

Long-term trends of Total Gaseous Mercury concentrations from selected CAMNet sites (1995-2005)

CAMNet

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Environment Canada

GLBTS mercury meeting, May 17th 2006, Toronto

Introduction

Emission data
CAMNet TGM dataset
Trend analysis
Conclusions

Outline

Where do we look?
The measurement parameter
What is CAMNet?

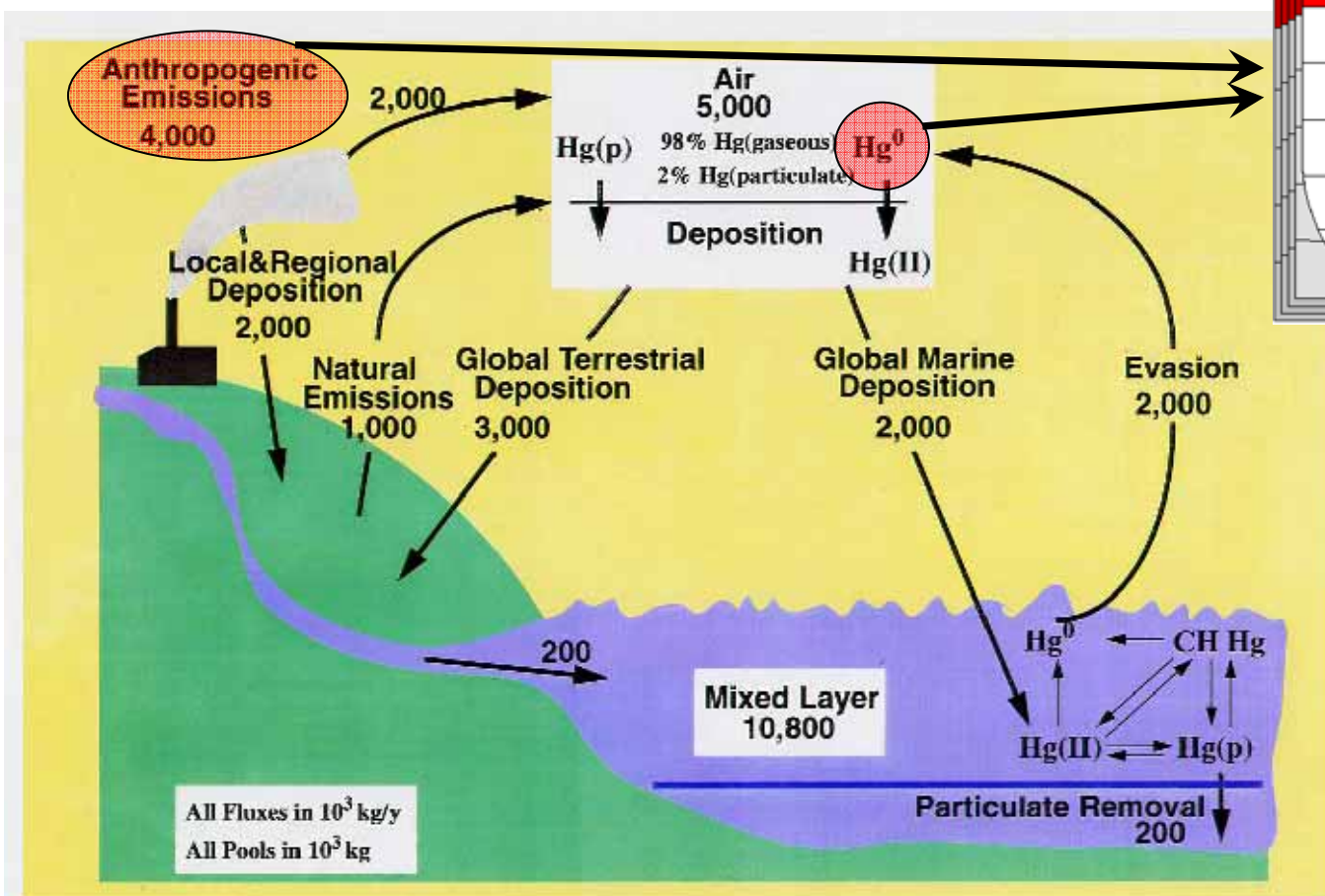
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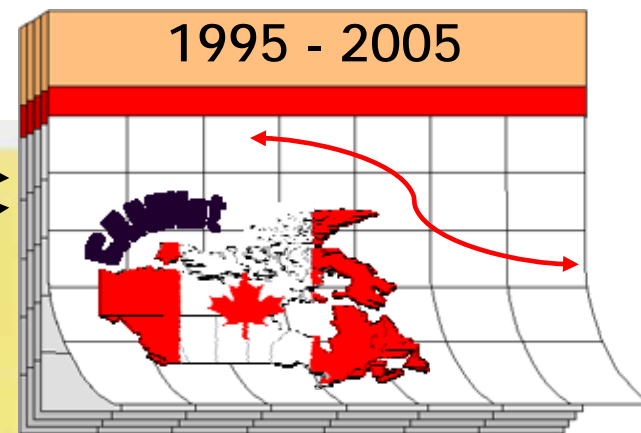
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Where do we look at?



Current Mercury Budgets and Fluxes (adapted from Mason et al., 1994)



- spatial and temporal distribution
- significant time trends
- absolute and relative increase/decrease
- target time periods
- Canadian perspective
- only gaseous Hg
- daily averages

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Measurements of Total Gaseous Mercury (TGM)

TGM = Elemental Mercury (Hg^0 ; >98%) + Reactive Gaseous Mercury (RGM)

TGM is detected with a TEKRAN analyser

Instrument features:

- gold amalgamation technique with subsequent AFS-detection
- two parallel gold cartridges operating in alternating modes (continuous)
- time resolution up to 5 min. → *daily averages are used for further analysis*
- detection limit of $< 0.1 \text{ ng/m}^3$ (20 ppq @ 7,5 L samples)
- relative measurement uncertainty of 4-5%



Distance Moon-Earth: 384403 km



⇒ 20 ppq = 8 μm

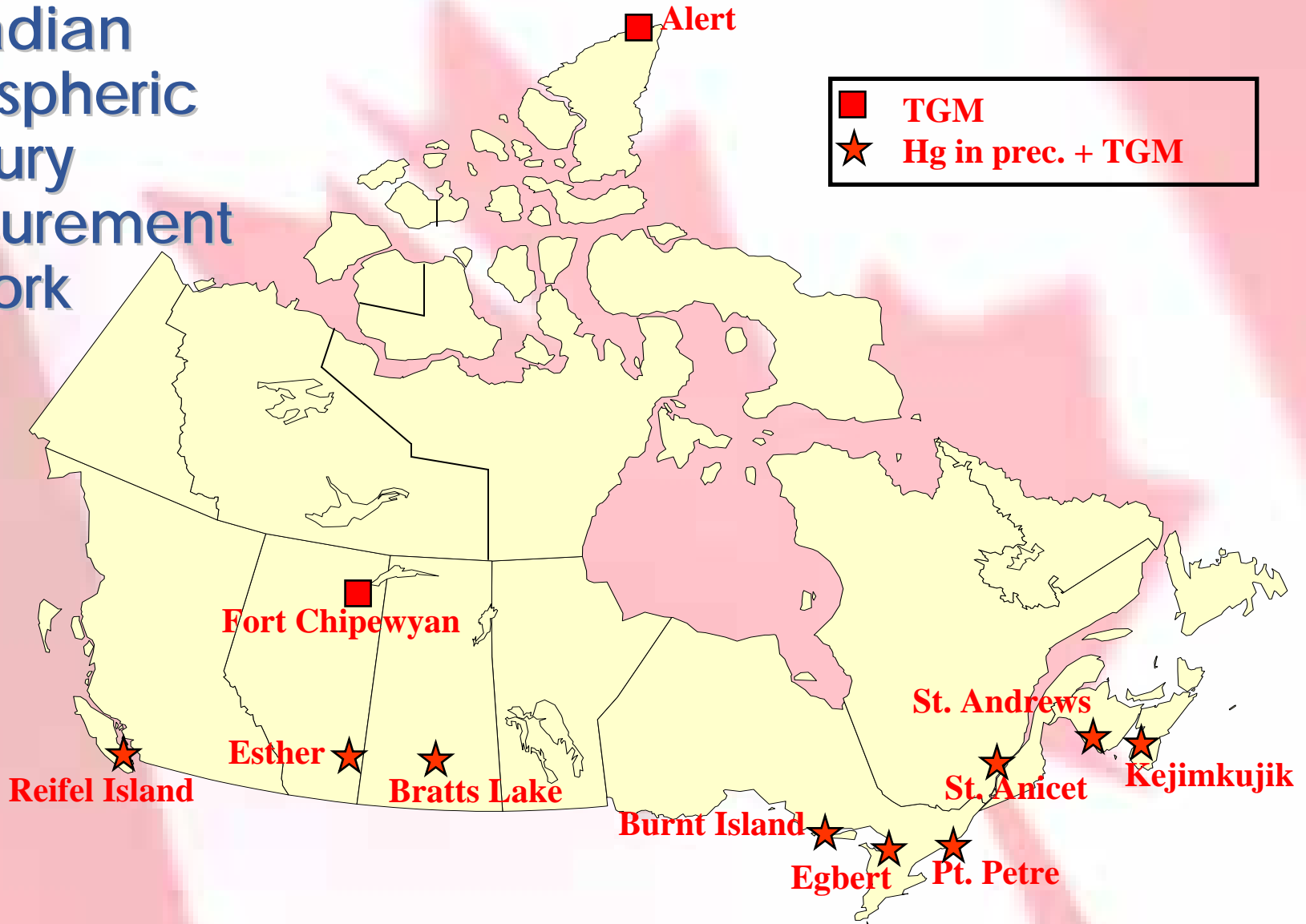
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**Canadian
Atmospheric
Mercury
Measurement
Network**



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Canadian Atmospheric Mercury Measurement Network

