

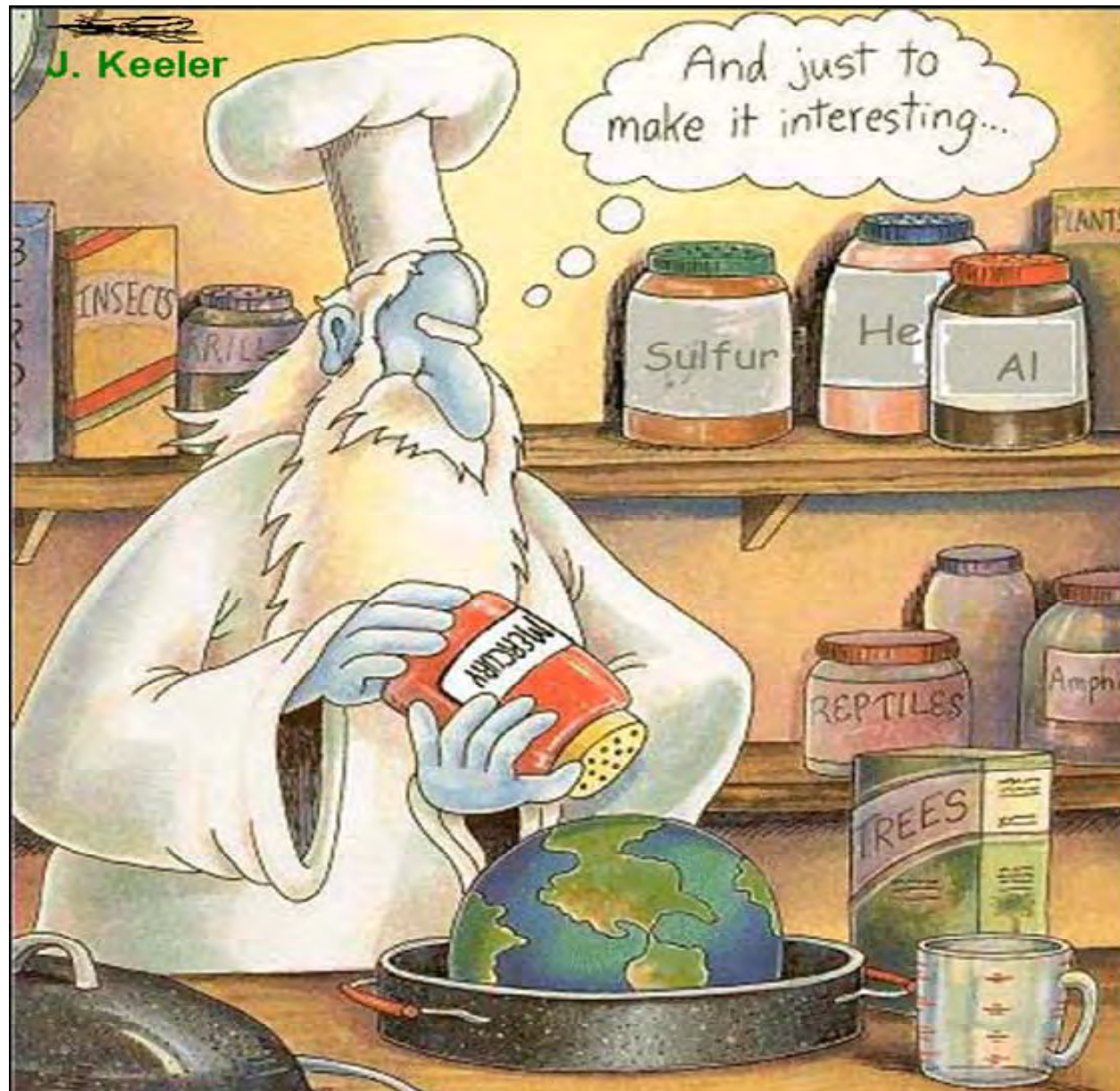
THE ESTIMATION OF ATMOSPHERIC MERCURY LOADINGS: THE LAKE ONTARIO AIR DEPOSITION STUDY (LOADS)

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Kelly

J. Keeler

And just to
make it interesting...

