EVALUATION OF CONTAMINANT SOURCES AND EXPORT IN A WATERSHED

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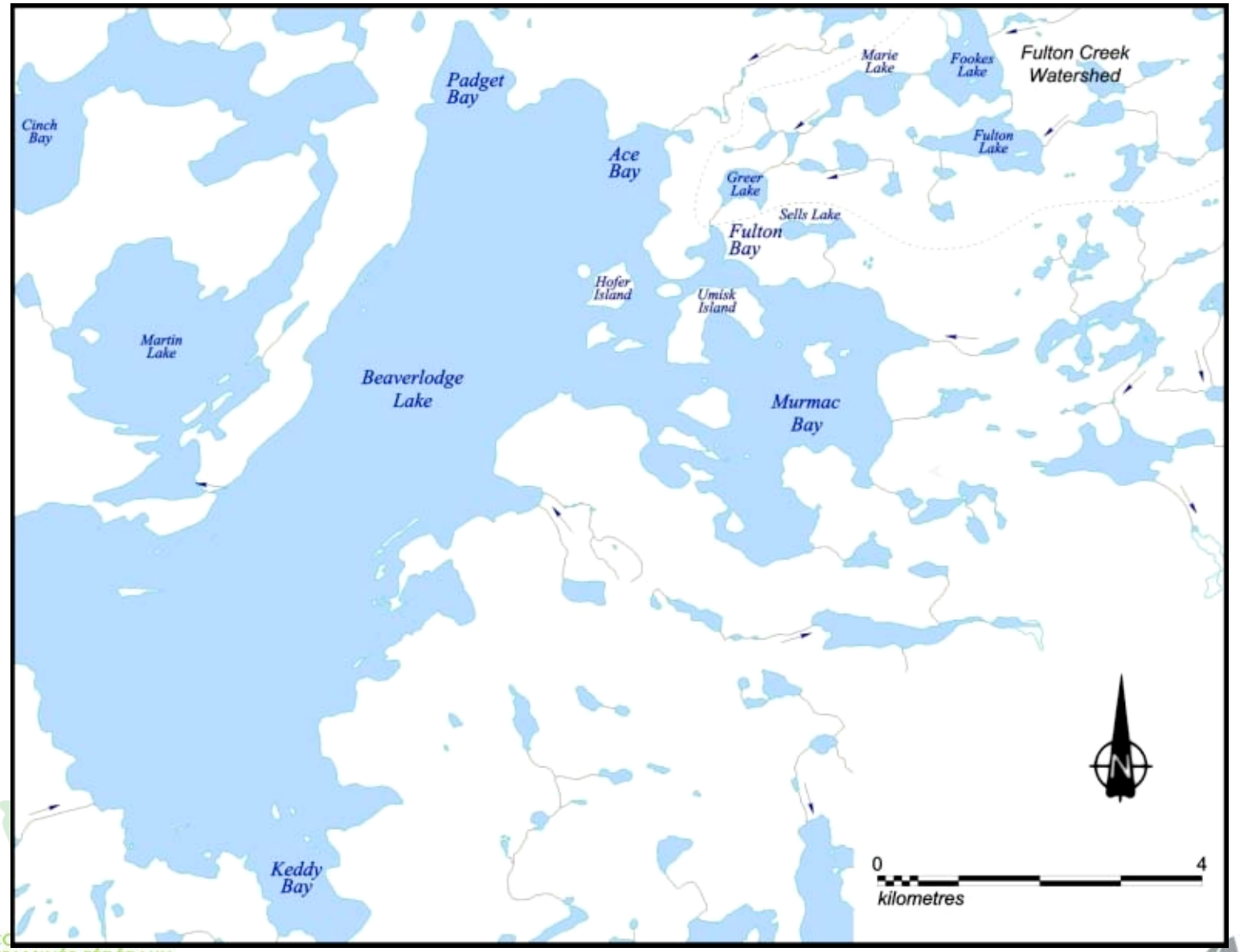
BACKGROUND

- Fulton Creek Watershed - former uranium mining waste management area in Northern Saskatchewan
- Mining activity ceased 25 years ago
- Contaminants from the watershed continue to impact Beaverlodge Lake


Padget Bay
Cinch Bay
Ace Bay
Marie Lake
Fookes Lake
Fulton Creek Watershed
Fulton Lake
Greer Lake
Sells Lake
Fulton Bay
Hofer Island
Umisk Island
Martin Lake
Beaverlodge Lake
Murmac Bay
Keddy Bay
N
0
4
kilometres

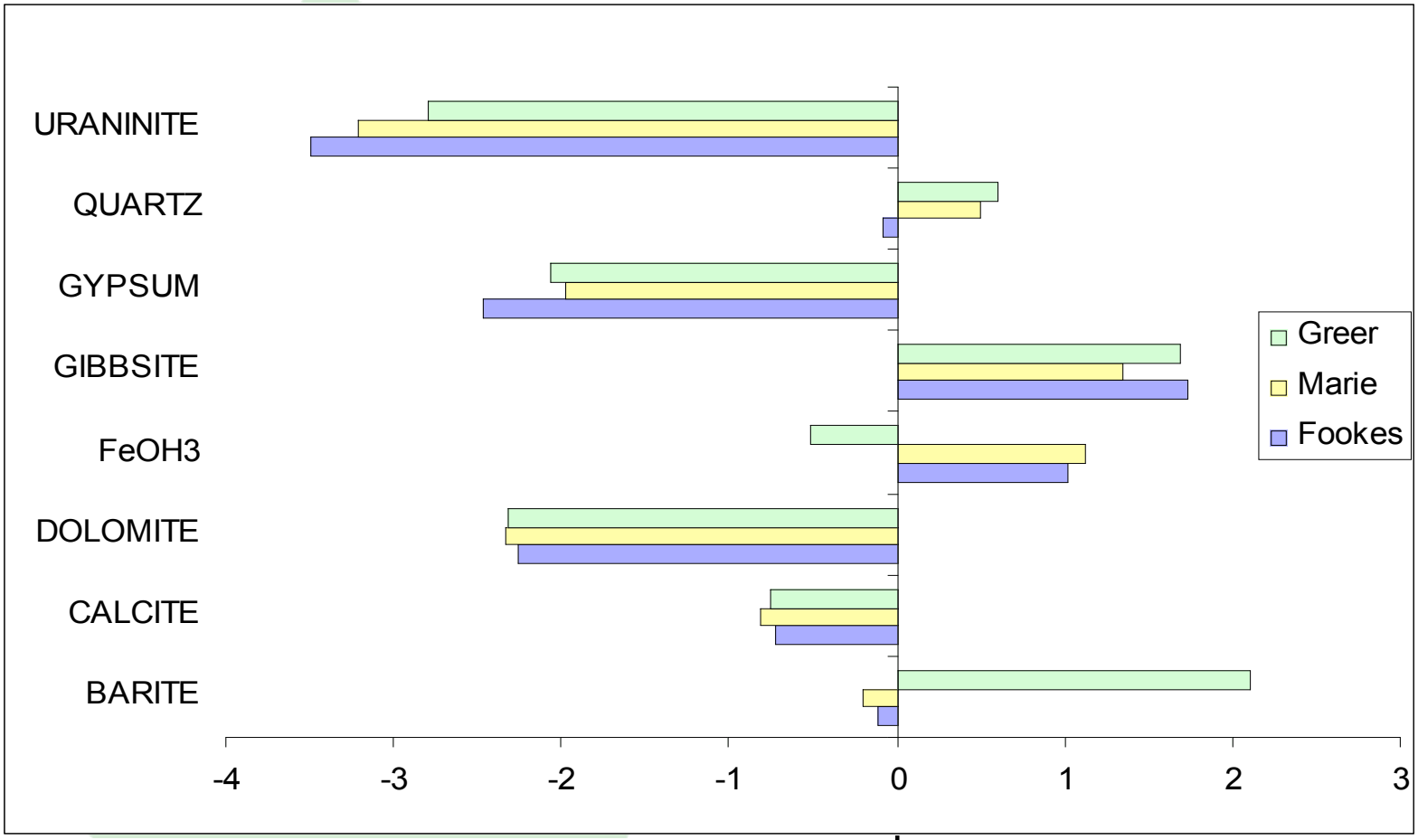
OBJECTIVES

- Identify sources of contaminants
- Assess current and future contaminant export by geochemical modeling
- Determine the impact of contaminant source reduction on Beaverlodge Lake water quality