Station	Code	Province	Latitude	Longitude	Altitude	Period
Alert	ALT	NU	82.50	-62.33	210	01/95-12/05
Kejimkujik	KEJ	NS	44.43	-65.21	127	01/96-12/04
St. Andrews	STA	NB	45.09	-67.08	80	01/96-12/04
St. Anicet	WBZ	QC	45.12	-74.28	49	01/97-12/05
Point Petre	PPT	ON	43.84	-77.15	75	11/96-12/05
Egbert	EGB	ON	44.23	-79.78	251	12/96-12/05
Burnt Island	BNT	ON	45.81	-82.95	75	05/98-12/05
Bratt's Lake	BRL	SK	50.20	-104.72	577	05/01-12/05
Esther	EST	AB	51.67	-110.20	707	06/98-04/01
Fort Chipewyan	FCH	AB	58.78	-111.12	232	06/00- 07/01
Reifel Island	RFL	BC	49.10	-123.17	2	03/99-02/04

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Latest newspaper article
U.S. and Canadian emissions

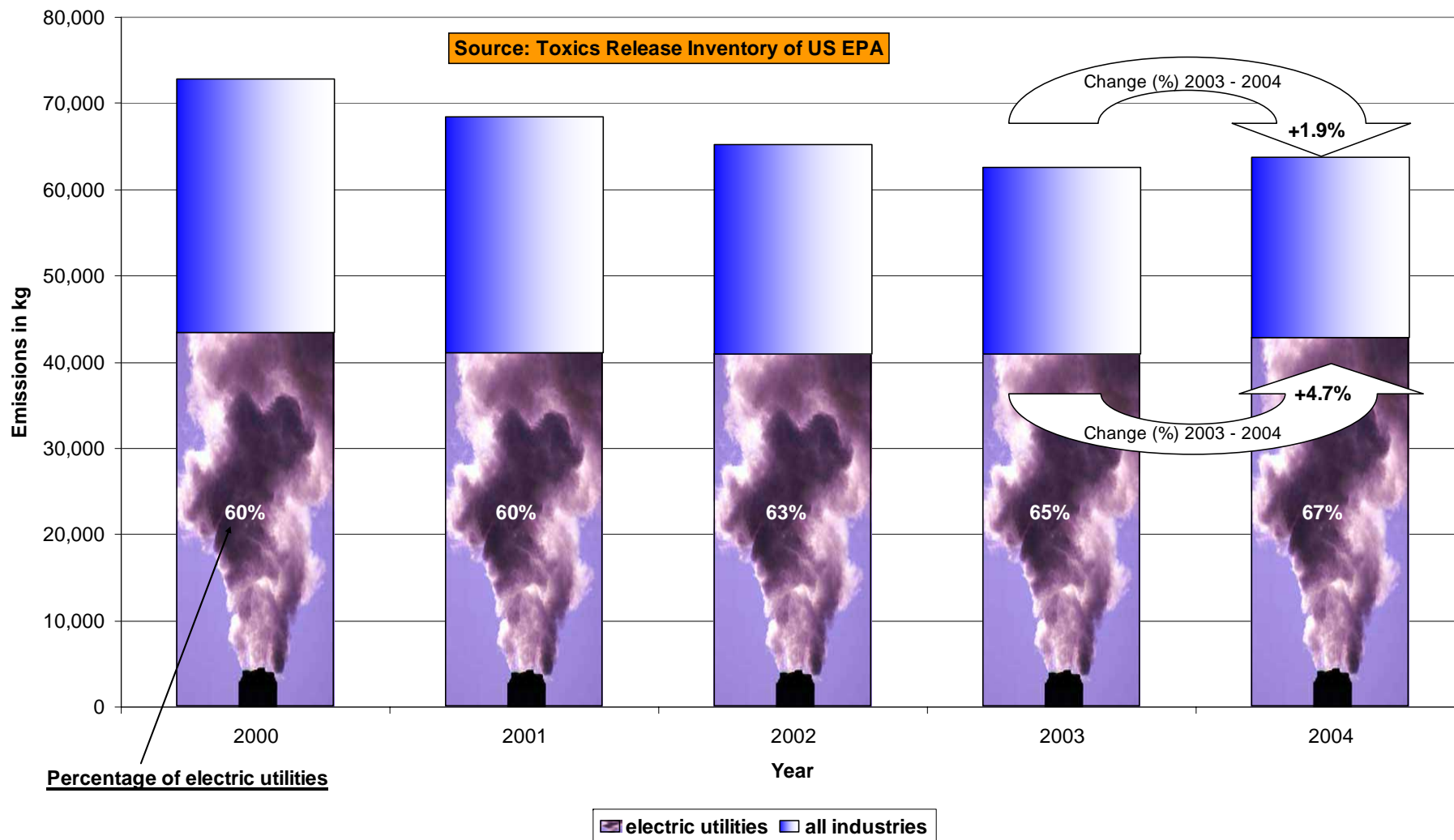
Up-to-dateness:

Change in U.S.
Hg emissions
reflected in the
newspaper

The screenshot shows a Chicago Tribune webpage. At the top left is a logo for 'Chicago Tribune SUBSCRIBER ADVANTAGE' with the text 'The day's top stories e-mailed to subscribers'. The main header features the 'Chicago Tribune' name in a large, white, serif font on a dark blue background. Below the header is a pink banner with a floral image and the text 'It's not too late! Send Mother's Day Flowers from \$2. Mother's Day is Sunday, May 14th'. The article's title is 'Coal plants spew more mercury' in a large, bold, black font. Below the title is a sub-headline: 'Emissions grow in Illinois, nation despite drop in other pollutants'. The author is 'By Michael Hawthorne', a Tribune staff reporter, published on April 29, 2006. The main text of the article states that mercury pollution from coal-fired power plants is increasing nationwide, even as the Bush administration touts an overall decline in toxic chemicals released by industry into the environment. A highlighted text box contains the following information: 'Though total mercury emissions decreased less than 2 percent from 2003 to 2004, the amount blown into the air by power plants increased 4 percent, a Tribune analysis of newly released federal data shows.' Below this, the text continues: 'Coal plants in 28 states, including Illinois, put more mercury into the air during 2004 than the year before, offsetting lower amounts of the hazardous metal from plants elsewhere. The increase is of particular concern in states like Illinois that rely heavily on coal to generate electricity, environmental groups say, because mercury tends to fall back to earth close to its source, and it takes only a small amount to contaminate waterways.' On the left side of the page, there are navigation links: 'E-mail this story', 'Printable format', and 'Search archives'. Below these are 'Most e-mailed (last 24 hours)' links, including 'U. of I. admission about to get harder for residents', 'Daddy material? It takes just 1 look', 'Rape suspect caught after escape', 'Rosemont drops casino, eyes family friendly project', and 'Food show's exit takes bite out of city's status'. There are also links for 'More from today' and 'Past week'. At the bottom left, there is a section titled 'Images in the news' with a small image of a volcano erupting.

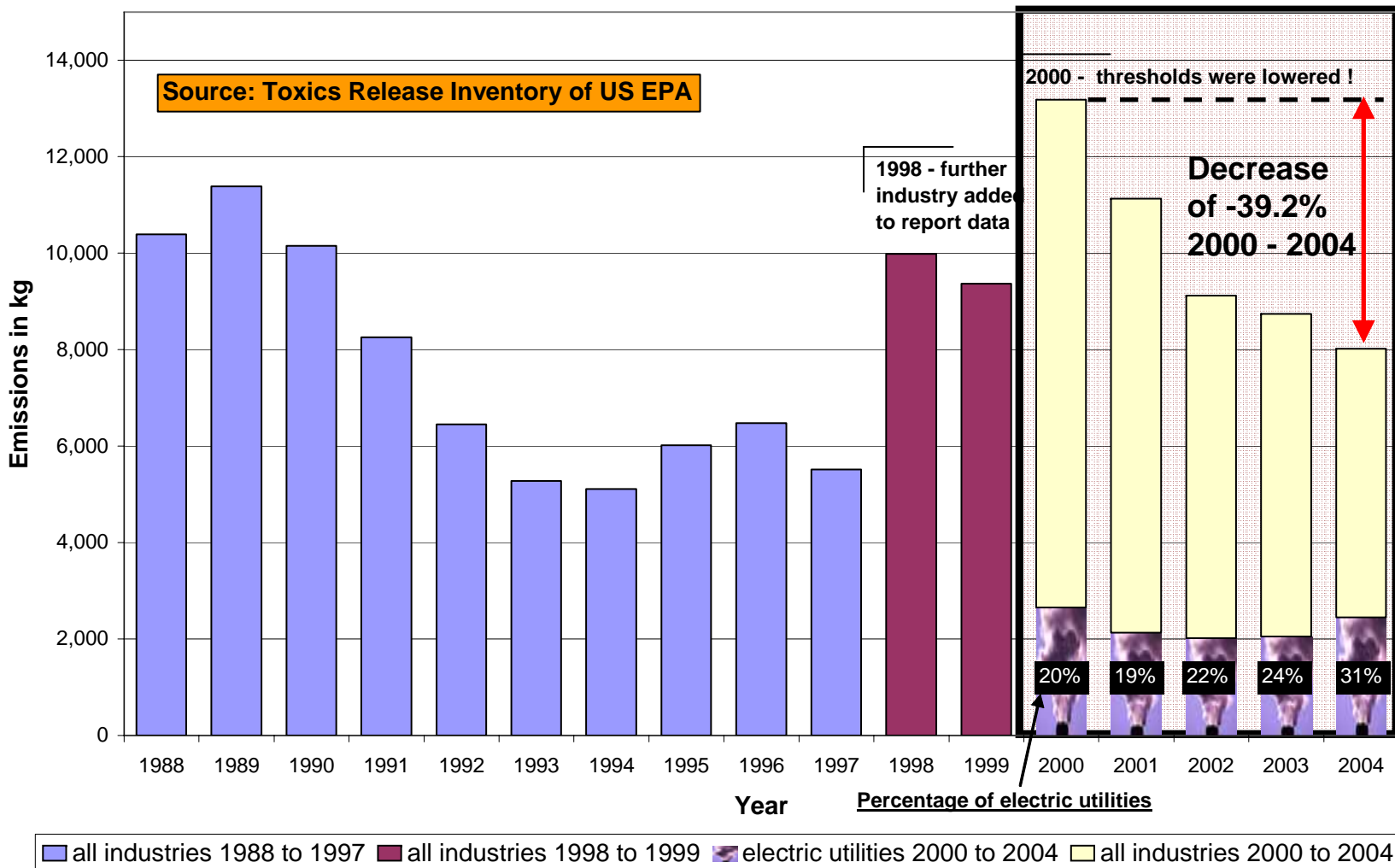
Reported U.S. atmospheric Hg emissions

Total atmospheric mercury (Hg^0 + compounds) emissions in the U.S.