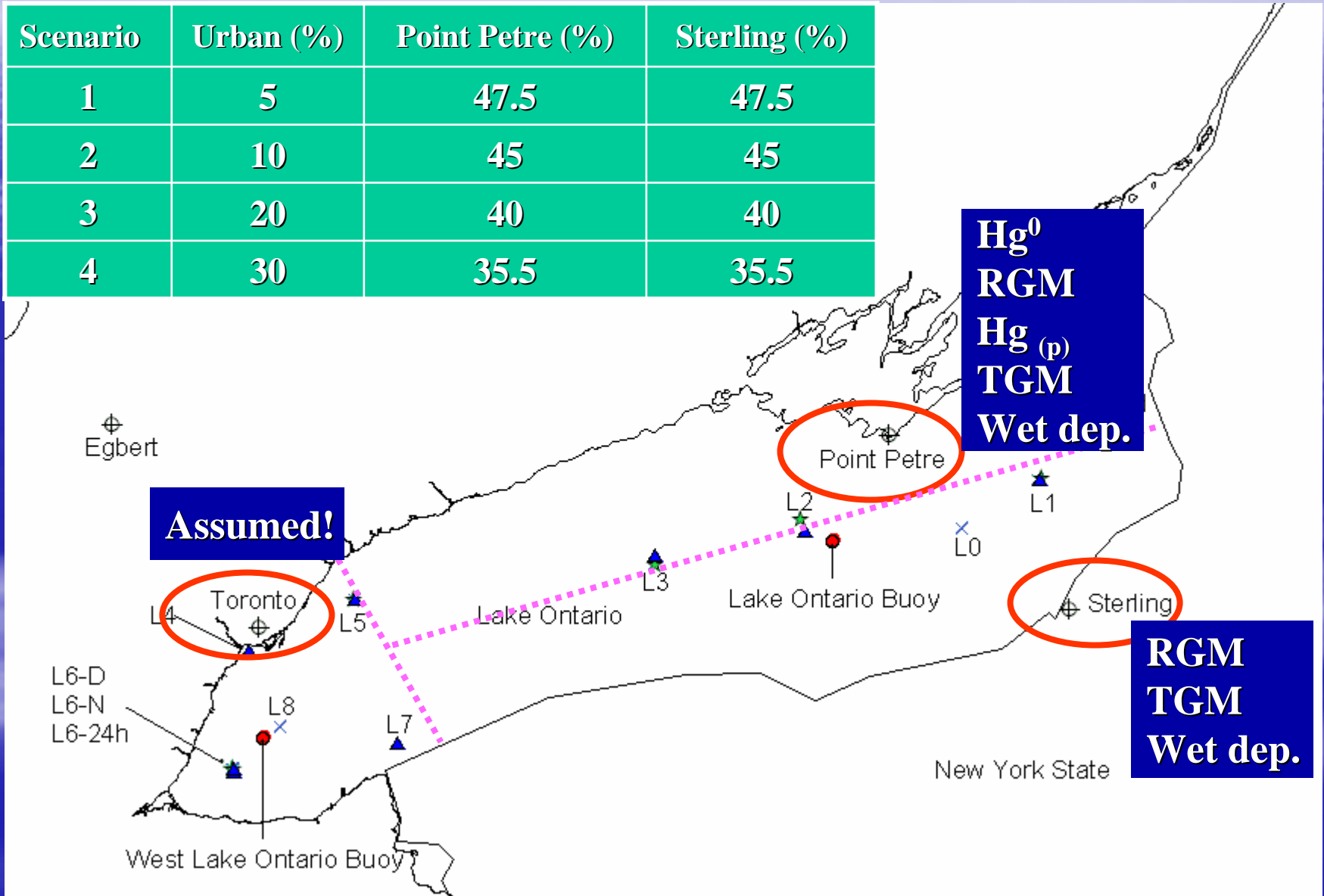


Objectives

- To investigate the seasonal variations of Hg concentrations and fluxes around and over Lake Ontario.
- To estimate atmospheric loadings of Hg to Lake Ontario on seasonal and annual basis.

Modeling Scenarios and Sampling sites

Scenario	Urban (%)	Point Petre (%)	Sterling (%)
1	5	47.5	47.5
2	10	45	45
3	20	40	40
4	30	35.5	35.5



Modeling Approaches

□ Total Atmospheric Loadings of Mercury into Lake Ontario

= Wet deposition (Sterling, Pt. Petre, urban = PPT*2)

+ Air-water exchange of Hg^0 and RGM (Sterling, Pt. Petre, urban = PPT*2)

+ Dry deposition of $\text{Hg}_{(p)}$ (Sterling = PPT, Pt. Petre, urban = PPT*6)

Wet Deposition

- ❖ *Wet deposition = Hg concentration in precipitation x precipitation depth*
- ❖ Both Hg measurements and rainfall amounts were collected at Point Petre and Sterling (*J. Keeler, U. MI*).
- ❖ Areal average precipitation depth computed by NOAA GLERL

Air-Water Exchange of Hg⁰

- ❖ Deposition-emission of Hg⁰: Two-film model (Liss and Slater, 1974)

$$\frac{1}{K_{OL}} = \frac{1}{k_w}$$

Hg⁰ emission flux (ng m⁻² h⁻¹)

$$F_{Hg^0} = k_w \left(\frac{TGM}{H'} - DGM \right)$$

Assume constant DGM concentration (15.7 pg L⁻¹)

Transfer velocity $k_w = f(U_{10}, T_w)$

Sanemesa (1975), $f(T_w)$

$$k_w = 0.31(U_{10}^2)(Sc_{Hg} / Sc_{CO_2})^{-0.5}$$

(Wanninkhof, 1992)

Air-Water Exchange of RGM

Tekran RGM concentration
(Urban ratio: PPT = 2:1)

RGM deposition flux
($\text{ng m}^{-2} \text{h}^{-1}$)

$$F_{RGM} = RGM \times k_a$$

- ❖ Transfer velocities k_a were estimated with Lo's model (1996)
Point Petre: 2.06 cm s^{-1} **Sterling: 2.02 cm s^{-1}**
- ❖ Literature values: $0.25 - 4 \text{ cm s}^{-1}$

- ❖ In Lo's model, single-level atmospheric parameter including U_{10} , T_a and T_w were utilized to calculate the surface parameters of u_* , z_0 and z/L .
- ❖ The molecular diffusivity of RGM was calculated and combined with the atmospheric parameters to obtain capture length (z_c).
- ❖ The RGM transfer velocity was calculated as

$$k_a \approx \frac{\kappa U_*}{[\ln(z/z_c) - \psi_{RGM}(z/L)]}$$

Hg_(p) Dry Deposition

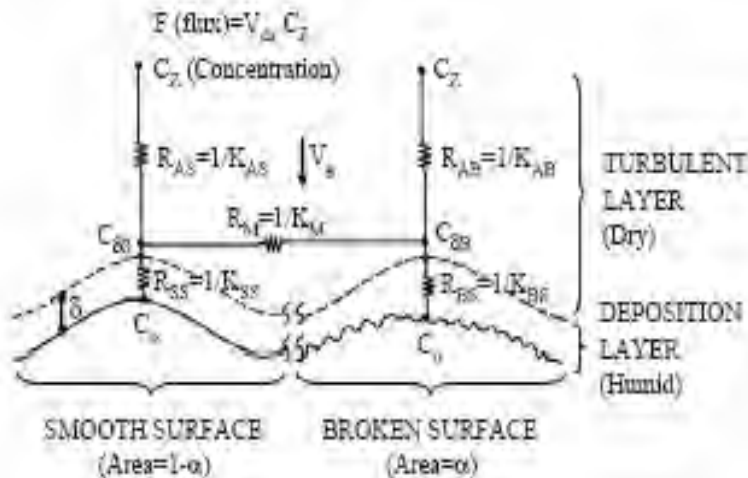
Tekran Hg_(p) concentrations

(Urban ratio: PPT = 6:1, Sterling = PPT)

