L]
Elevation at the top of the source	6.000	Z_2	[L]
Elevation at the bottom of the source	3.000	Z_1	[L]
SOURCE TYPE	Constant Concentration		
Source Concentration	253	Co	$[ML^{-3}]$

MODEL DISCRETIZATION

Starting coordinate (x axis)	Xmin [L]	0
Ending coordinate (x axis)	Xmax [L]	250
Number of discretization Points (x)	NX [-]	20
Starting coordinate (y axis)	Ymin [L]	-80
Ending coordinate (y axis)	Ymax [L]	80
Number of discretization Points (y)	NY [-]	20
Modeled Area Bottom Elevation	Zmin	1
Modeled Area Top Elevation	Zmax	6
Number of discretization Points (z)	NZ [-]	3

OBSERVATION DATA

	Time Steps	Time Start	Time Increment	Time End
	100	0	0.5	50

Number of Observation Points: 3

Name	X coord.	Y coord.	Elevation	Measured Conc.
MW28	0	0	6	SHOW
MW-37	10	0	5	
MW-25	50	5	4	

TIME DISCRETIZATION

NTIMES: 20

#	Time
1	25
2	50
3	75
4	100
5	125
6	150
7	175
8	200
9	225
10	250

OUTPUT

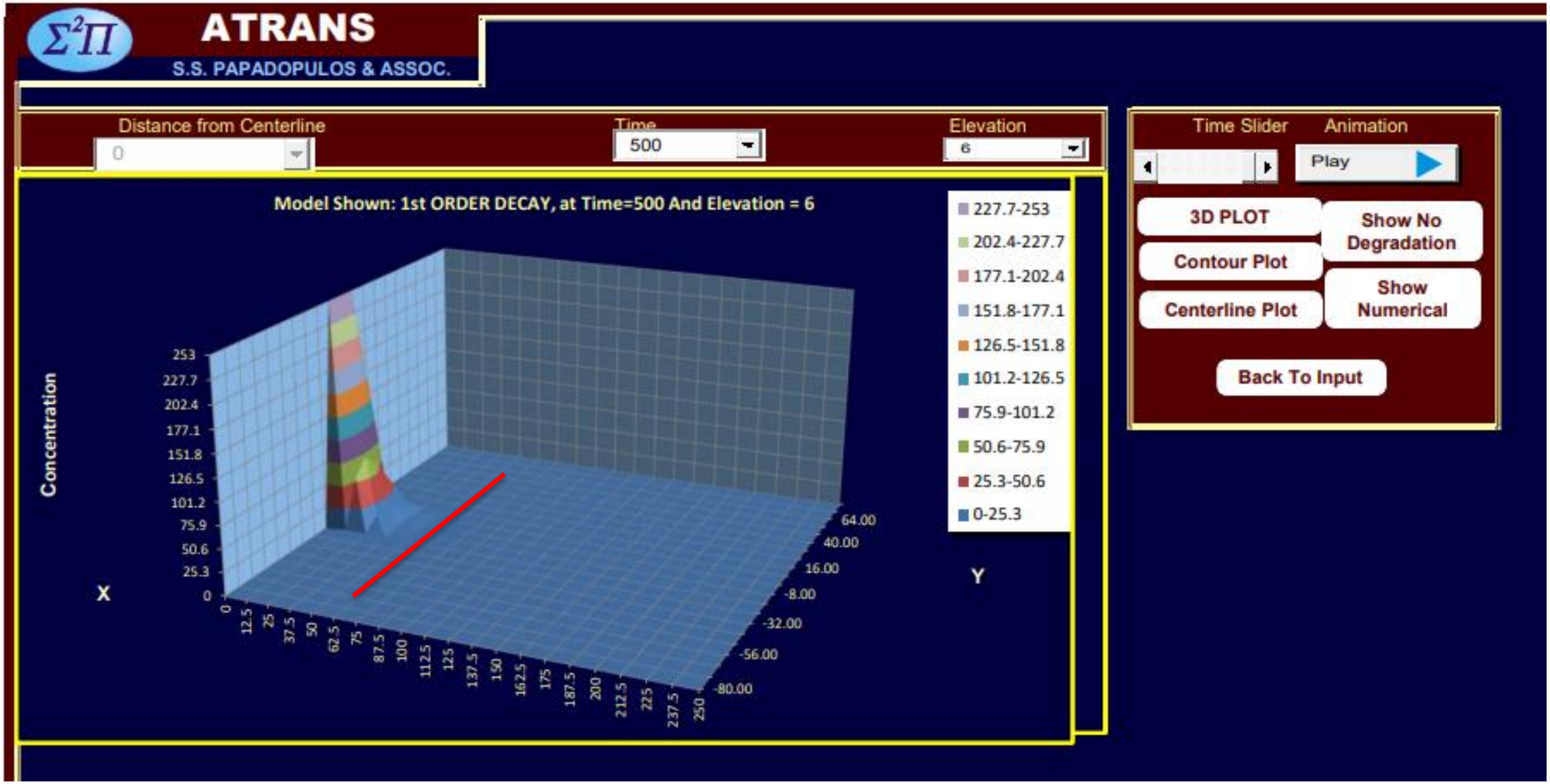
SHOW RESULTS

SHOW SOURCE

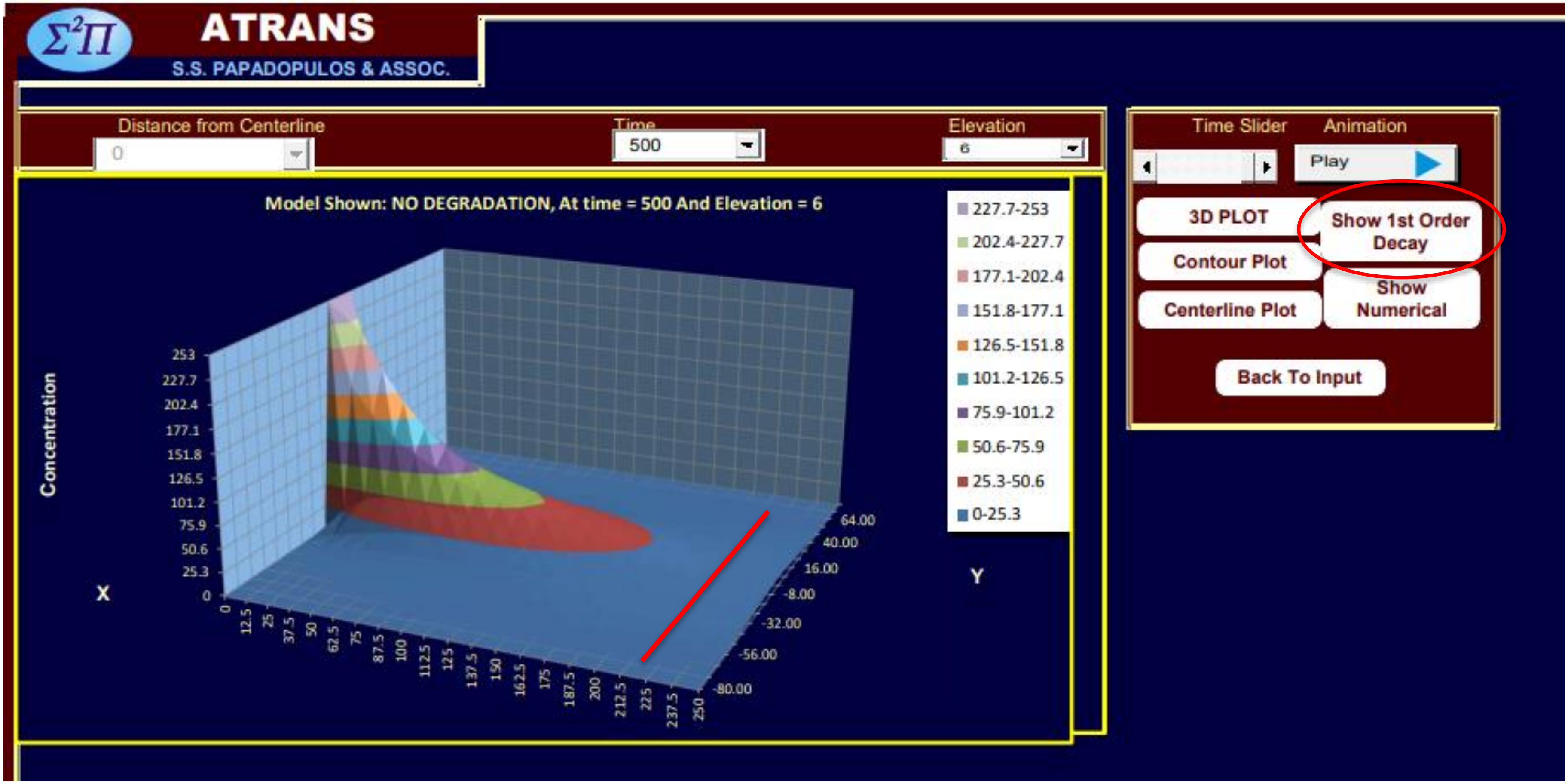
SHOW

SHOW

3. Nitrate Modeling #2



3. Nitrate Modeling #2



3. Nitrate Modeling #2

ATRANS Findings

- Measurable nitrate concentrations are not expected to extend beyond a distance of roughly 60 m, assuming nitrate degradation is occurring.
- 3D model is easy to use, various functionalities, and provides nice visuals.