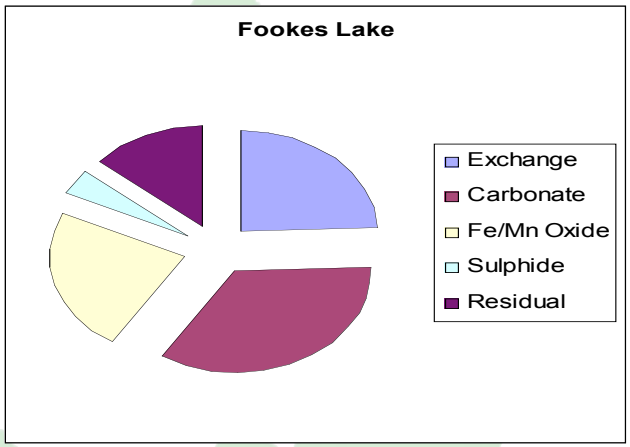
SEDIMENT PORE WATER AND SOLIDS ANALYSIS

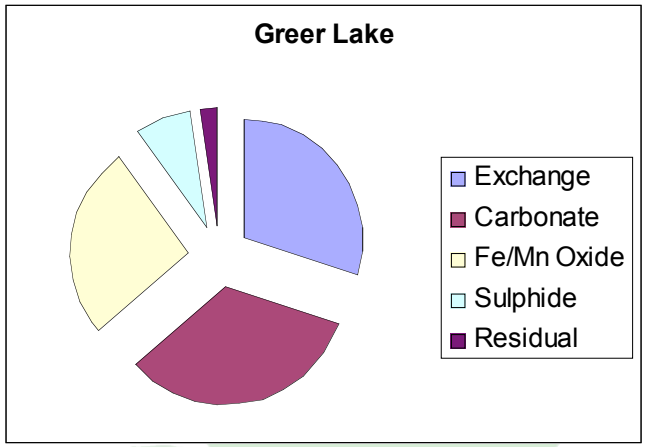
- Pore water samples were analyzed using USDA PHREEQC program
- Saturation indices of potential solid phases were determined.
- Sediment solids were partitioned by modified Tessier extraction procedure.

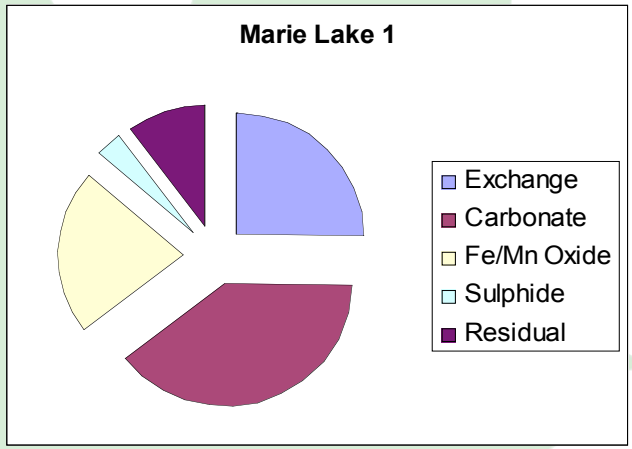
Sediment Pore Water Saturation Indices (PHREEQC)