Hg_(p) dry deposition flux
(ng m⁻² h⁻¹)

$$F_{\text{Hg}(p)} = \text{Hg}_{(p)1} \times V_{d,1} + \text{Hg}_{(p)2} \times V_{d,2} + \dots$$

$$V_d = (A/B) \left[(1-\alpha)(K_{ss} + v_{gw}) + \frac{K_m \alpha (K_{bs} + v_{gw})}{K_m + \alpha (K_{ab} + K_{bs} + v_{gw})} \right] + \frac{\alpha (K_{bs} + v_{gw}) \alpha (K_{ab} + v_{gd})}{K_m + \alpha (K_{ab} + K_{bs} + v_{gw})}$$



❖ Deposition velocities were estimated with Williams' model (1982)

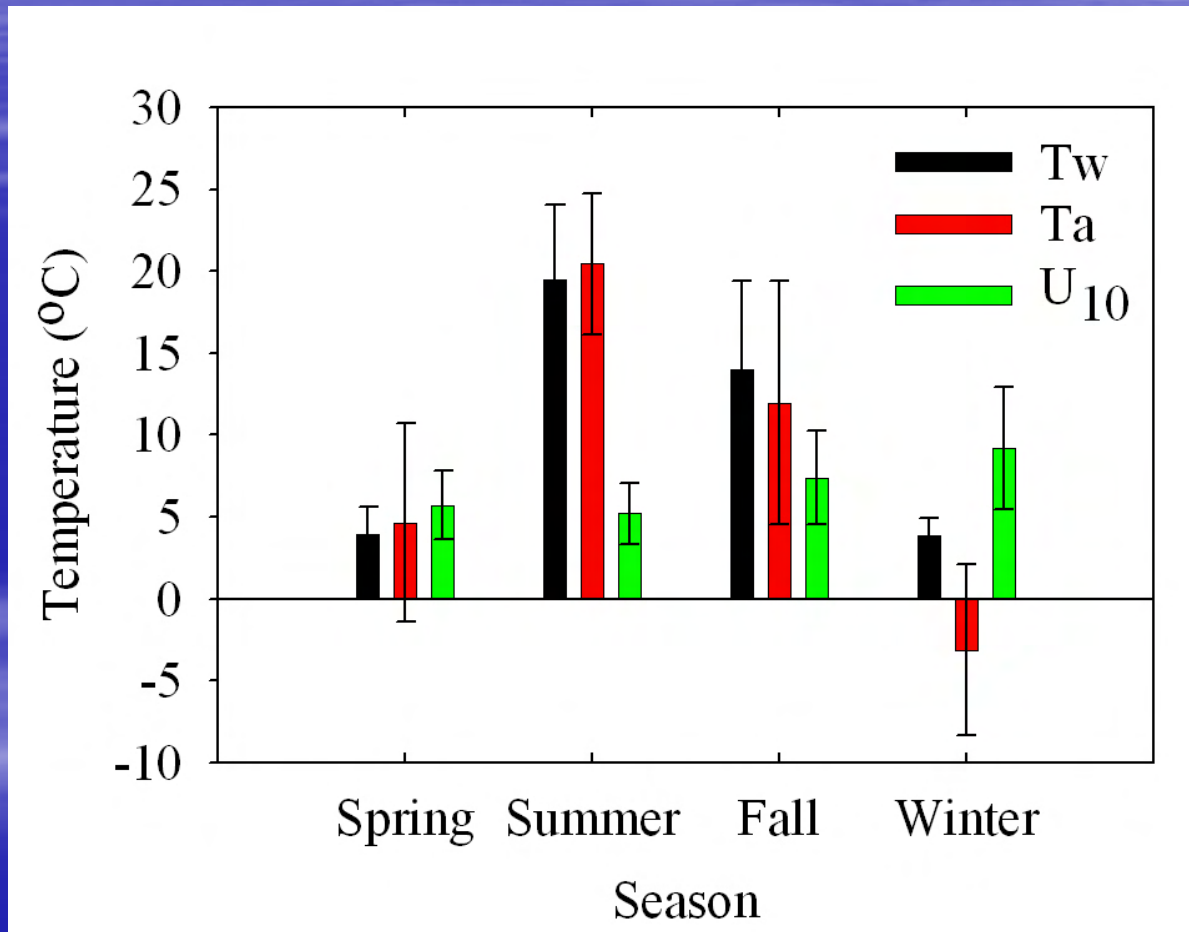
Fine fraction Hg_(p): 70%, 0.68 μm
Coarse fraction Hg_(p): 30%, 3.8 μm
(Keeler et al., 1995)

Fine: 0.23 cm s⁻¹

Coarse: 0.33 cm s⁻¹

❖ Literature values: 0.01 – 0.59 cm s⁻¹

Summary of Seasonal Meteorological Parameters



Comparisons with other studies

Hg deposition	LOADS (This study)				LMMBS (2002)	
	Flux ($\mu\text{g m}^{-2} \text{yr}^{-1}$)		Loading (kg yr^{-1})		Flux ($\mu\text{g m}^{-2} \text{yr}^{-1}$)	Loading (kg yr^{-1})
	Min	Max	Min	Max		
Wet	8.4	9.7	160	190	11	614
Hg _(p)	0.90	1.8	17	34	1.2	69
RGM	3.4	4.1	64	77	8.5	490
Hg ⁰	-5.9	-4.3	-110	-82	-7.8	-453
Total	6.8	11.3	140	220	12	720

Note: Negative values represent Re-emission.

Sensitivity Analysis

- ❖ Extent of urban influence
- ❖ response of the models to increases and decreases of 20%.