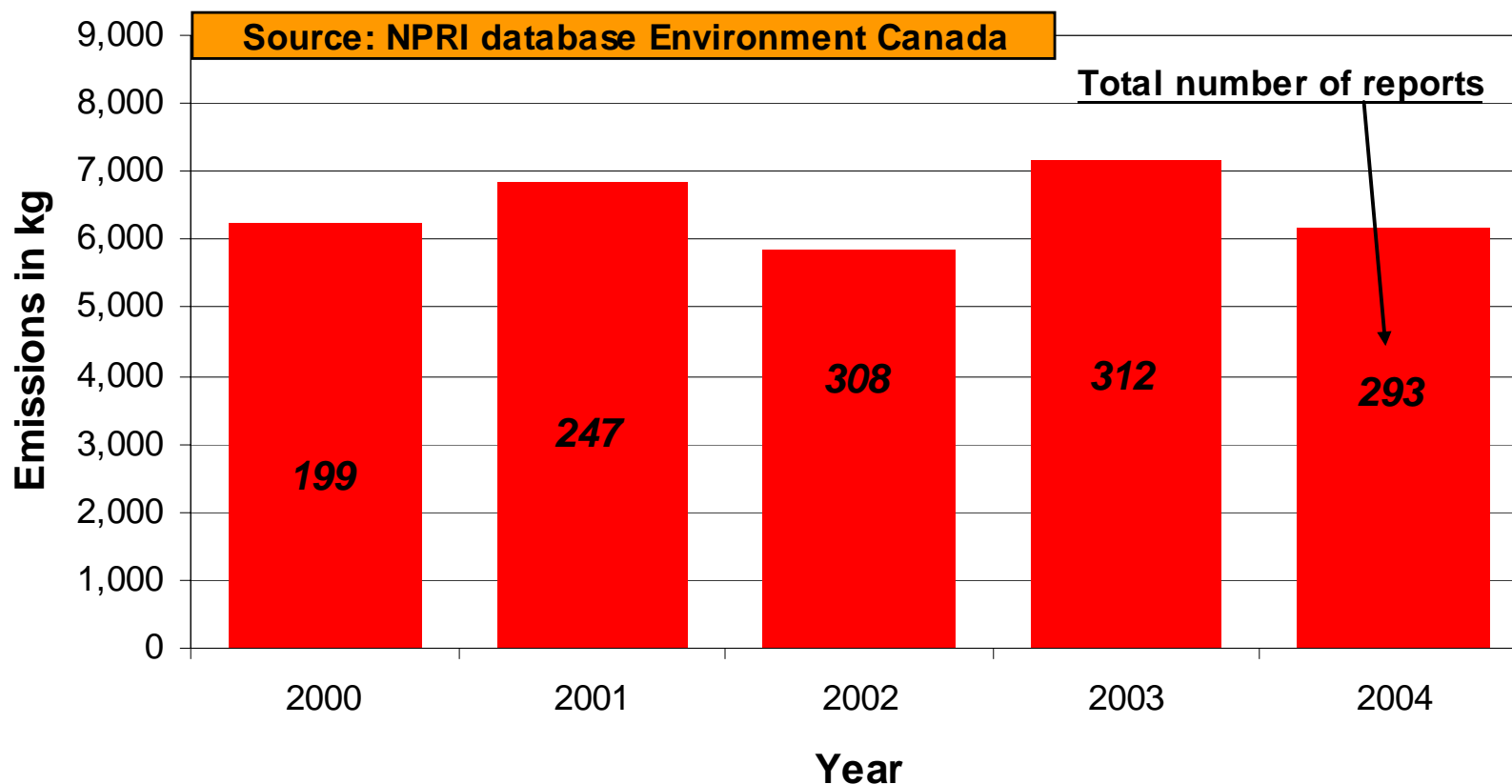
Reported U.S. emissions of elemental mercury (Hg⁰)

Total atmospheric Hg⁰ emissions in the U.S.



Canadian atmospheric (?) Hg emissions

Canadian on-site releases of mercury compounds in kg



Low comparability to U.S. data:

- high variation in number of reports
- releases to surface water and land included
- no information on Hg⁰ fraction

Facts:

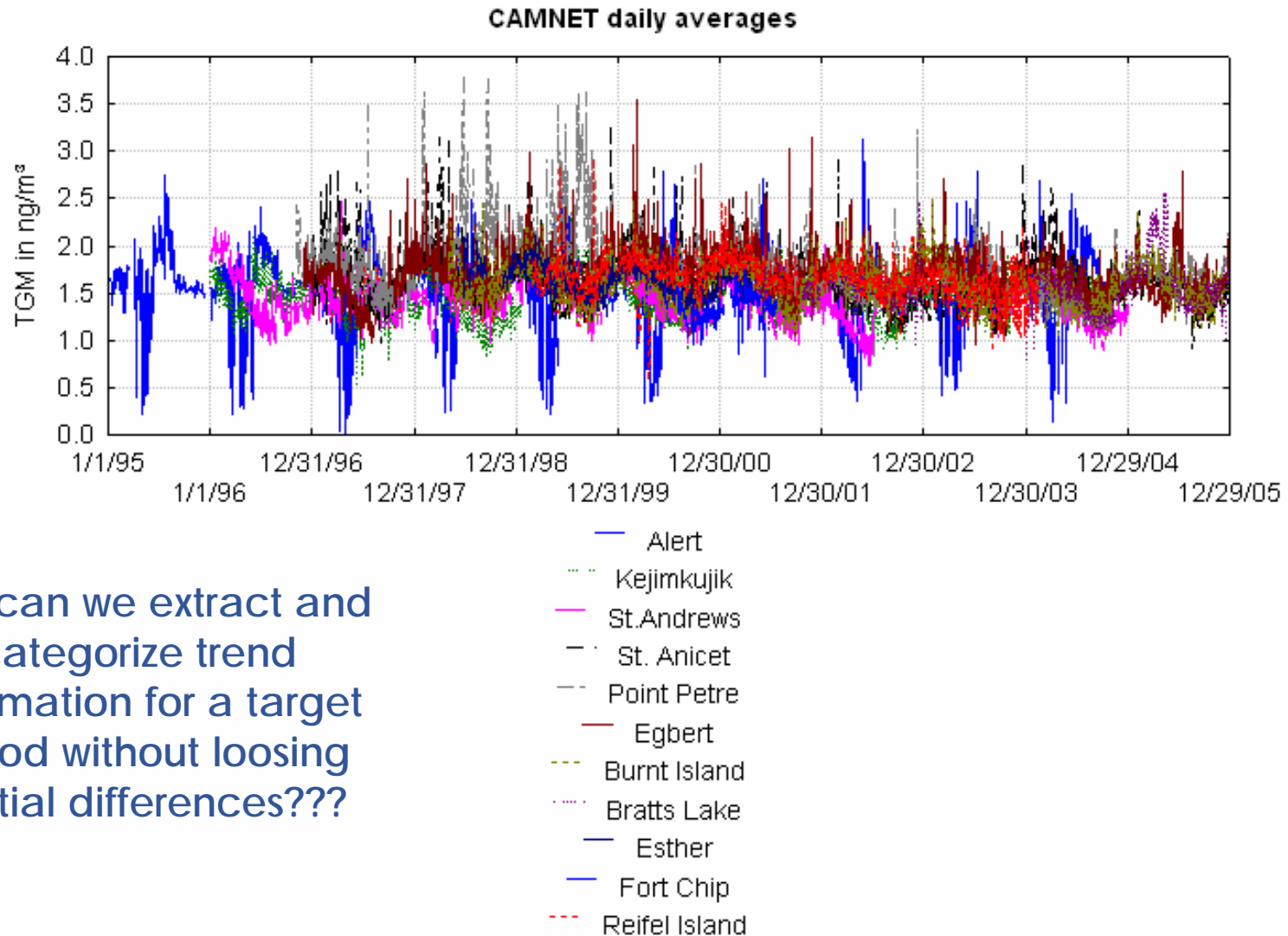
1. Decrease in reported U.S. Hg^0 emissions from all industries by 39.2% between 2000 and 2004
2. Canadian Hg emissions from all industries are at least 10 times lower than U.S. but trends can not be quantified with same consistency and precision



Questions:

1. How do we get equivalent information on the atmospheric concentrations of Hg^0 from CAMNet data for the same time period (target period)?
2. What are the spatial differences?