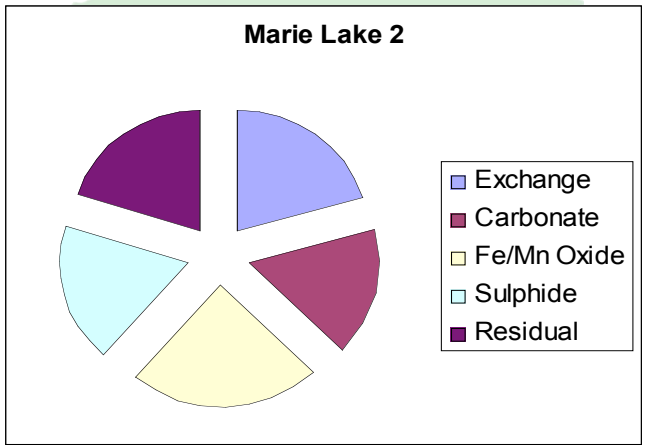


Distribution of Uranium in Sediments

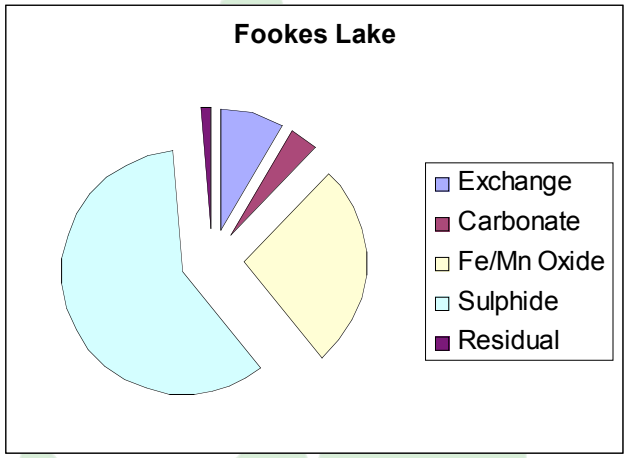


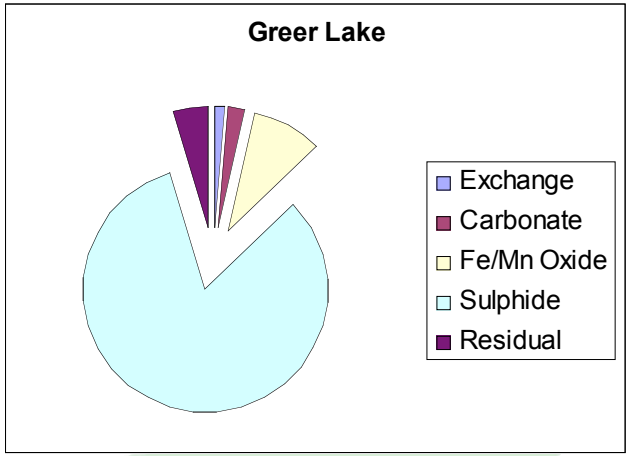


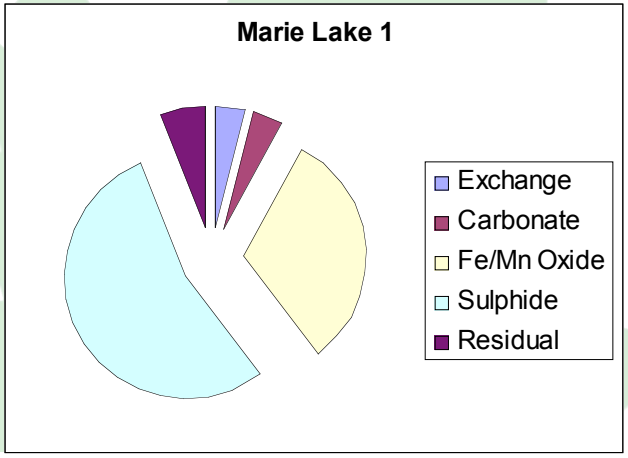


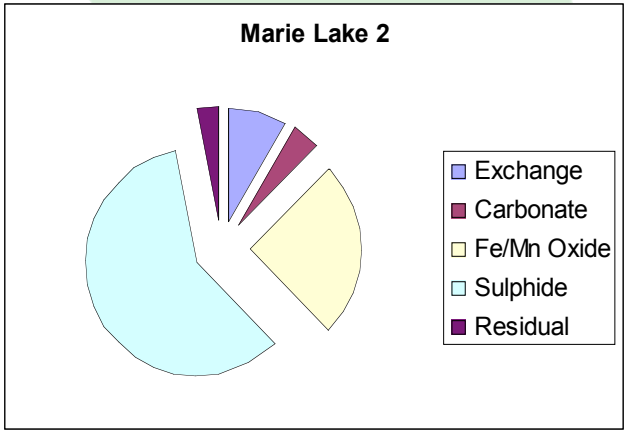


Distribution of Selenium in Sediments

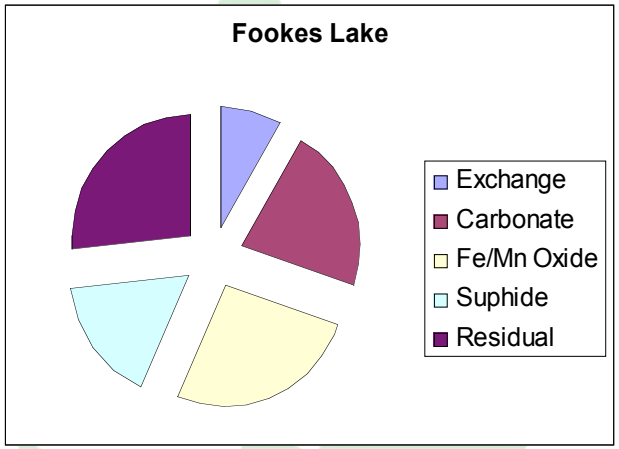


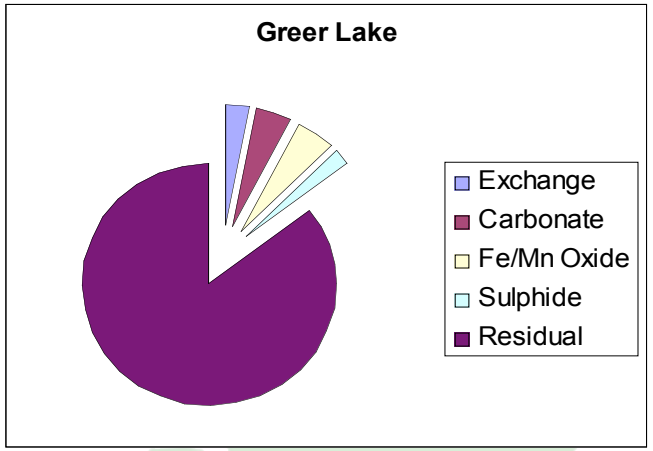


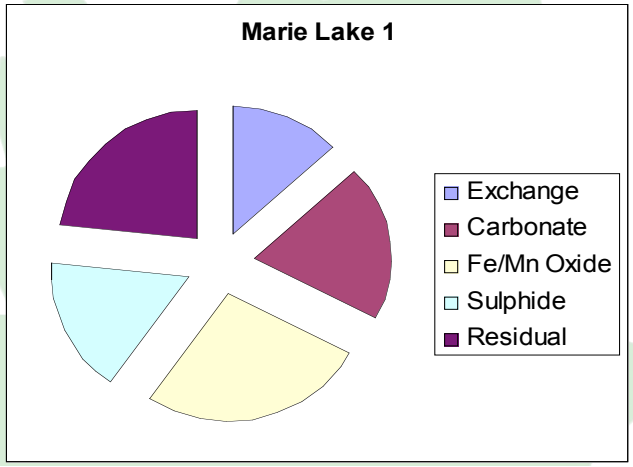


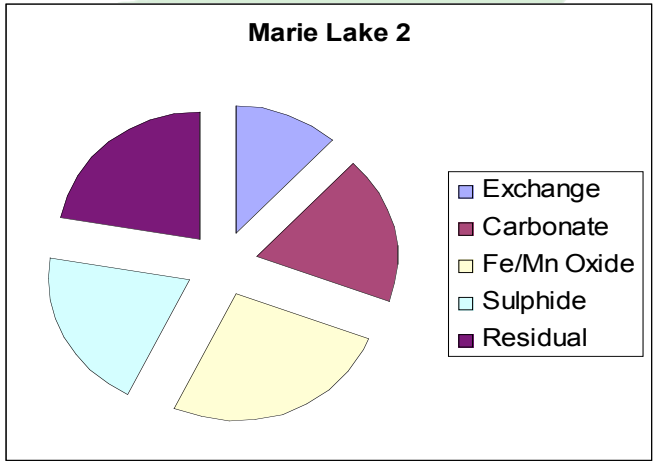


Distribution of Radium-226 in Sediments



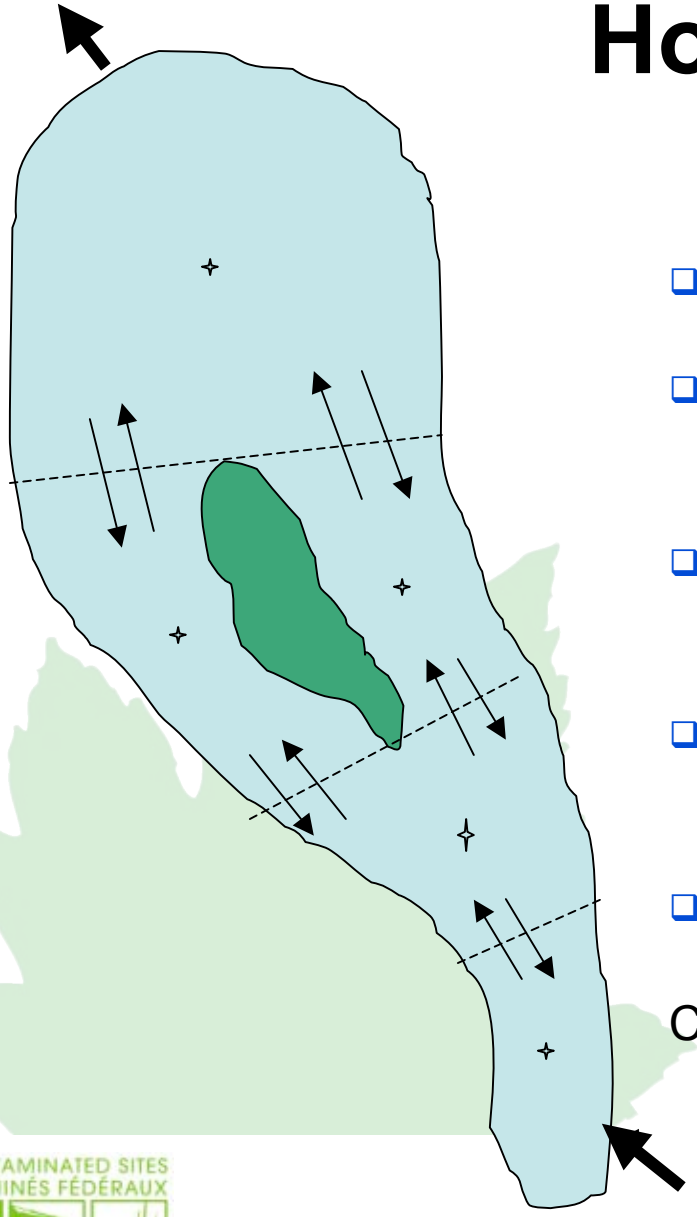






LAKEVIEW MODELING CONCEPTS

- CONTAMINANT LOADINGS:
  - MEASURED
  - ESTIMATED
- HORIZONTAL TRANSPORT PROCESSES
- VERTICAL TRANSPORT PROCESSES

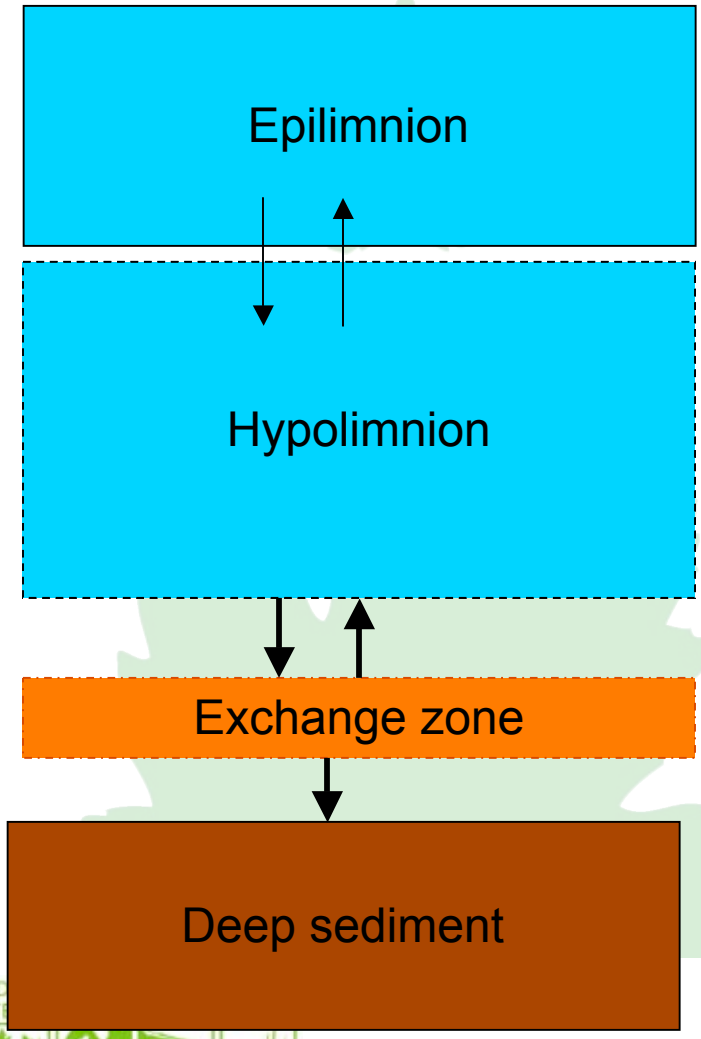


Horizontal Transport Processes

- Large lakes are segmented
- Point source and/or diffuse contaminant load to segments
- Contaminant load (dissolved & suspended)