4. Nitrate Modeling #3

Subsoil Salinity Tool

- A software program for development of soil salinity guidelines that are applicable below the root zone (>1.5 mbgs).
- Two software models are used to estimate the fate & transport of chloride:
    - LEACHM – vertical transport in vadose and saturated zones
    - 3DADE – lateral transport to FAL and attenuation of chloride plume leaching vertically toward DUA

3DADE

is a Fortran computer program for evaluating a series of analytical solutions of the 3-Dimensional Advection-Dispersion Equation. The analytical solutions pertain to three-dimensional solute transport during steady unidirectional water flow in porous media with uniform transport and flow properties. The transport equation contains terms accounting for

4. Nitrate Modeling #3

Subsoil Salinity Tool

- Nitrate is a 'conservative' solute similar to chloride.
- The SST is readily available to many, buy-in from the regulators, so perhaps use as a screening tool.
- SST can calculate subsoil guidelines for 5 exposure pathways:
    - Protection of root zone
    - Livestock watering
    - Irrigation watering
    - **Aquatic life**
    - **Domestic use aquifer**

4. Nitrate Modeling #3

Subsoil Salinity Tool

- Important input parameters:
    - Tier 2B, agricultural
    - Subregion is Dry Mixedwood
    - Shallow GW - coarse-grained, k=13.9 m/yr, gradient=0.008
    - Depth to DUA, 10 mbgs
    - Distance to FAL, 218 m
    - Depth of impact 3 to 5 mbgs
    - One Subarea w/ source dimension of 30 m

4. Nitrate Modeling #3

Pathway	SubArea 1		SubArea 2		SubArea 3		SubArea 4		SubArea 5	
	Guideline (mg/kg)	Time to peak breakthrough (Year)	Guideline (mg/kg)	Time to peak breakthrough (Year)	Guideline (mg/kg)	Time to peak breakthrough (Year)	Guideline (mg/kg)	Time to peak breakthrough (Year)	Guideline (mg/kg)	Time to peak breakthrough (Year)
Root Zone	2200	~ 250								
Livestock Watering	ML (54000)	~ 20								
Irrigation Watering	ML (35000)	~ 20								
Aquatic Life	ML (14000)	~ 300								
DUA	5300	~ 350								
Minimum Chloride Guideline (mg/kg)	**2200**									
Groundwater Guideline (mg/L)	6600									

Surface Water Quality Guidelines

Chloride - 120 mg/L

Nitrate - 3 mg/L 40x difference

5. Conclusions

- Have successfully used the dilution factor approach for nitrate at several contaminated sites.
  - DUA evaluation using a modified version of the DF4 equation to represent DF2 (considering saturated transport).
- Currently using ATRANS at a number of former fertilizer storage sites. Hoping will be considered acceptable!
  - ADE approach, 3D dispersivity, robust modeling approach
- SST for nitrate? Not there yet……

Questions?