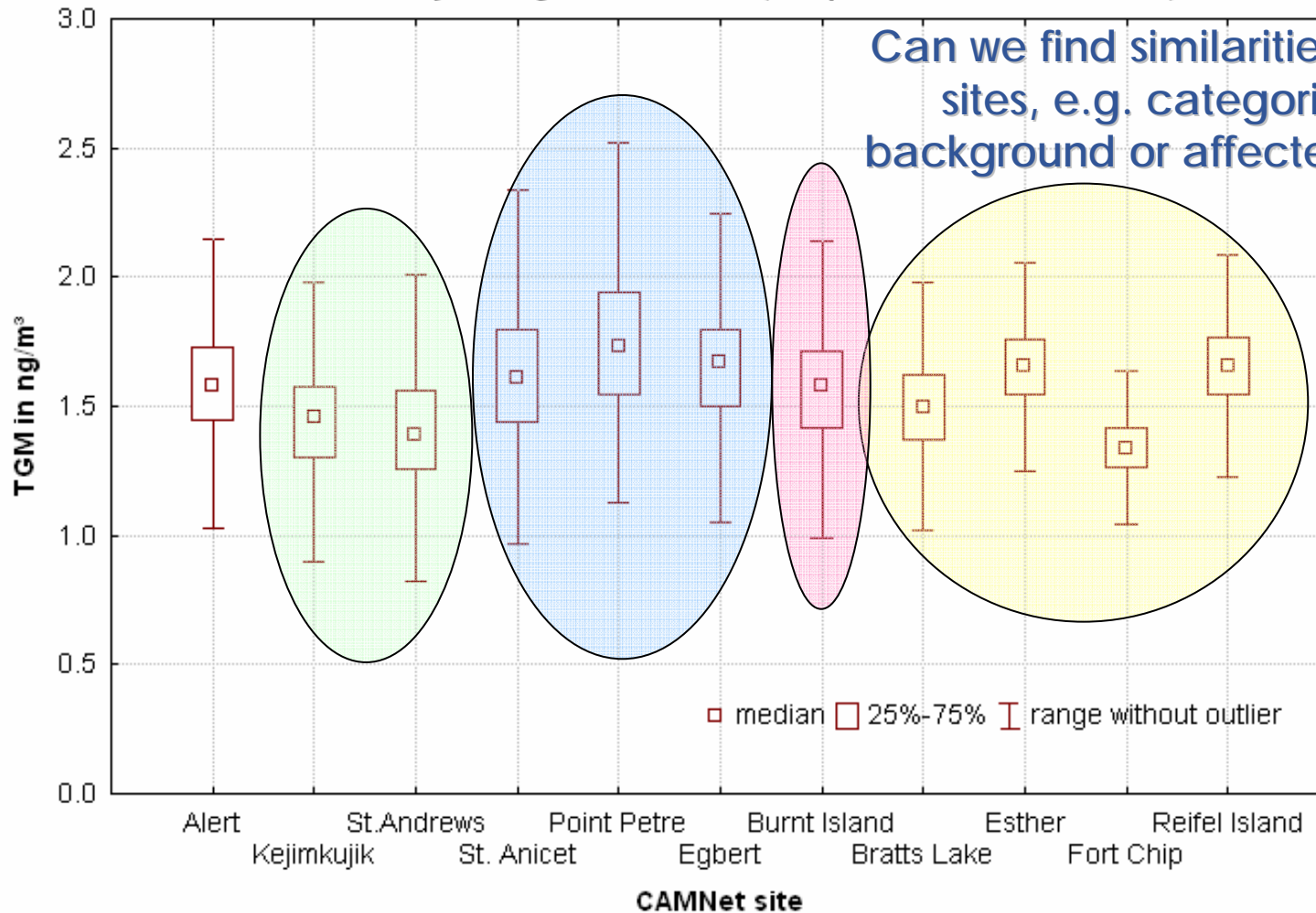
CAMNet dataset (daily averages)



How can we extract and categorize trend information for a target period without losing spatial differences???

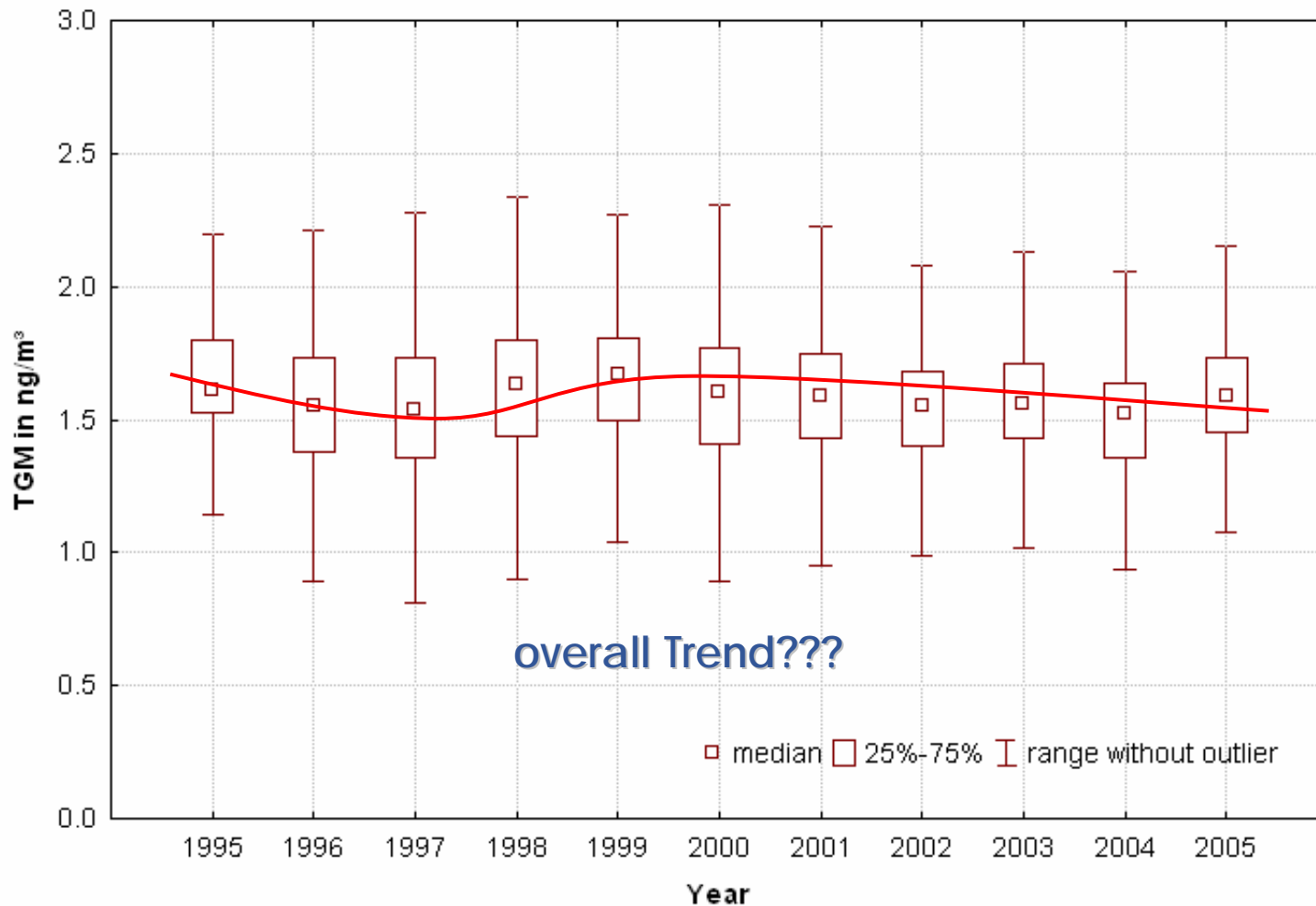
CAMNet – spatial distribution

Total gaseous mercury concentrations at selected CAMNet sites - Box and Whisker plot calculated from daily averages of each site (complete datasets 1995-2005)



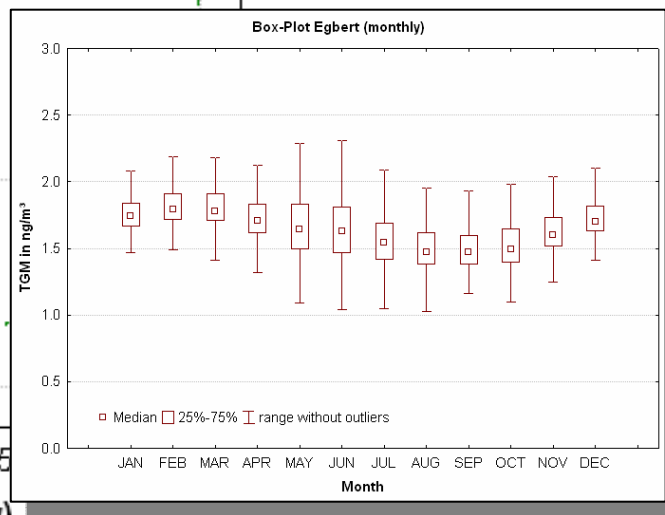
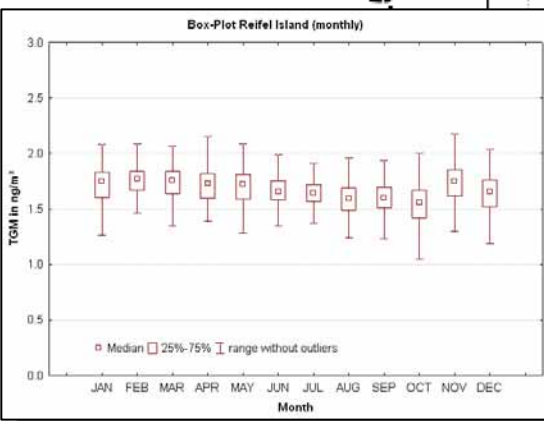
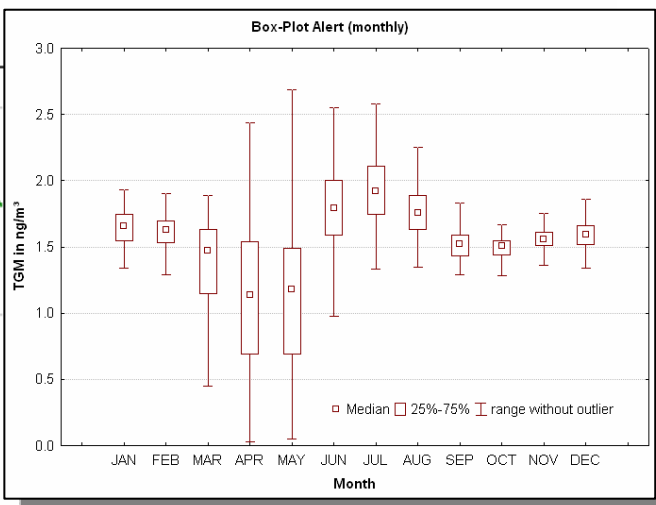
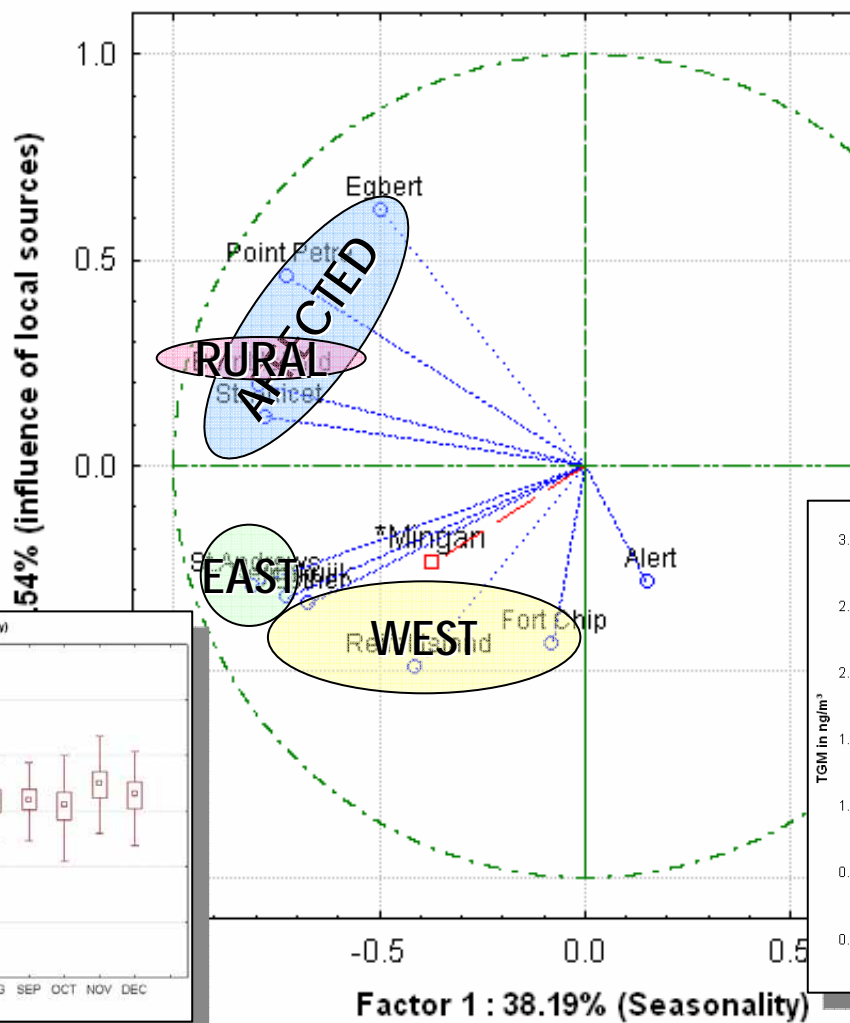
CAMNet – temporal distribution