- Convective and dispersive transport between segments
- Distance averaged dispersion

CONTAMINANT LOAD

Vertical Chemical Transport Processes



Processes in water column

- mass transport across stratified layers (optional)
- settling

Processes in water & sediment

- diffusive transport (water column / sediment pore water)
- kinetics of transformation (formation / decay)

Processes in sediment exchange zone

- adsorption
- dissolution / precipitation
- sediment mixing (bio-perturbation)
- burial
- re-suspension (river sections)

PARAMETER ESTIMATION

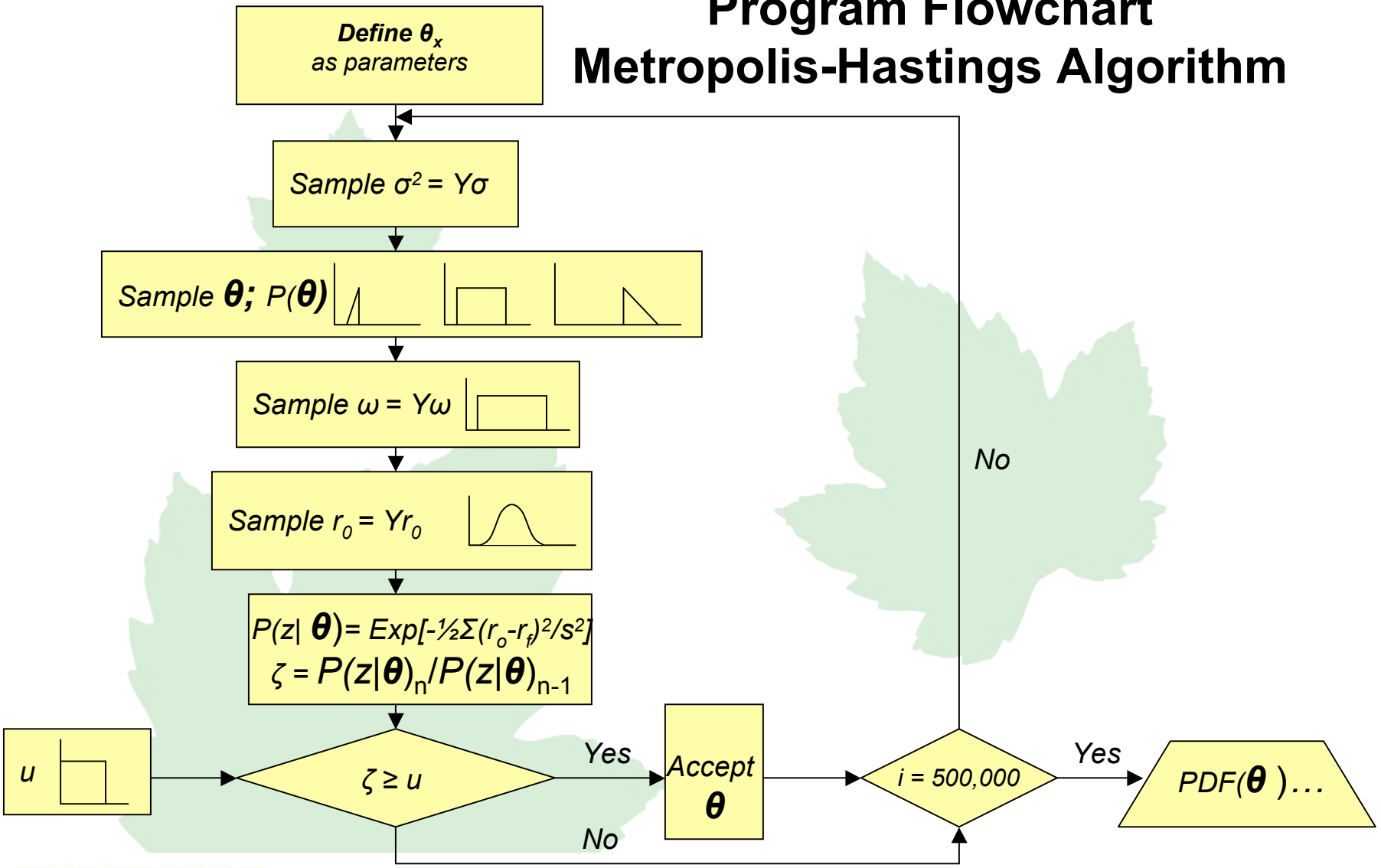
- Markov chain modeling

$$P(X_n|X_{n-i}) = P(X_n)$$

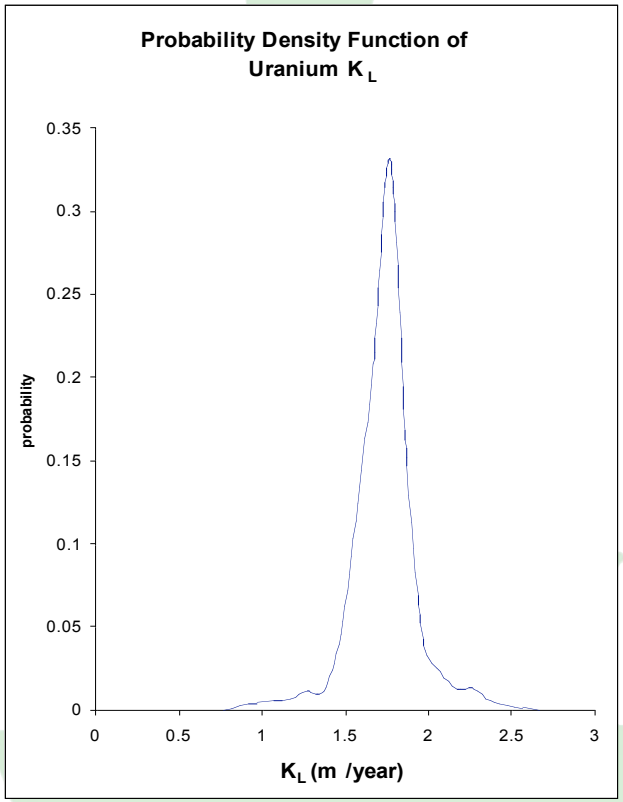
For all values of i unless i = 1

- "Future" is independent of "Past" given "Present".
- Memory-less – no consideration beyond the present.
- Useful for modeling and analyzing real systems.