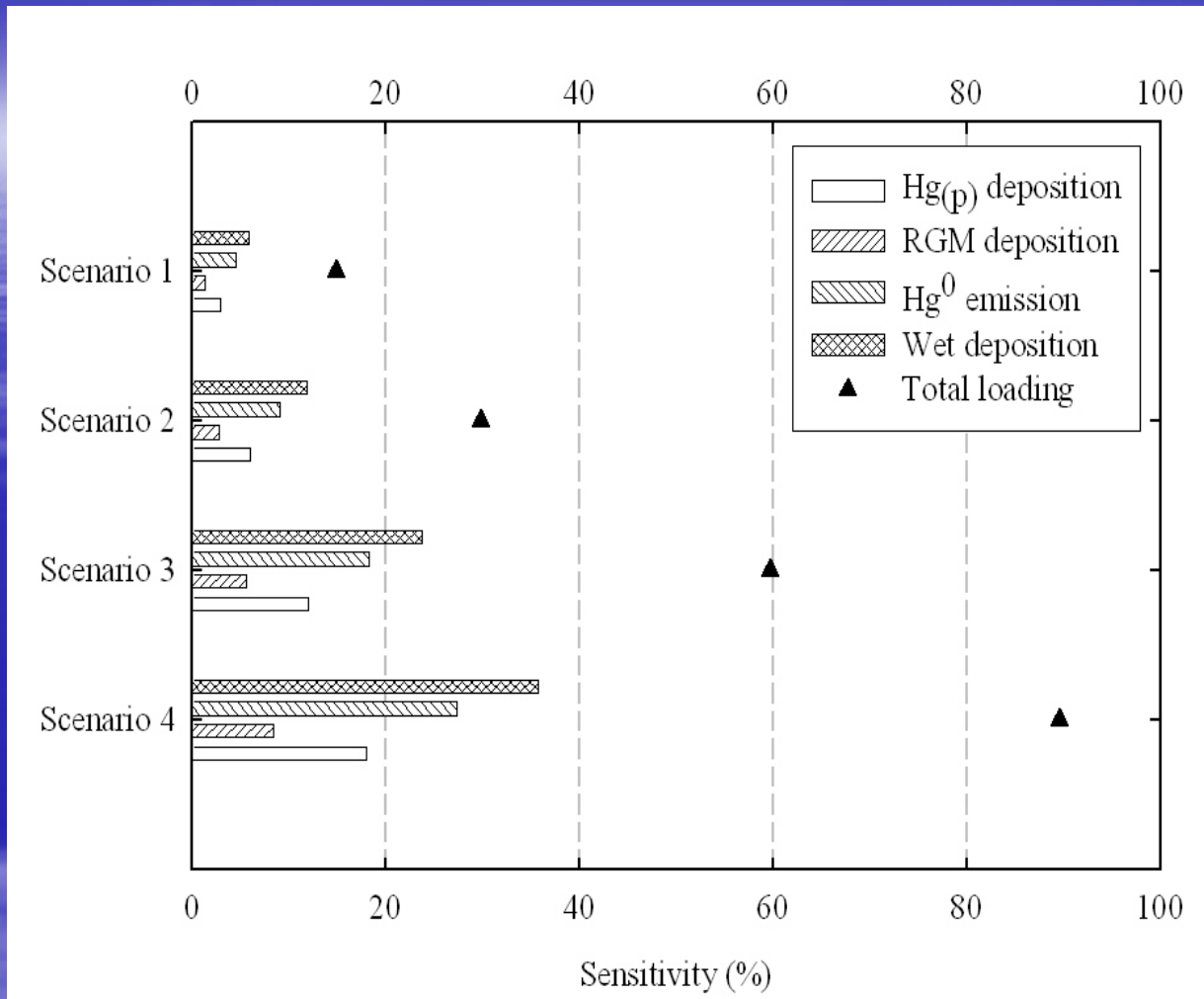
$$F_{\text{Total}} = C_{\text{Precip.}} \times \text{Depth}_{\text{Precip.}} + k_w \left(\frac{\text{TGM}}{H'} - \text{DGM} \right) + C_{\text{RGM}} \times k_a + \sum_{i=1}^n \left(C_{\text{Hg}(p)} \times V_{d,i} \right)$$