Total gaseous mercury concentrations at selected CAMNet sites - Box and Whisker plot calculated from daily averages of all stations for each year



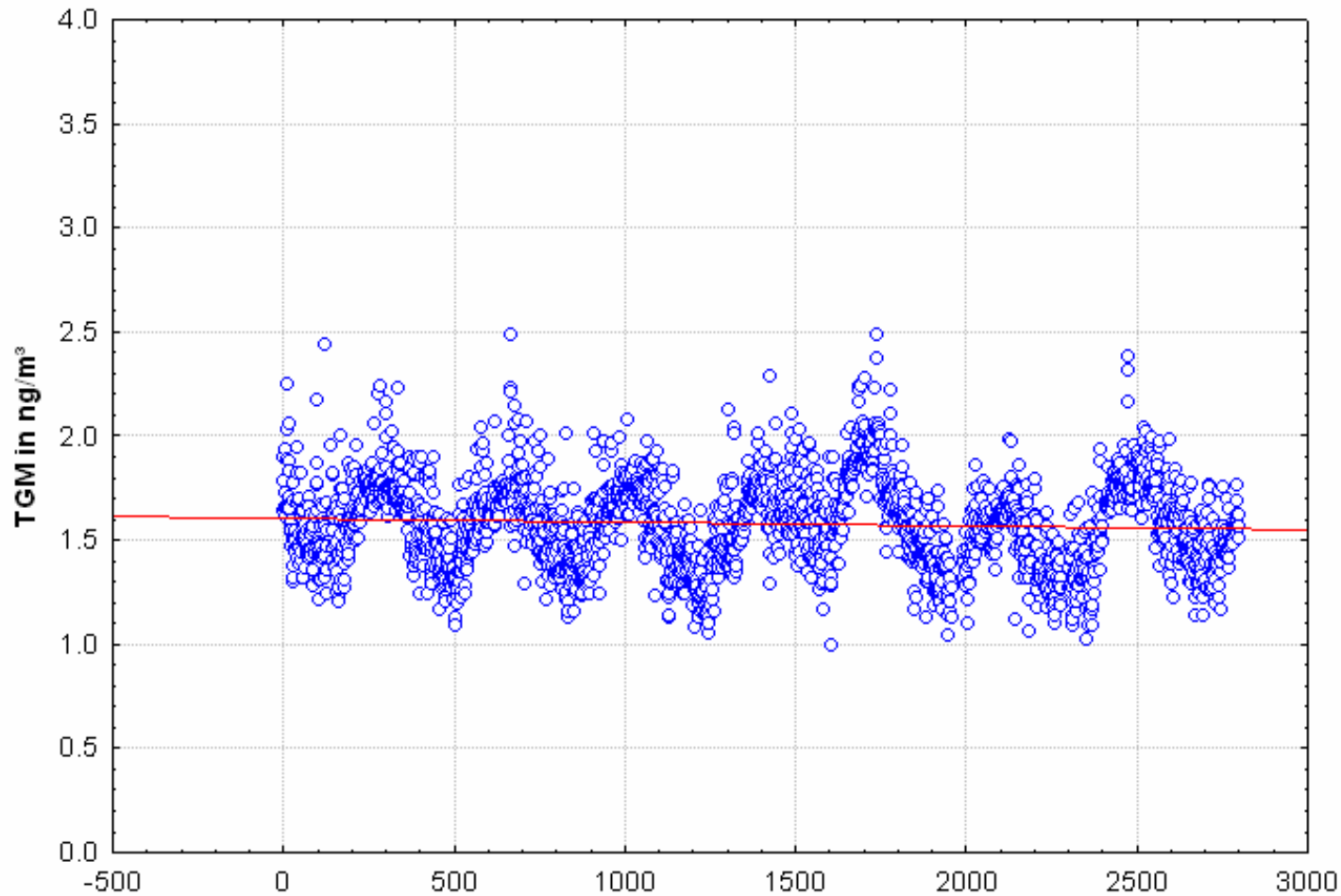
Explaining spatial variance in the TGM data

PCA for daily averages 2000 - factor plot



Linear regressions - slope and significance

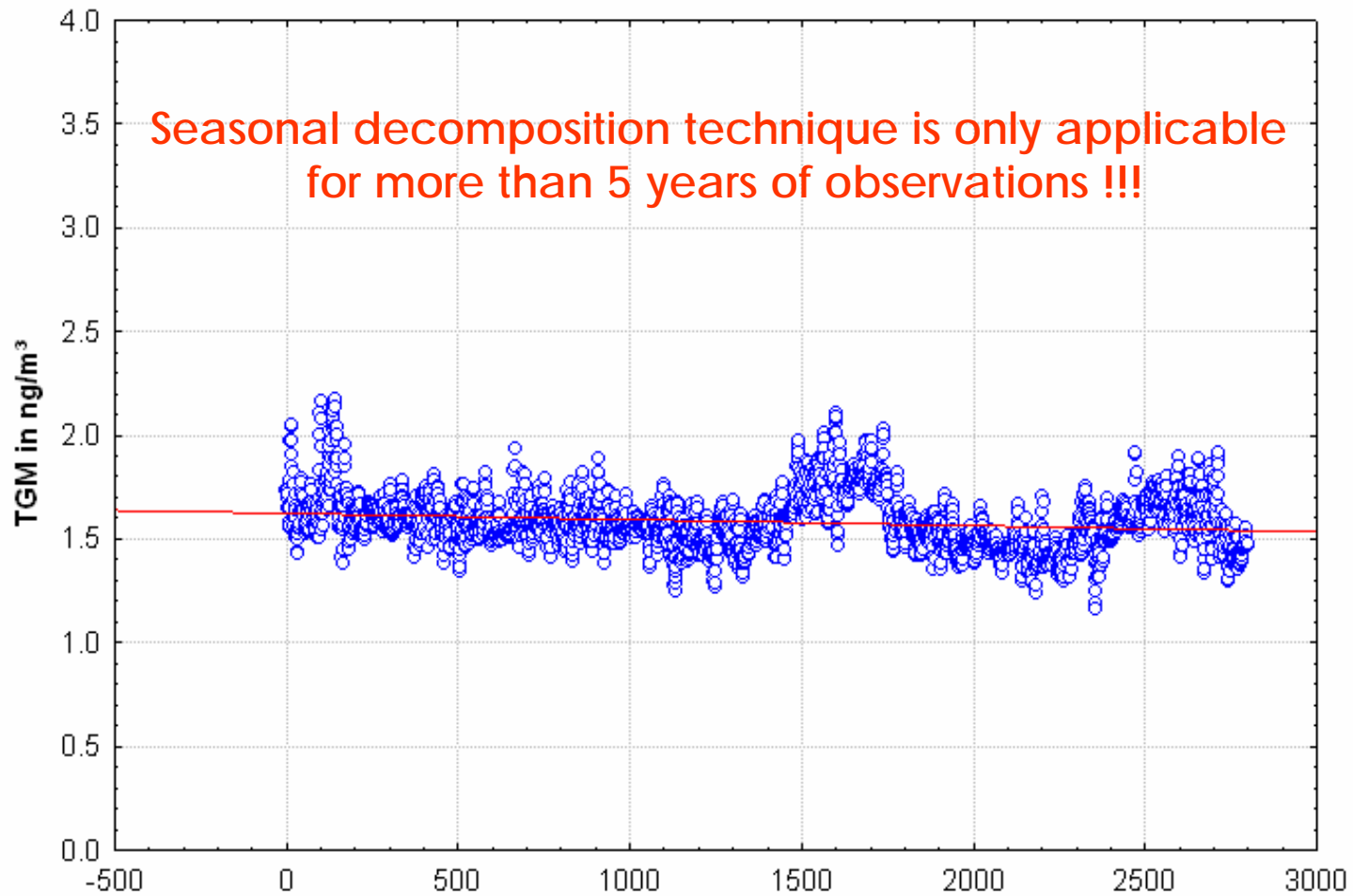
Burnt Island - daily averages and linear regression



Burnt Island: $r^2 = 0.0048$; $r = -0.0694$, $p = 0.0003$; $y = 1.6044 - 1.8058E-5x$