Program Flowchart
Metropolis-Hastings Algorithm



Estimation of K_L Value for Uranium



LAKE: FOOKES

 # trials: 2960

Max. likelihood: 1.67

Median value: 1.69

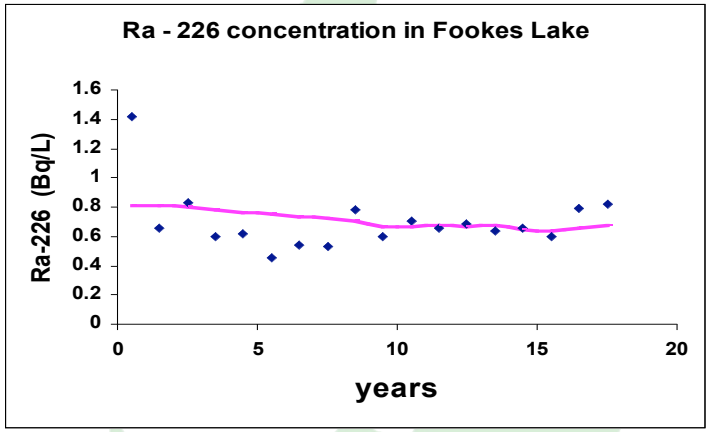
Mean value: 1.67

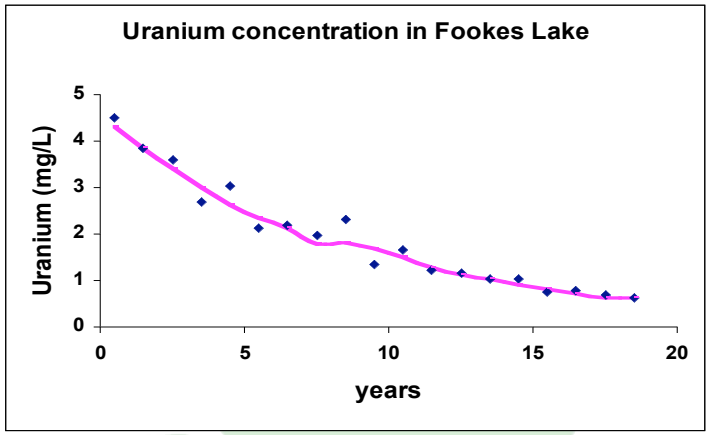
Std. Deviation: 0.21

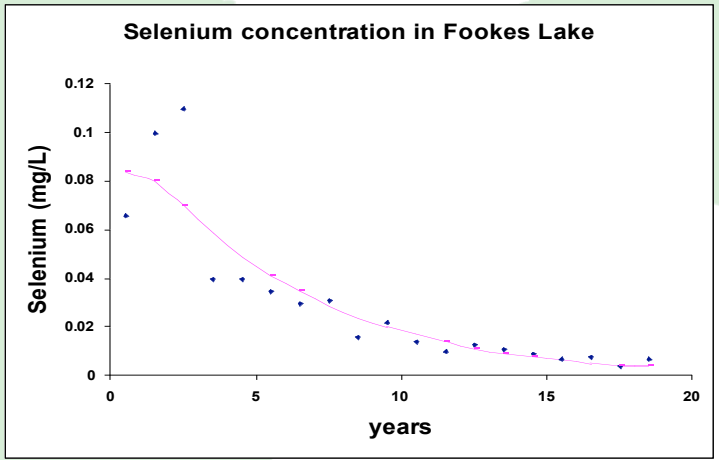
$FLUX = K_L(C_{SED} - C_{WAT})$