$$H' = f(T_w)$$

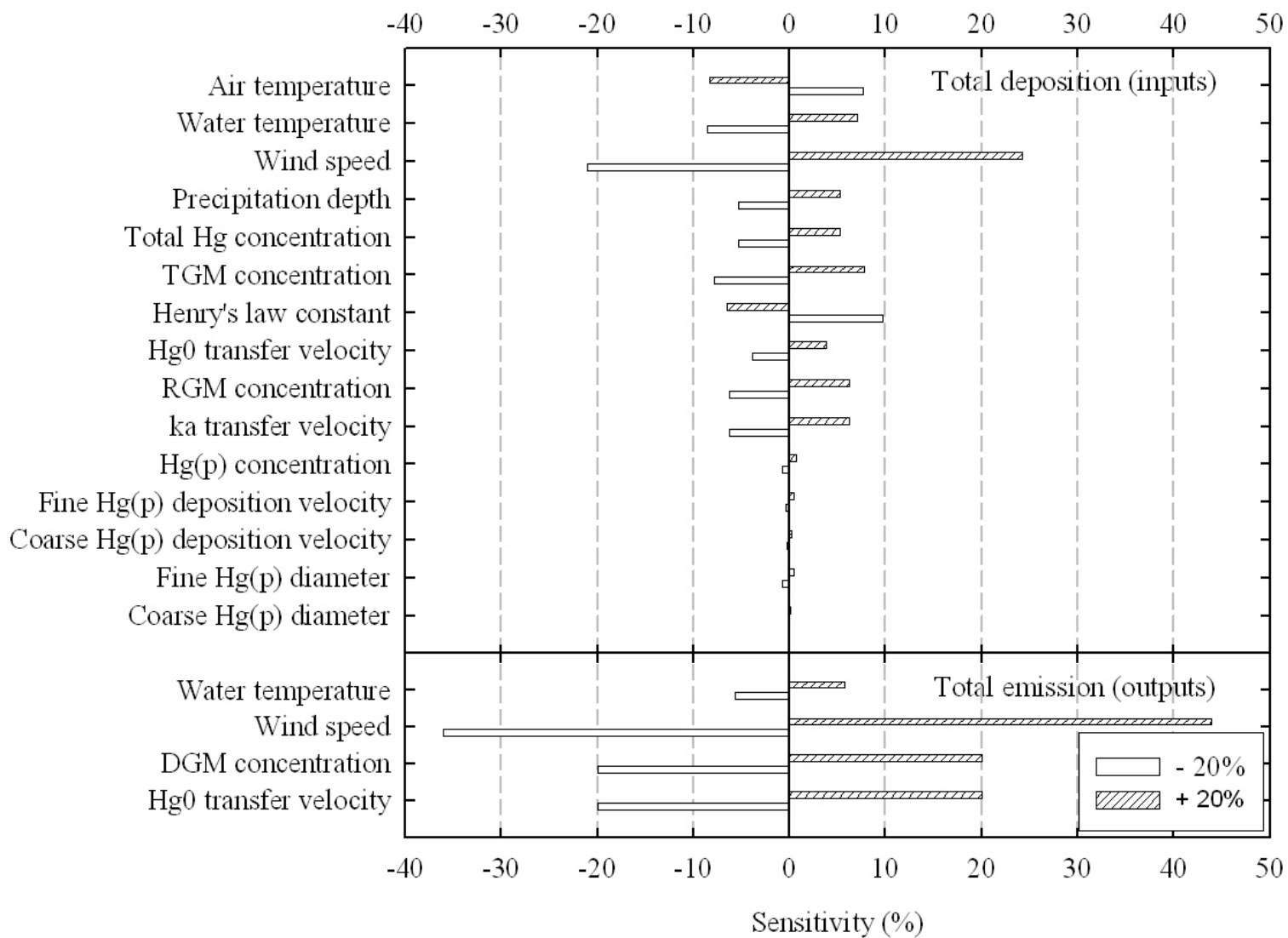
$$k_w = f(U_{10}, T_w)$$

$$k_a = f(U_{10}, T_w, T_a)$$

$$V_d = f(U_{10}, T_w, T_a, D_p, RH)$$



Urban area influence varied from 5 to 30%
 - loading approx doubles



Conclusions

❖ The contributions to Lake Ontario:

Wet deposition: **170** kg yr⁻¹

RGM dry gaseous deposition: **70** kg yr⁻¹

Hg_(p) dry particle deposition: **25** kg yr⁻¹

DGM re-emission: **-100** kg yr⁻¹

❖ The net Hg loading: **165** kg yr⁻¹

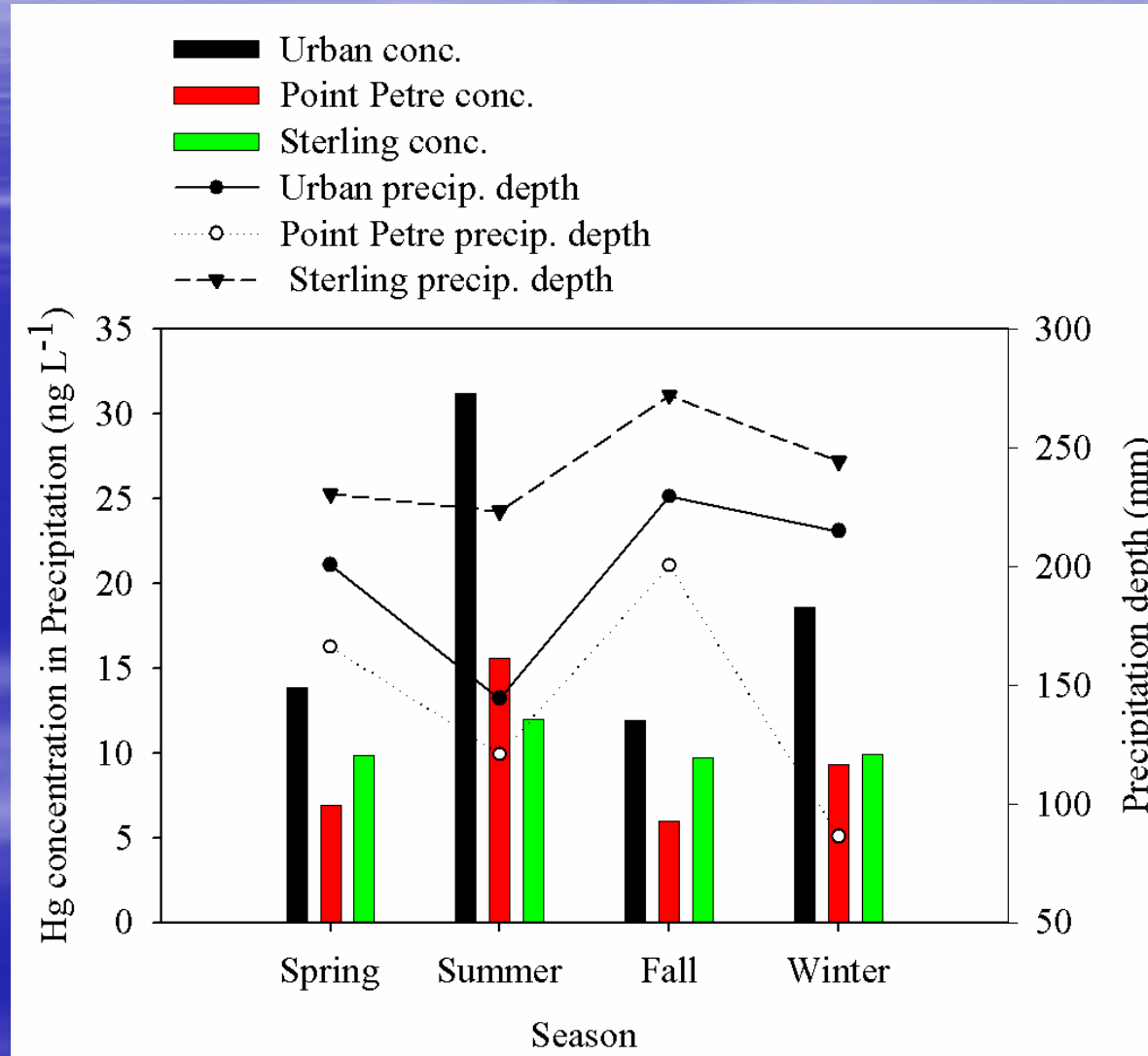
❖ Most sensitive inputs:

extent of urban influence, air temperature, wind speed,
DGM, RGM, k_a

Acknowledgments

- ❖ USEPA Region 2 and 5, GLNPO
- ❖ Environment Canada
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- ❖ Dr. Han, Dr. Yi, Hyun-Deok Choi, Francis
- ❖ Dr. Keeler, Dr. Landis

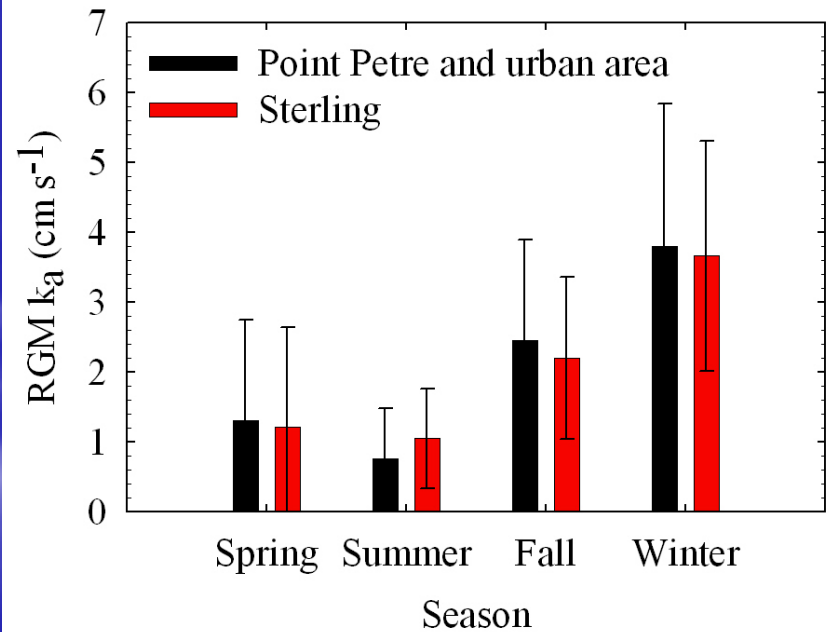
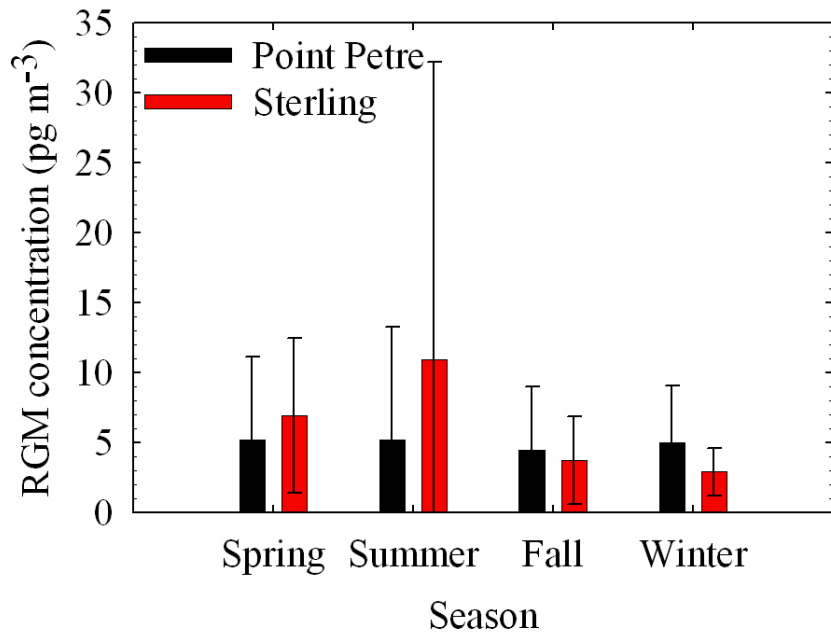
Wet deposition



Wet deposition = Hg concentration in precipitation x precipitation depth.