Time series analysis – seasonal decomposition

Burnt Island daily averages after seasonal decomposition



Burnt Island_1: $r^2 = 0.0323$; $r = -0.1796$, $p = 00.0000$; $y = 1.6231 - 2.9597E-5*x$

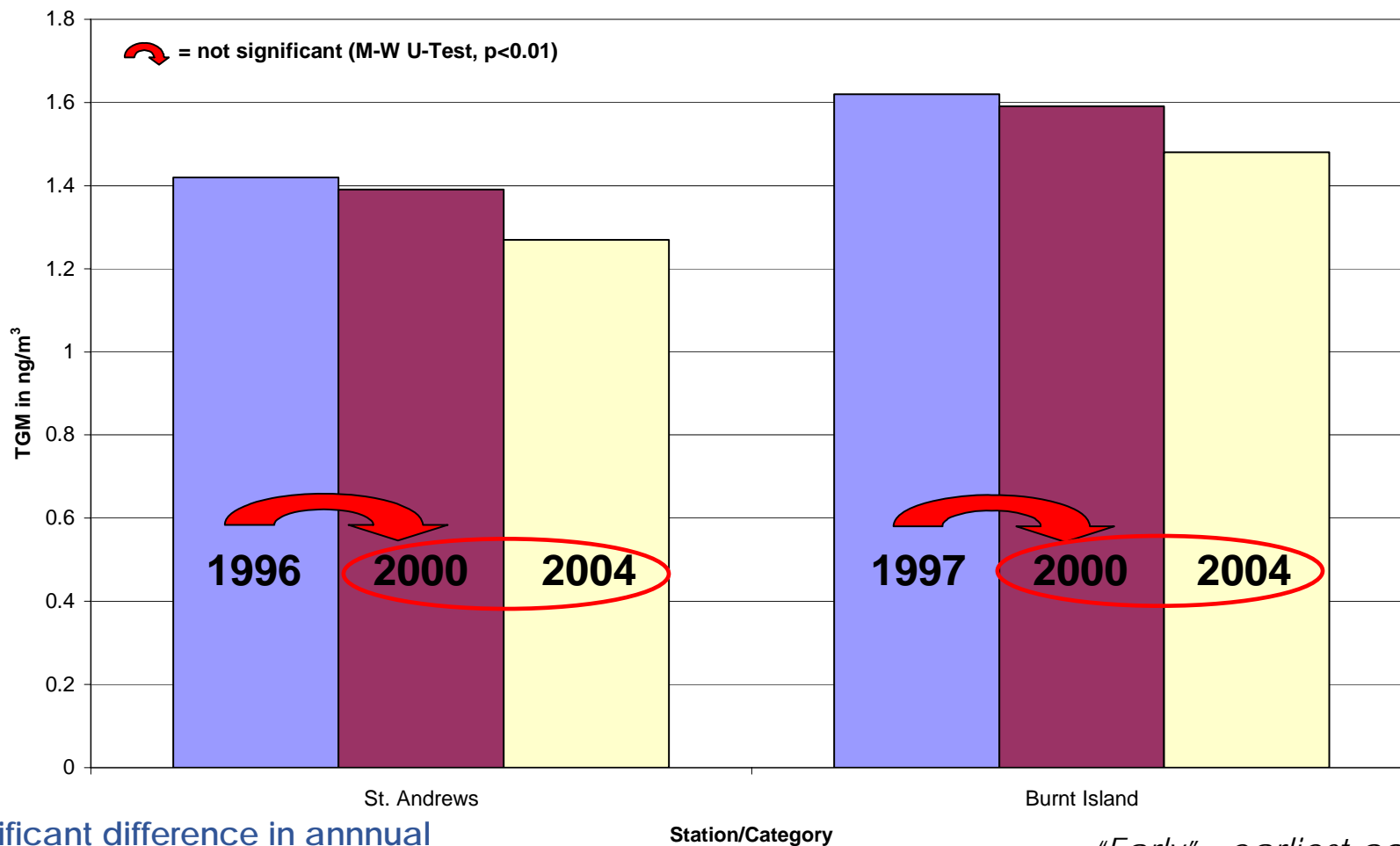
Linear trend after seasonal decomposition

Trend after Seasonal Decomposition									
Station	Start	End	Days	Intercept	Slope	overall Change	yearly Change	overall Change	Significant
	dd/mm/yy	dd/mm/yy		ng/m3	ng/(m3 day)	ng/m3	%	%	p<0.01
Alert	1/1/1995	31/12/2005	4009	1.577	-0.0000136	-0.05	-0.71	-3.46	yes
Kejimkujik	1/1/1996	31/12/2004	3287	1.425	0.0000144	0.05	0.37	3.32	yes
St. Andrews	1/1/1996	31/12/2004	3288	1.486	-0.0000333	-0.11	-0.82	-7.37	yes
St. Anicet	1/1/1997	31/12/2005	3286	1.75	-0.0000698	-0.23	-1.46	-13.11	yes
Point Petre	5/11/1996	31/12/2005	3340	2.015	-0.0001	-0.33	-1.81	-16.58	yes
Egbert	30/11/1996	31/12/2005	3318	1.689	-0.0000111	-0.04	-0.24	-2.18	yes
Burnt Island	1/5/1998	31/12/2005	2800	1.623	-0.0000296	-0.08	-0.67	-5.11	yes
Bratt's Lake	2/5/2001	31/12/2005	1702	not possible (less than 5 years of observations)					
Esther	26/06/1998	22/4/2001	1032	not possible (less than 5 years of observations)					
Fort Chipewyan	17/06/2000	19/07/2001	398	not possible (less than 5 years of observations)					
Reifel Island	3/3/1999	11/2/2004	1807	not possible (less than 5 years of observations)					
Category									
WEST	26/06/1998	31/12/2005	2745	1.712	-0.0000755	-0.21	-1.61	-12.11	yes
(Median RFL,EST,FOH,BRL)									
EAST	1/1/1996	31/12/2004	3288	1.465	-0.0000195	-0.06	-0.49	-4.38	yes
(Median KEJ,STA)									
AFFECTED	5/11/1996	31/12/2005	3343	1.77	-0.000055	-0.18	-1.13	-10.39	yes
(Median WBZ,PPT,EGB)									
RURAL	1/5/1998	31/12/2005	2800	1.623	-0.0000296	-0.08	-0.67	-5.11	yes
(BNT)									
ALL	1/1/1995	31/12/2005	4009	1.613	-0.0000151	-0.06	-0.34	-3.75	yes
(Median All)									

**BUT is the overall trend comparable within CAMNet
AND is the trend representative for the target period (2000 – 2004) ???**

Which time period is dominating the trend ?

Mann-Witney U-test - a robust non-parametric test as an alternative to the t-test

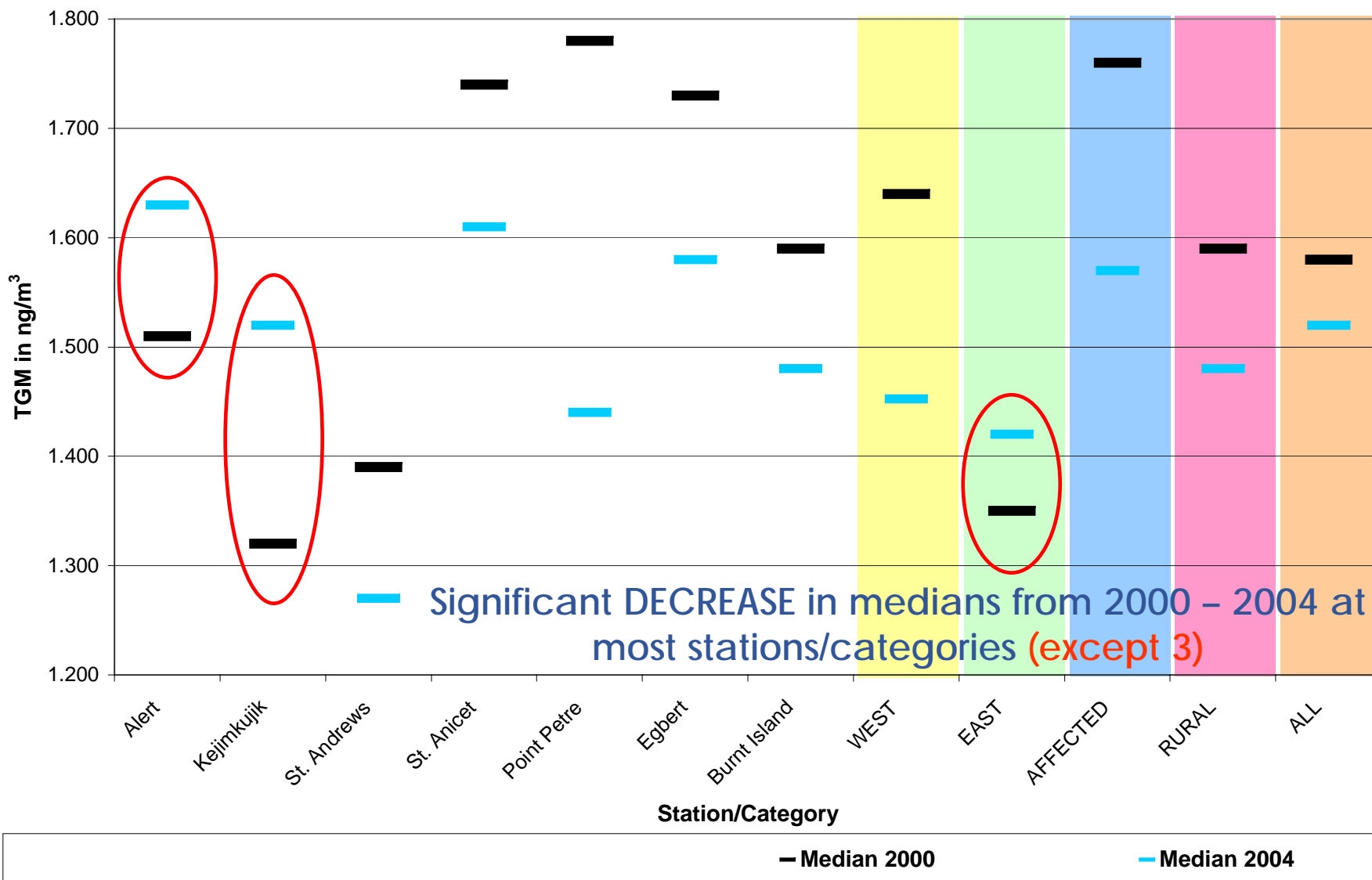


→ Significant difference in annual median for all stations/categories for 2000 - 2004