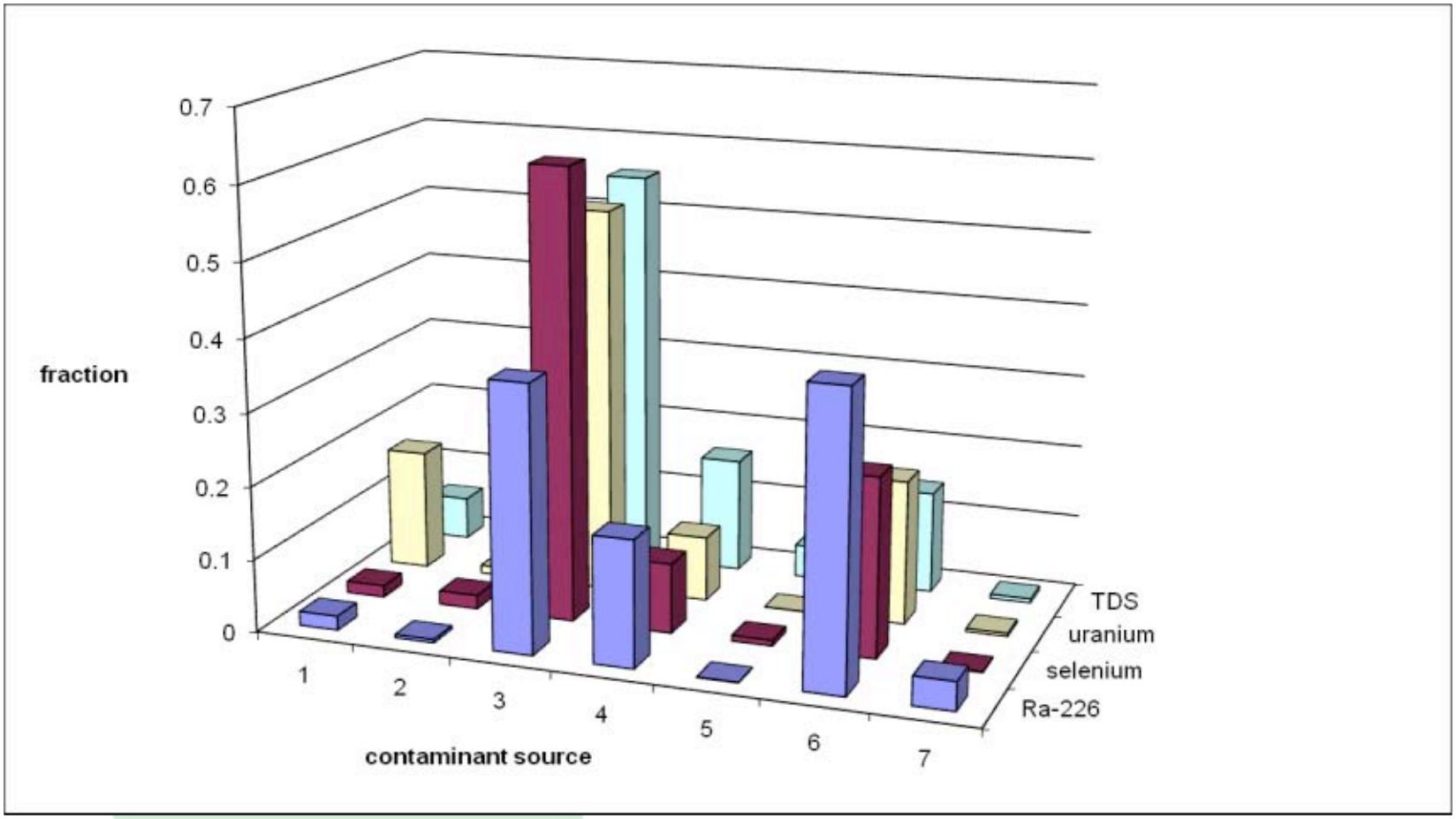
Sediment to Water Column Flux

Comparison of Measured and Predicted Concentrations in Fookes Lake





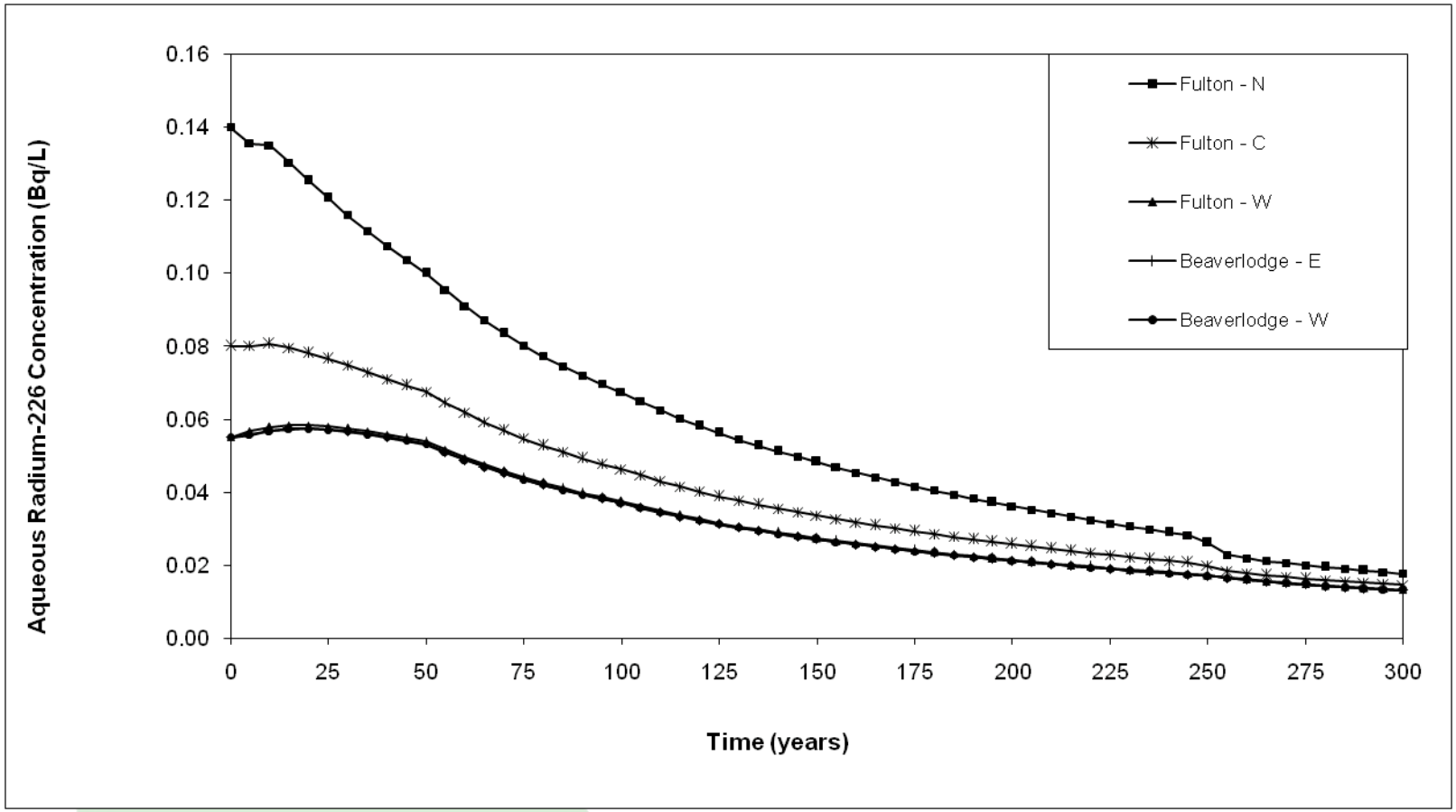




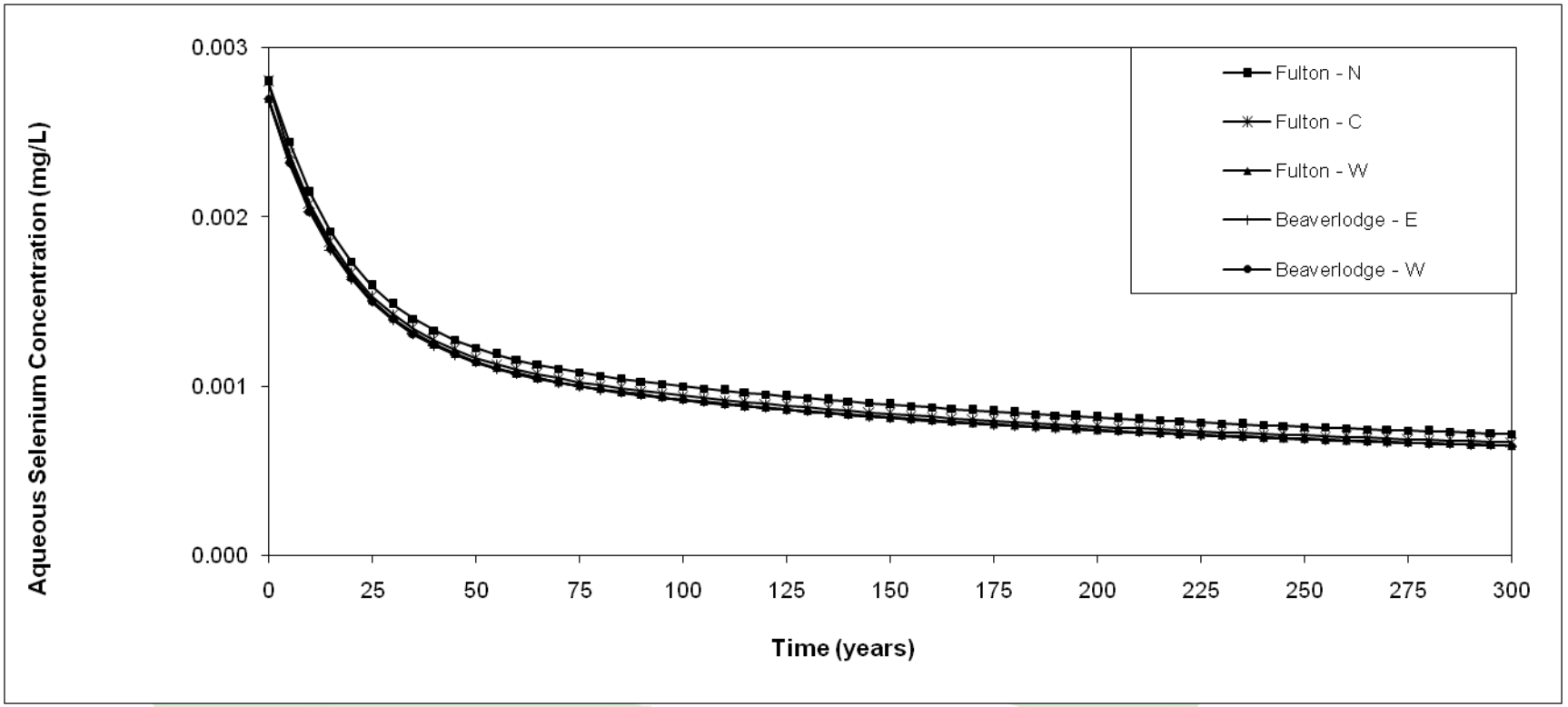
Distribution of contaminant sources: 1) Fookes Delta, 2) Minewater tailings, 3) Fookes, 4) Marie, 5) Meadow, 6) Greer 7) Unnamed Lake sediments