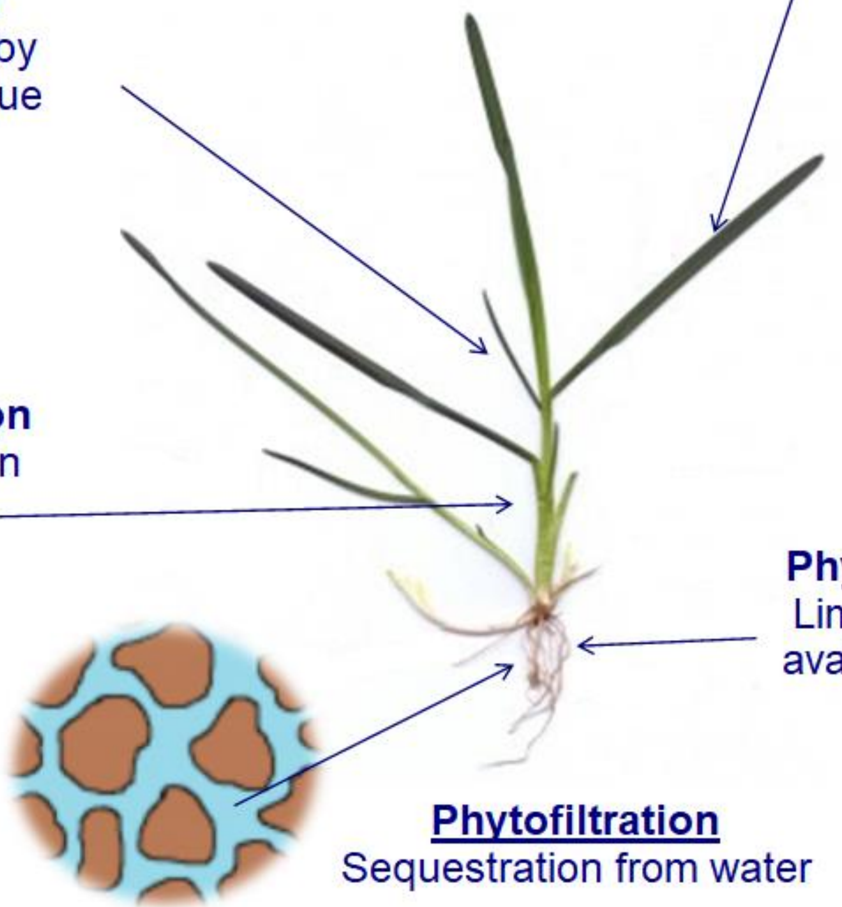
Thank You!

VERTEX

ADBE

Phytovolatilization
Converts to volatile form, releases to atmosphere through leaf surface

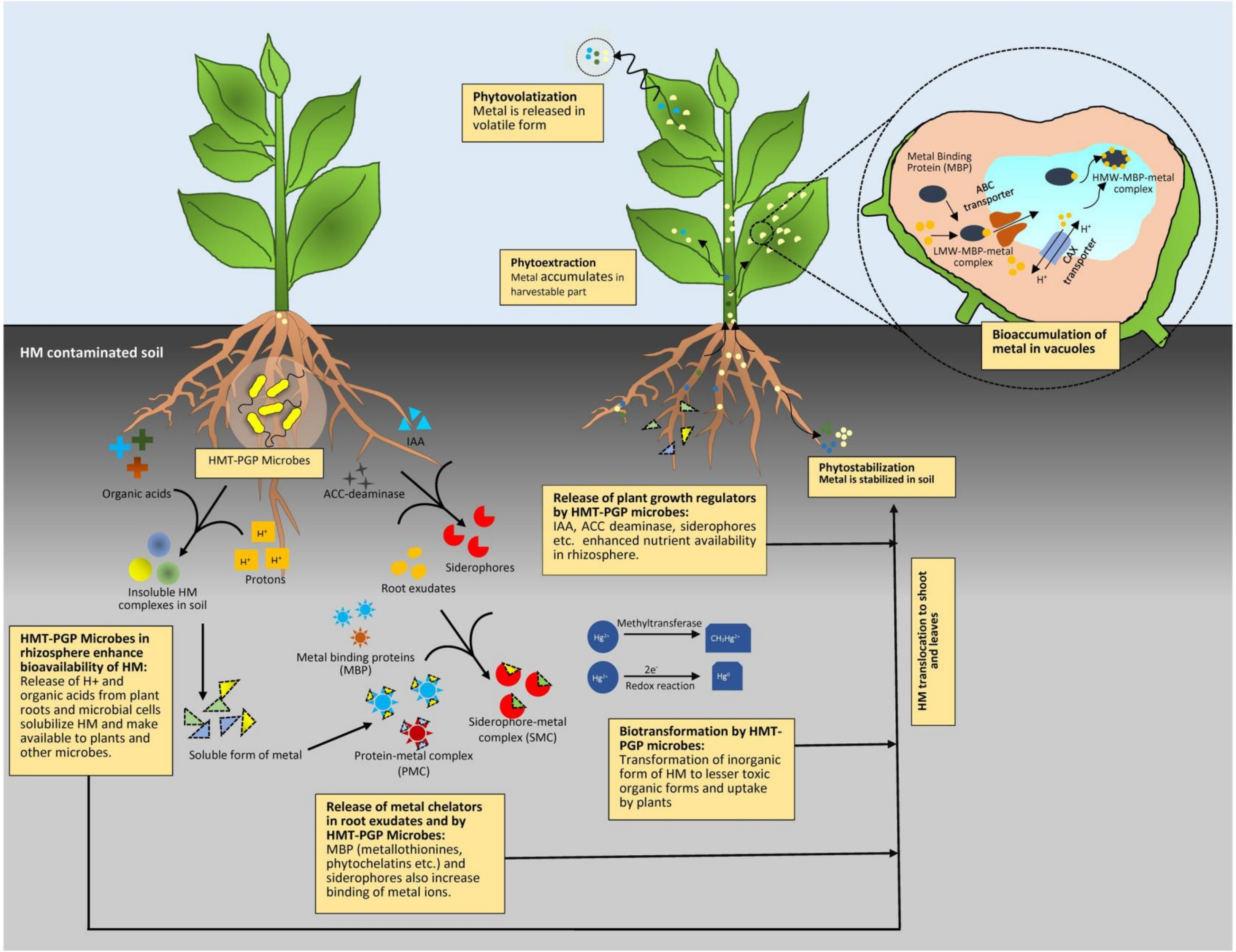
Phytodegradation
Breakdown or transformation by enzymes in tissue