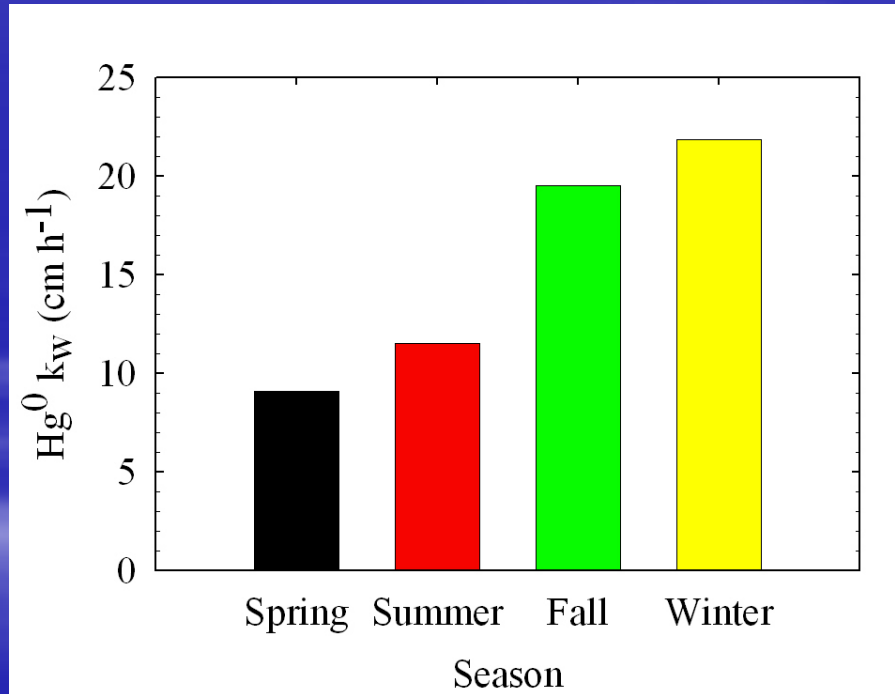
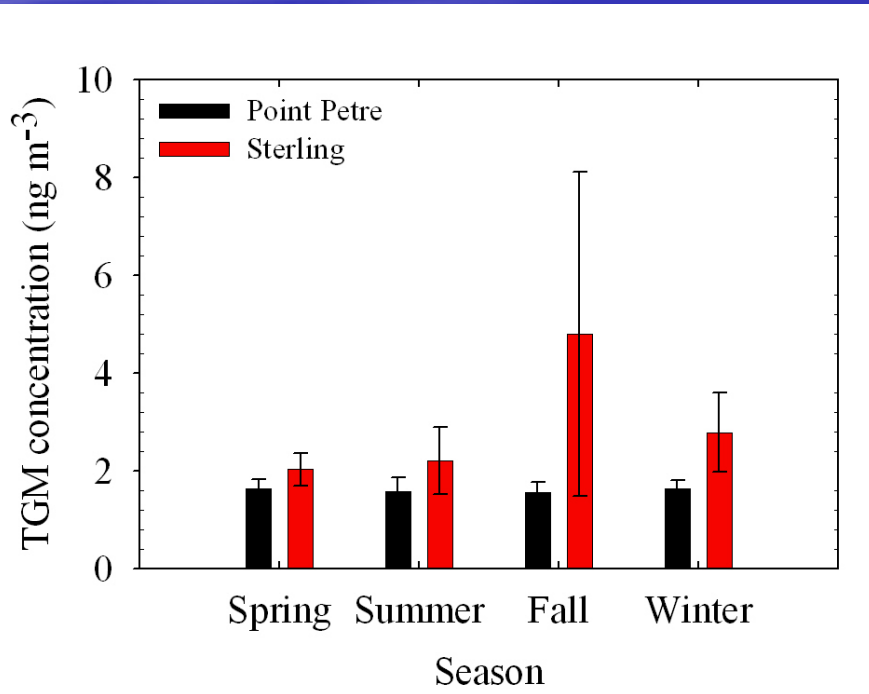
Air-Water Flux of RGM

$$F_{RGM} = RGM \times k_a$$



Air-Water Exchange

$$F_{Hg^0} = k_w \left(\frac{TGM}{H} - DGM \right)$$



Air-Water Exchange of Hg⁰

Seasonal Flux ($\mu\text{g m}^{-2} \text{ season}^{-1}$)	Range	Average
Spring	-0.67 – -1.1	-0.90
Summer	-1.9 – -2.2	-2.1
Fall	-0.94 – -1.1	-1.1
Winter	-0.81 – -1.5	-1.2
Annual*	-4.3 – -5.9	-5.2
Seasonal Loading (kg season ⁻¹)	Range	Average
Spring	-13 – -20	-17
Summer	-36 – -42	-40
Fall	-18 – -21	-20
Winter	-15 – -28	-23
Annual*	-82 – -110	-100

* Annual flux ($\mu\text{g m}^{-2} \text{ yr}^{-1}$)/loading (kg yr⁻¹)

Negative values represent Re-emission.

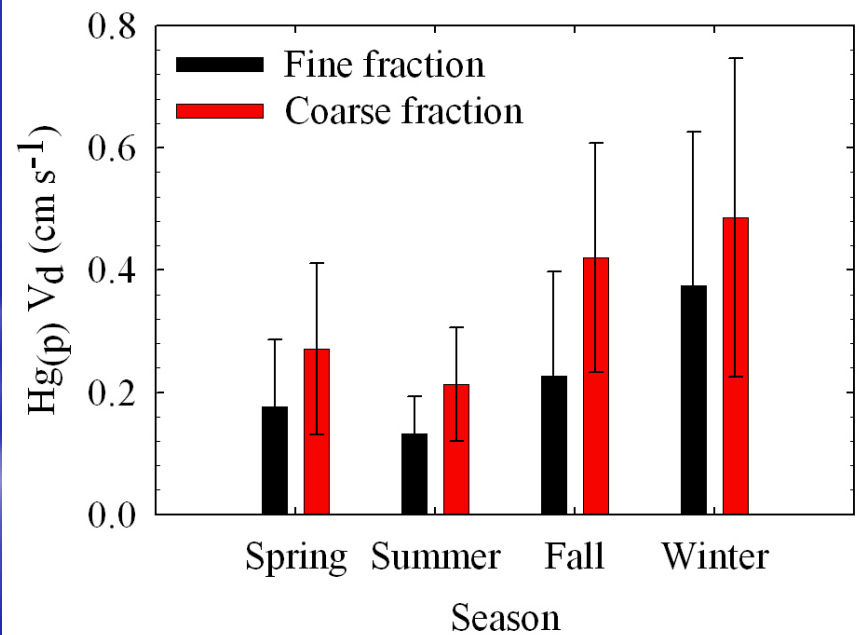
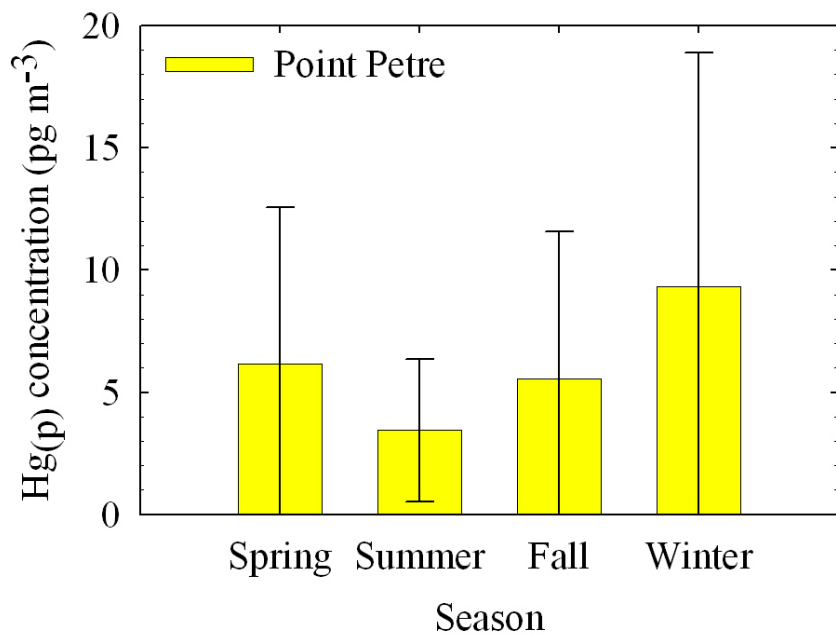
Air-Water Exchange of RGM