WATER QUALITY SIMULATIONS IN BEAVERLODGE LAKE

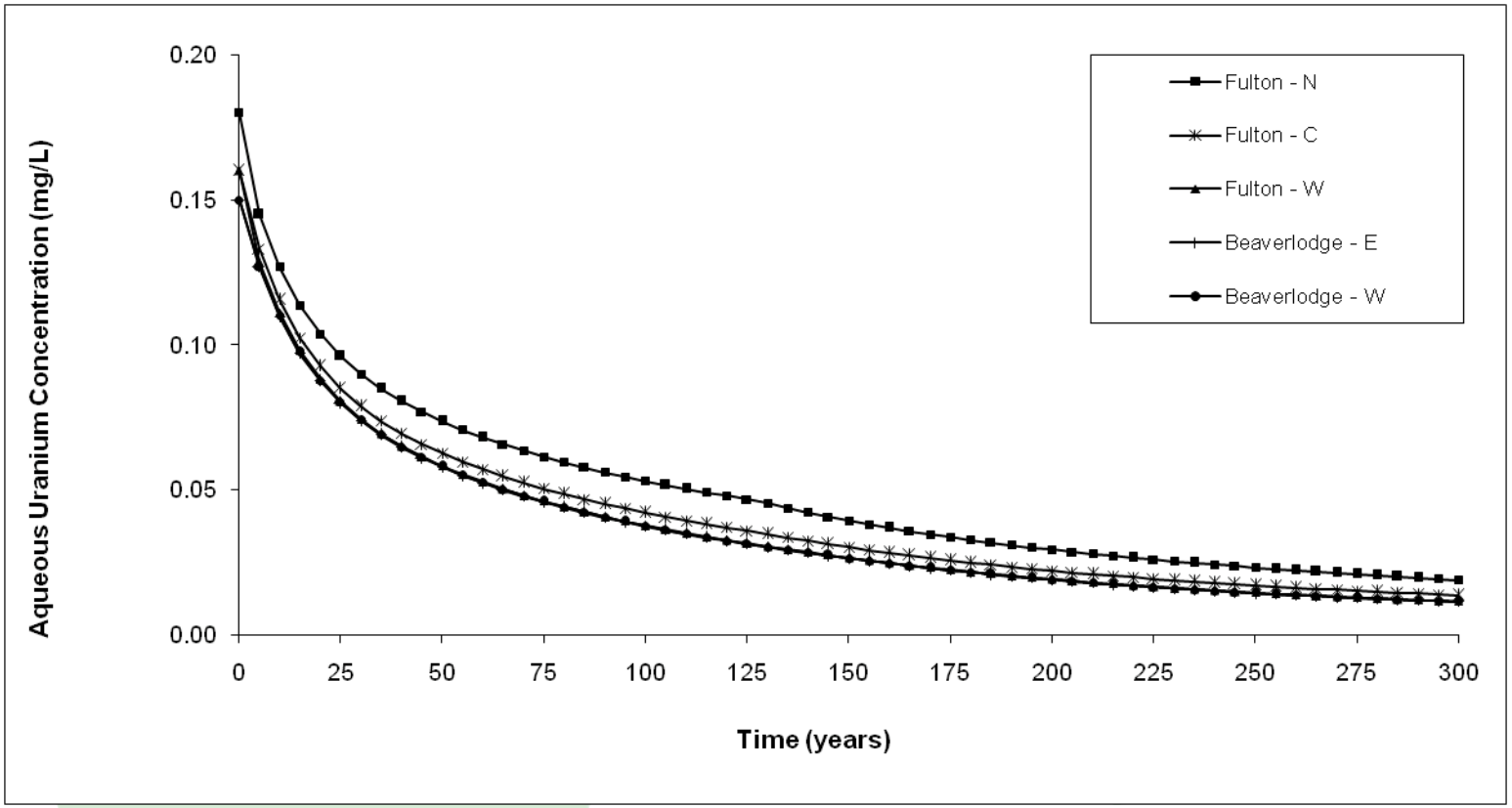
- Water and sediment concentrations in Beaverlodge and Martin Lakes were simulated for 300 year periods
- Simulations included hypothetical 50% and 90% sediment flux reductions
- Impact of flux reduction was evaluated as time averaged logarithmic sensitivity response



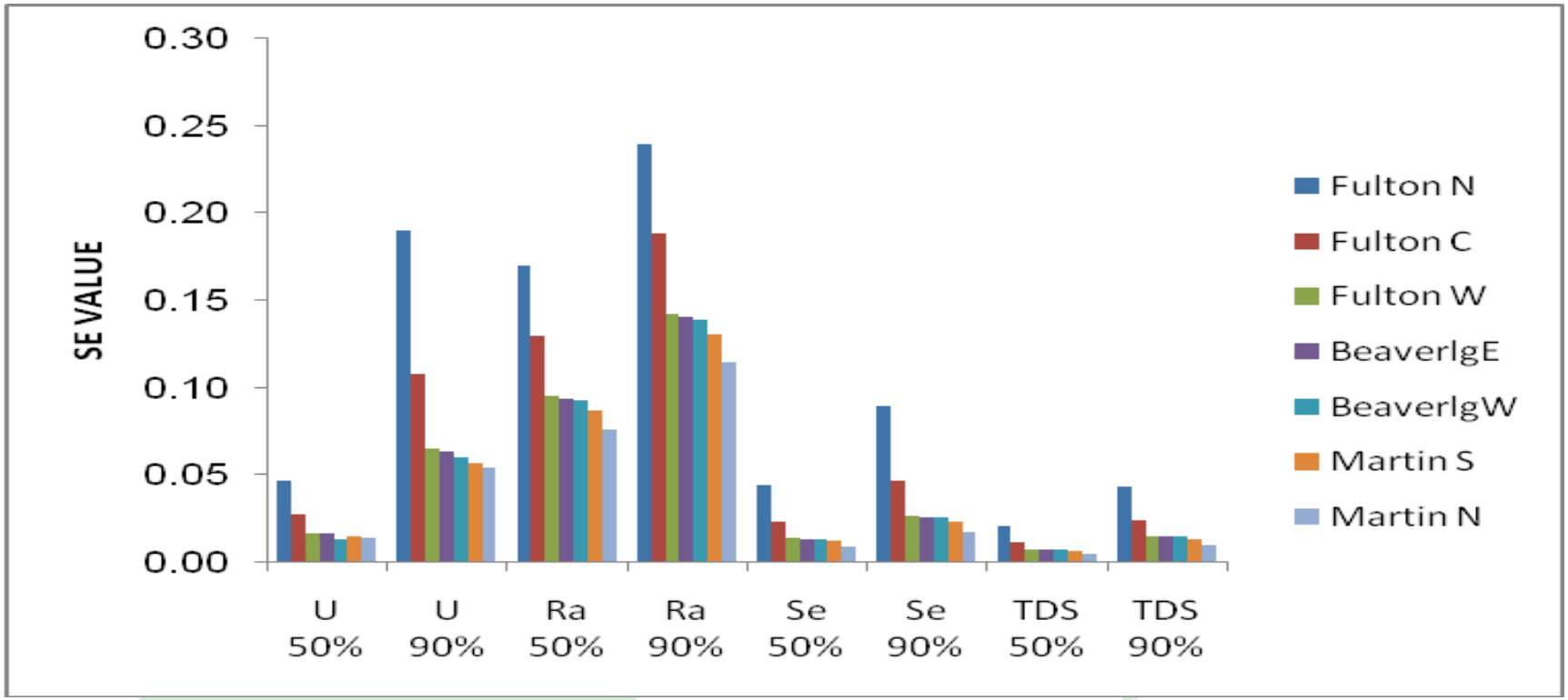
Predicted concentration of Radium-226 in Beaverlodge Lake



Predicted concentration of Selenium in Beaverlodge Lake



Predicted concentration of Uranium in Beaverlodge Lake



Normalized Sensitivity Response to Sediment Flux Load Reductions in Beaverlodge Lake and Martin Lake.

CONCLUSIONS (1 of 2)

- Sediments of Fookes and Greer lakes were proven to be the major sources of contaminants in the watershed
- Pore water and sediment analysis allowed identification of solid phases and the important sediment to water column transfer processes.
- The LAKEVIEW model was calibrated and shown to adequately simulate water quality in Fookes, Marie and Greer Lakes.

CONCLUSIONS (2 of 2)

- Parameter estimates were reasonable and consistent with previously published values.
- Application of LAKEVIEW model to Fulton Bay, Ace Bay and Beaverlodge Lake predicted consistent contaminant decline and Saskatchewan water quality objectives are expected to be met in 50 years
- The hypothetical reduction of sediment loads resulted in only slight improvements in most of Beaverlodge Lake.

Thank-you For Your Attention !