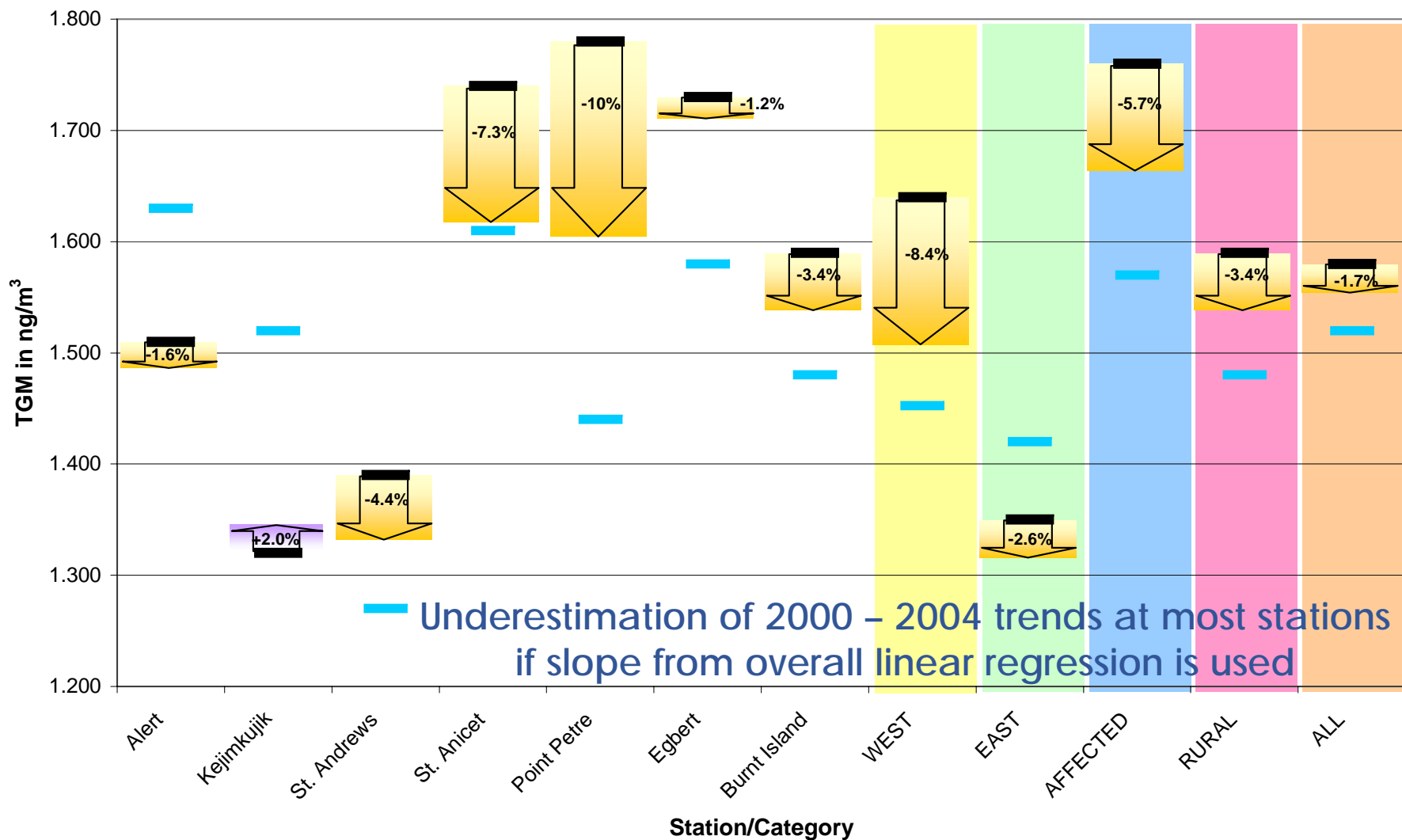
■ Median "EARLY" ■ Median 2000 □ Median 2004

"Early" = earliest complete year of data

Trend 2000 to 2004 for selected CAMNet stations/categories

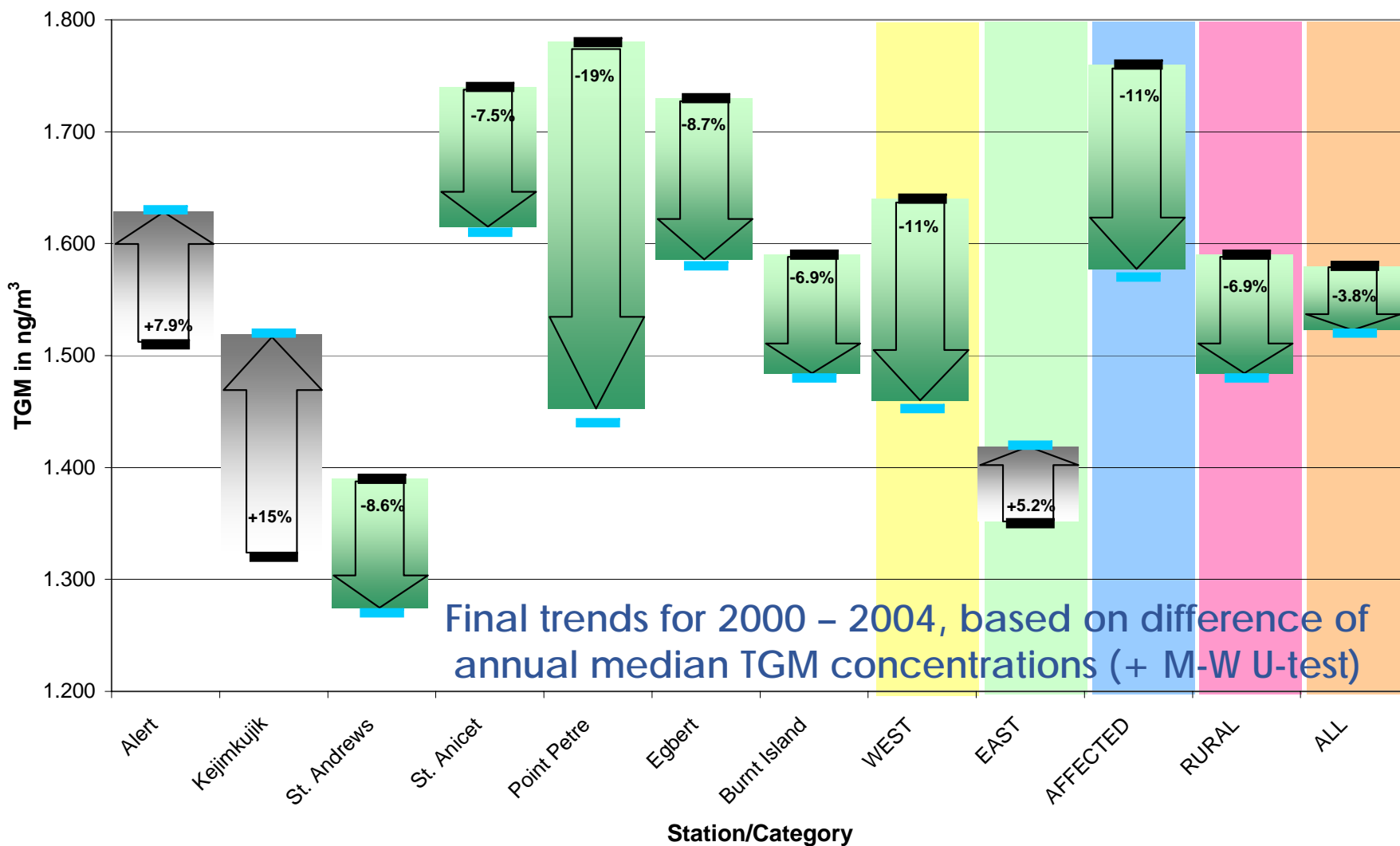


Trend 2000 to 2004 for selected CAMNet stations/categories



▾ abs. trend from linear regression (-)
 ▴ abs. trend from linear regression (+)
 — Median 2000
 — Median 2004

Trend 2000 to 2004 for selected CAMNet stations/categories



diff. Median (-)

diff. Median (+)

Median 2000

Median 2004

Conclusions I

- Comparability, accuracy and spatial distribution of CAMNet TGM data are outstanding
- U.S. emission data are consistent and comparable for 2000-2004
→ decrease in reported U.S. Hg⁰ emissions from all industries of -39.2%
- Canadian Hg⁰ emissions from all industries are at least a factor of 10 lower but trends can not be quantified with same consistency and precision

Conclusions II

- CAMNet stations can be categorized by 4 major categories (supported by multivariate techniques)
- Time series analysis helps to reveal linear trends for long-term datasets
- Nearly all stations and categories show significant decrease of TGM within the time period 1995 to 2005
- absolute trend for target time period (2000 – 2004) is underestimated if overall linear trend (slope) is applied
- Better to use difference in annual median TGM conc. for target period
→ mostly decreasing trend 2000 – 2004 ranging from -3.8% up to -19%
- reasons for spatial differences should be further investigated

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Acknowledgments

Data Analysis

- Julie Narayan
- Bill Sukloff

Scholarship

- German Academic
Exchange Service
- Environment Canada
- GKSS Research Centre

Thank you for your attention



Backup slides

Why Mercury?

- Mercury is a potent neurotoxin - that can cross the blood/brain barrier
- Escapes emission controls
- Susceptible to long range transport
- Biologically methylated
- Highly bioconcentrated

Sources of mercury to the atmosphere?