Seasonal Flux ($\mu\text{g m}^{-2} \text{ season}^{-1}$)	Range	Average
Spring	0.51 – 0.69	0.59
Summer	0.45 – 0.69	0.57
Fall	1.2 – 1.3	1.2
Winter	1.2 – 1.4	1.3
Annual*	3.4 – 4.1	3.7
Seasonal Loading (kg season^{-1})	Range	Average
Spring	10 – 13	11
Summer	8 – 13	11
Fall	23– 24	24
Winter	23 – 27	25
Annual*	64 – 77	70

* Annual flux ($\mu\text{g m}^{-2} \text{ yr}^{-1}$)/loading (kg yr^{-1})

Hg_(p) Dry Deposition

$$F_{\text{Hg}(p)} = \text{Hg}_{(p)1} \times V_{d,1} + \text{Hg}_{(p)2} \times V_{d,2} + \dots$$



Wet deposition

Seasonal Flux ($\mu\text{g m}^{-2} \text{ season}^{-1}$)	Range	Average
Spring	2.2 – 2.6	2.3
Summer	2.4 – 3.0	2.7
Fall	2.0 – 2.2	2.1
Winter	1.8 – 2.4	2.0
Annual*	8.4 – 9.7	9.1
Seasonal Loading (kg season^{-1})	Range	Average
Spring	41 – 49	44
Summer	46 – 56	50
Fall	38 – 41	40
Winter	34 – 45	38
Annual*	160 – 190	170

* Annual flux ($\mu\text{g m}^{-2} \text{ yr}^{-1}$)/loading (kg yr^{-1})

Future Work

Estimation of Hg loadings to Lake Ontario will be continued and improved.

- a. Kriging can be used to interpolate spatially meteorological parameters over the whole lake.
- b. DGM concentrations can be estimated using model proposed by Vette et al. (2002).
- c. Uncertainties in estimated deposition will be performed with perturbation analysis.
- d. Comparisons of different k_w models.

Sensitivity Analysis

Input parameters

Air temperature

RGM concentration

RGM transfer velocity

TGM concentration

Dimensionless Henry's Law constant

Sampling Strategies

Period	Sterling	PPT	Urban area	Ship
Total Hg in precip.	Apr. 02 – Mar. 03 (six-day)	Apr. 02 – Mar. 03 (weekly)	NA	Apr. 02, Sept. 02, and Jul. 03
TGM	Apr. 02 – Mar. 03 (six-day)	Apr. 02 – Mar. 03 (continuously)	NA	Apr. 02, Sept. 02, and Jul. 03
RGM	Apr. 02 – Mar. 03 (six-day)	Sept. 02 – Sept. 03 ^a (continuously)	NA	Apr. 02, Sept. 02, and Jul. 03
Hg _(p)	NA	Sept. 02 – Sept. 03 ^a (continuously)	NA	NA
DGM	NA	NA	NA	Jul. 03

Method	Sterling	PPT	Urban area	Ship
Total Hg in precip.	MIC-B	MDN collector	Urban:PPT = 2:1 ^b	Manual
TGM	Manual gold trap	Tekran 2537A	Urban:PPT = 2:1 ^b	Manual gold trap
RGM	KCl-coated denuder	Tekran Hg speciation system	Urban:PPT = 2:1 ^b	KCl-coated denuder
Hg _(p)	Sterling: PPT = 1:1 ^c	Tekran Hg speciation system	Urban:PPT = 6:1 ^b	NA
DGM	Mean DGM conc	Mean DGM conc	Mean DGM conc	Tekran 2537A

Note: a Similar seasonal variations of RGM and Hg(p) were assumed in 2002 and 2003. b The Hg concentrations in urban areas used in each mechanism were determined based on those measured at Point Petre. c The Hg(p) concentrations at Sterling were assumed to be the same as those measured at Point Petre. NA: Not available.

Hg_(p) Dry Deposition

Seasonal Flux ($\mu\text{g m}^{-2} \text{ season}^{-1}$)	Range	Average
Spring	0.17 – 0.35	0.25
Summer	0.07 – 0.14	0.10
Fall	0.20 – 0.40	0.29
Winter	0.45 – 0.90	0.65
Annual*	0.90 – 1.8	1.3
Seasonal Loading (kg season^{-1})	Range	Average
Spring	3.3 – 6.6	4.8
Summer	1.4 – 2.7	2.0
Fall	3.8 – 7.6	5.5
Winter	8.5 – 17	12
Annual*	17 – 34	25

* Annual flux ($\mu\text{g m}^{-2} \text{ yr}^{-1}$)/loading (kg yr^{-1})