Phytoextraction
Accumulation in shoots

Phytostabiliaztion
Limits mobility and availability in soil by roots

Phytofiltration
Sequestration from water



Phytovolatization
Metal is released in volatile form
Phytoextraction
Metal accumulates in harvestable part
Metal Binding Protein (MBP)
ABC transporter
HMW-MBP-metal complex
LMW-MBP-metal complex
CAX transporter
H⁺
Bioaccumulation of metal in vacuoles
HM contaminated soil
IAA
HMT-PGP Microbes
Organic acids
ACC-deaminase
H⁺
Protons
Insoluble HM complexes in soil
Siderophores
Root exudates
Phytostabilization
Metal is stabilized in soil
Release of plant growth regulators by HMT-PGP microbes:
IAA, ACC deaminase, siderophores etc. enhanced nutrient availability in rhizosphere.
HM translocation to shoot and leaves
HMT-PGP Microbes in rhizosphere enhance bioavailability of HM:
Release of H+ and organic acids from plant roots and microbial cells solubilize HM and make available to plants and other microbes.
Metal binding proteins (MBP)
Methyltransferase
Hg²⁺
CH₃Hg²⁺
2e⁻
Redox reaction
Hg⁰
Soluble form of metal
Protein-metal complex (PMC)
Siderophore-metal complex (SMC)
Biotransformation by HMT-PGP microbes:
Transformation of inorganic form of HM to lesser toxic organic forms and uptake by plants
Release of metal chelators in root exudates and by HMT-PGP Microbes:
MBP (metallothionines, phytochelatins etc.) and siderophores also increase binding of metal ions.

Project Team

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Alberta Upstream Petroleum Research Fund (AUPRF)

PTAC PETROLEUM TECHNOLOGY ALLIANCE CANADA

1. Project Background

Ecological CSM

Source Media	Exposure Media	Potential Exposure Pathways	Bird (waterfowl)	Bird (omnivore)	Large Mammal (herbivore)	Medium Mammal (omnivore)	Small Mammal (omnivore)	Amphibian	Freshwater Aquatic Life	Soil Organisms	Terrestrial Plants
Soil / Groundwater	Surface Soil	Ingestion	X	X	X	X	X	X		X	
	Surface Soil	Dermal Contact								X	
	Surface Soil	Root Uptake									X
	Terrestrial Invertebrate Prey	Ingestion	X	X		X	X	X			
[uptake]	Plant Food	Ingestion	X	X	X	X	X	X			
Runoff / Groundwater	Surface Water	Ingestion	X	X	X	X	X	X			
	Surface Water	Direct Contact							X		

SOURCE → **RECEPTOR**

Note: **X** indicates a potentially complete exposure pathway

2. Work Plan and Methods

Plant Species

Functional Type	Common Name	Species	Range
Grass	Barley	*Hordeum vulgare*	Peace River Region, Central AB, and Southern/Southeastern AB
Grass	Italian ryegrass	*Lolium multiflorum*	Peace River Region, Central AB, and Southern AB (irrigation)
Grass	Corn (Maize)	*Zea mays*	Southern region of AB
Forb	Yarrow	*Achillea millefolium*	Throughout AB
Legume	Pea plant	*Pisum sativum*	Peace River Region, Central and Southern AB

- Plant species selection based on:
  - Presence in Alberta and Canada
  - Variety of functional types
  - Availability and ease to work with in the laboratory
  - Growth characteristics (e.g., speed of growth, time to flowering)