KEY CONTAMINANTS OF CONCERN

Uranium

Selenium

Radium – 226

PARAMETER ESTIMATION (Cont'd)

Bayes' Theorem

$$\theta = \grave{e}_1, \grave{e}_2, \grave{e}_3 \ldots \grave{e}_n$$

$$n = number\ of\ \ parameters$$

$$z = data$$

$$P(\theta \mid z) \propto P(\theta)\ P(z \mid \theta)$$

$$PDF \propto prior \text{ x } likelihood$$

PARAMETER ESTIMATION (Cont'd)

Metropolis-Hastings Algorithm

Start with some initial parameter values: $\left(\theta_1^{(1)}, \theta_2^{(1)}, \ldots, \theta_n^{(1)}\right)$

In some "random" way, select new candidate parameters:

$$\left(\theta_1^{(2)}, \theta_2^{(2)}, \ldots, \theta_n^{(2)}\right)$$

Calculate: $$\alpha = \frac{p\left(\vec{\theta}^{(2)}\right) p\left(z \mid \vec{\theta}^{(2)}\right)}{p\left(\vec{\theta}^{(1)}\right) p\left(z \mid \vec{\theta}^{(1)}\right)}$$

a) Generate random number l

b) Accept candidate as new chain member if $\alpha >= l$

c) If candidate is accepted, it also becomes the new chain value

d) Repeat numerous times.

Uranium Chemistry

- Solid phase equilibrium:

Solution

$$U_3O_8(s) + 12H^+ \leftrightarrow 2U^{6+} + UO_2(s) + 6H_2O$$

$$UO_2(s) + 4H^+ \leftrightarrow U^{4+} + 2H_2O$$

Adsorption

$$SOLID\{U(VI)\}_\chi \leftrightarrow SOLID + \chi\, U(VI)$$

CHI SQUARED TEST

- **Testing for model adequacy**

$$X^2 = \sum \frac{(o_i - e_i)^2}{e_i}$$

o_i = observed value
e_i = expected (modeled) value

Chi Square Goodness of Fit Test for Fookes, Marie, and Greer Lakes

LOCATION	Ra-226	Uranium	Selenium	TDS
FOOKES	**6.99 (27.79 / 17)**	**3.21 (27.79 / 17)**	**16.20 (23.68 /14)**	**9.62 (27.79 /17)**
MARIE	**8.59 (26.30 / 16)**	**24.72 (26.30 / 16)**	47.18 **(26.30 /16)**	**4.26 (27.79 / 17)**
GREER	**19.6 (22.36 / 13)**	**14.35 (25.00 /15)**	**21.00 (22.36 / 13)**	**18.44 (23.68 / 14)**

Beaverlodge Lake Water Quality Predicted vs Measured Levels

Constituent	Predicted Concentration in 2001	Measured Concentration Range in 2000/2001 Period
Radium-226 (Bq/L)	0.05	0.03 – 0.15
Selenium (µg/L)	3.25	1.0 – 4.0
TDS (mg/L)	155	150 – 180
Uranium (µg/L)	205	157 – 262

Parameter Estimates

	FOOKES	MARIE	GREER	Average
		Radium-226		
k_X (y^{--1})	**0.30**	**0.00**	**0.00**	0.10
K_L ($m\ y^{-1}$)	**1.82**	**1.82**	0.10	1.82
K_{Dsed} ($m^3 kg^{-1}$)	**0.10**	**0.20**	**0.21**	0.17
K_D ($m^3\ kg^{-1}$)	**2.50**	**2.50**	**2.52**	2.51
		Uranium		
k_X (y^{-1})	**0.00**	**0.00**	**0.07**	0.02
K_L ($m\ y^{-1}$)	**1.67**	**1.58**	**2.34**	1.87
K_{Dsed} ($m^3 kg^{-1}$)	**5.76**	**5.76**	**7.50**	6.34
K_D ($m^3\ kg^{-1}$)	**2.30**	**2.30**	**2.30**	2.30

FEDERAL CONTAMINATED SITES
SITES CONTAMINÉS FÉDÉRAUX
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Parameter Estimates

	FOOKES	MARIE	GREER	Average
		Selenium		
k_x (y^{--1})	**0.22**	**0.22**	**0.07**	0.17
K_L ($m\ y^{-1}$)	**3.67**	**3.14**	**2.04**	2.95
K_{Dsed} ($m^3 kg^{-1}$)	**5.85**	**5.75**	**7.50**	6.37
K_D ($m^3\ kg^{-1}$)	**4.82**	**4.82**	**4.82**	4.82

Selenium Chemistry

- Oxidation:

  $FeSe_xS_{2-x}(s) + (3.5-0.5x)\ O_2 + H_2O \rightarrow$
  $Fe^{2+} + 2H^+ + x\ SeO_3^{2-} + (2 - x)\ SO_4^{2-}$
  $SeO_3^{2-} + 0.5\ O_2 \rightarrow SeO_4^{2-}$

- Reduction:

  $SeO_4^{2-} + 2CH_2O \rightarrow Se^{2-} + 2H_2O + 2CO_2$

- Adsorption:

  $SOLID\{Se(IV\&VI)\}_x \rightarrow SOLID + x\ Se(IV\&VI)$

Uranium Chemistry (cont'd)

- **Liquid phase speciation:**

U^{4+}	U^{6+}
$U(OH)_{4\ (aq)}$	UO_2^{2+}
$U(OH)_5^-$	$UO_2(OH)^+$
	$(UO_2)_2OH_2^{2+}$
	$UO_2CO_{3\ (aq)}$
	$UO_2(CO_3)_2^{2-}$

Radium-226 Chemistry

- Solid phase equilibrium:

$$Ba_{1-x}(Ra)_x SO_4(s) \rightleftharpoons (1-x)Ba^{2+} + xRa^{2+} + SO_4^{2-}$$

$$x << 1$$

- Adsorption:

$$SOLID\{Ra\}_x \rightleftharpoons SOLID + x\ Ra^{2+}$$

ITEMS FOR DISCUSSION

- Chemistry of Water / Sediment
- Modeling Concepts
- Parameter Estimation

Sediment to Water Column Flux

$$FLUX = K_L(C_{SED} - C_{WAT})$$

$$FLUX = g\ m^{-2}\ yr^{-1}]$$

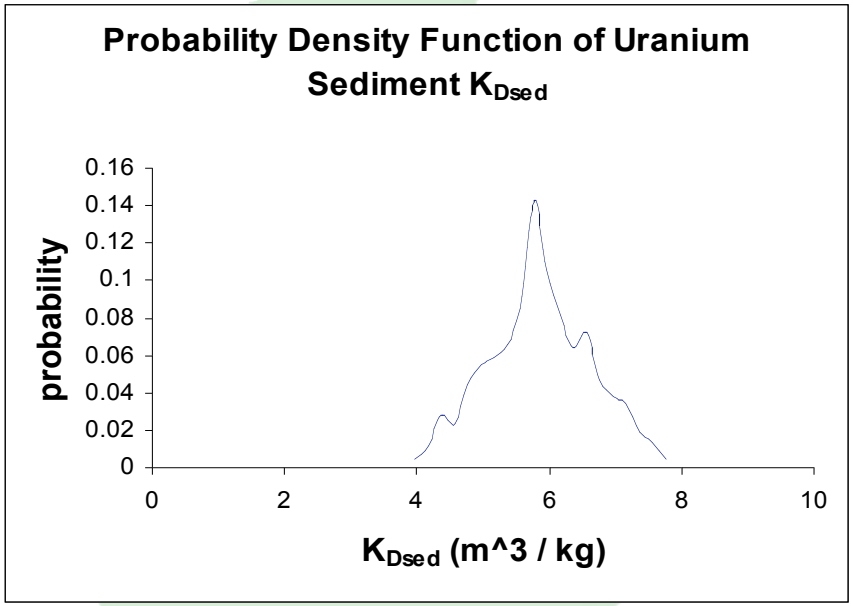
$$FLUX = Bq\ m^{-2}\ yr^{-1}]$$

K_L = mass transfer coefficient (m yr^{-1})

C_{SED} = concentration in sediment porewater

C_{WAT} = concentration in water column

Estimation of Sediment K_{Dsed} for Uranium



LAKE : FOOKES

 # trials: 2994

Max. likelihood: 5.76

Median value: 5.73

Mean value: 5.76

Std. Deviation: 0.78