Natural

- Forest fires
- evaporation from soil
- vegetation and water surfaces
- volcanoes

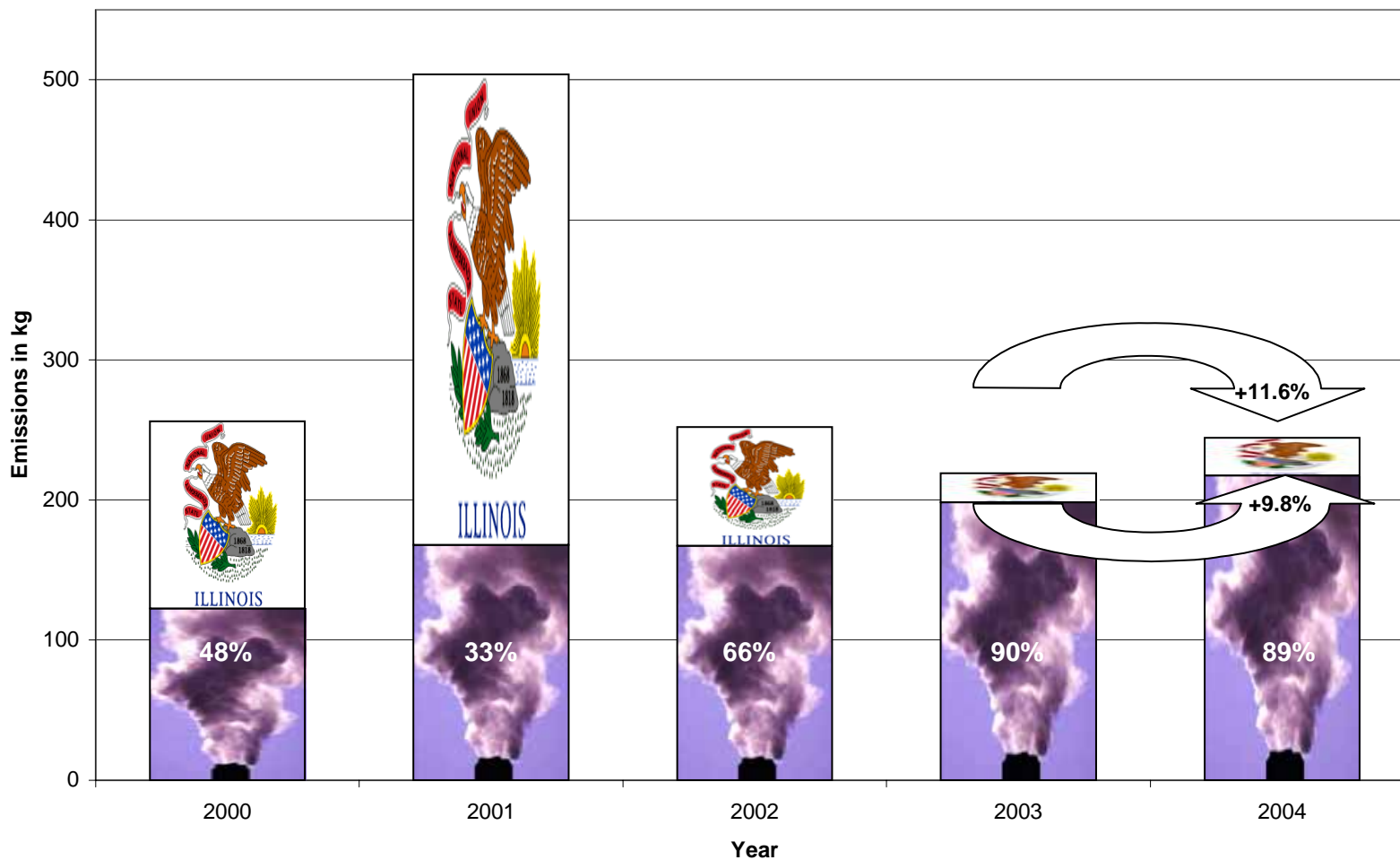
Resulting from human activities

- Mining
- burning of fossil fuels
- production of metals and cement
- landfills
- flooding
- incineration plants.
- fluorescent light bulbs
- thermometers
- batteries
- dental fillings
- electrical switches.

These human activities release considerable amount of Hg that would otherwise not be available for exposure.

U.S. emissions of elemental mercury (Hg^0)

Total atmospheric Hg^0 emissions in Illinois



Source: Toxics Release Inventory of US EPA

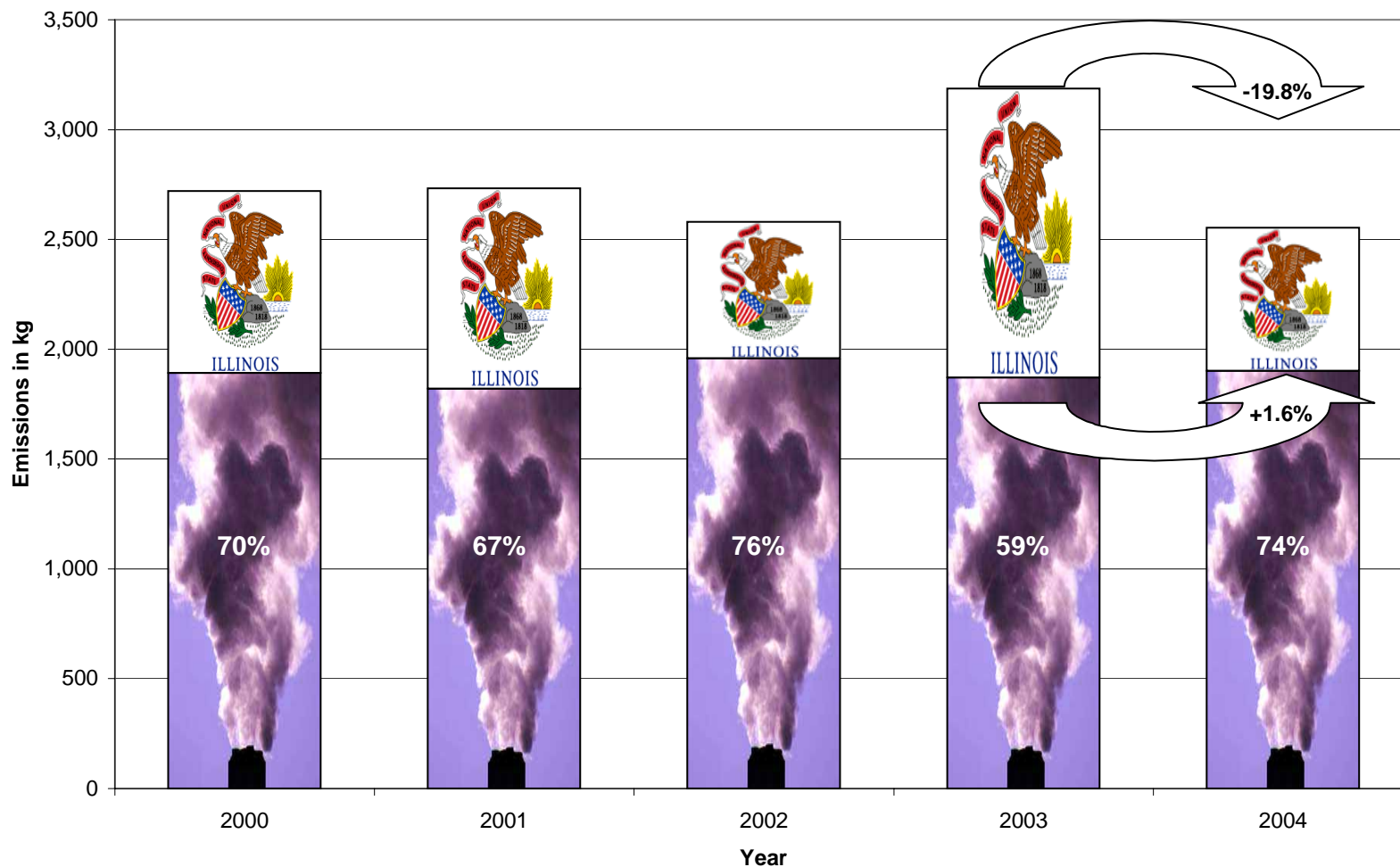
electric utilities all industries

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Latest newspaper article
U.S. and Canadian emissions

The true story about U.S. Hg emissions

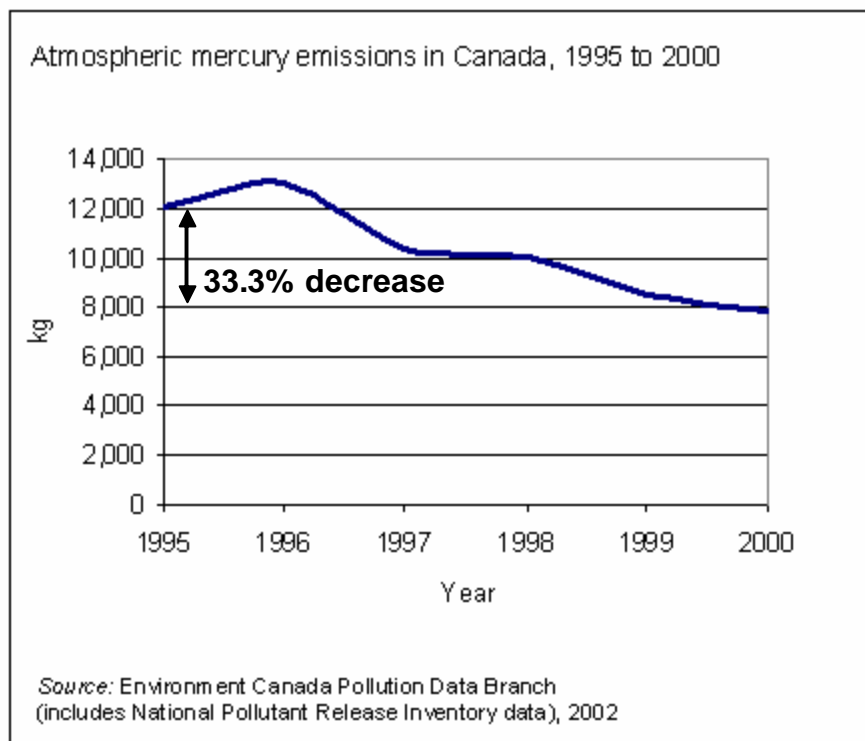
Total atmospheric mercury (Hg^0 + compounds) emissions in Illinois



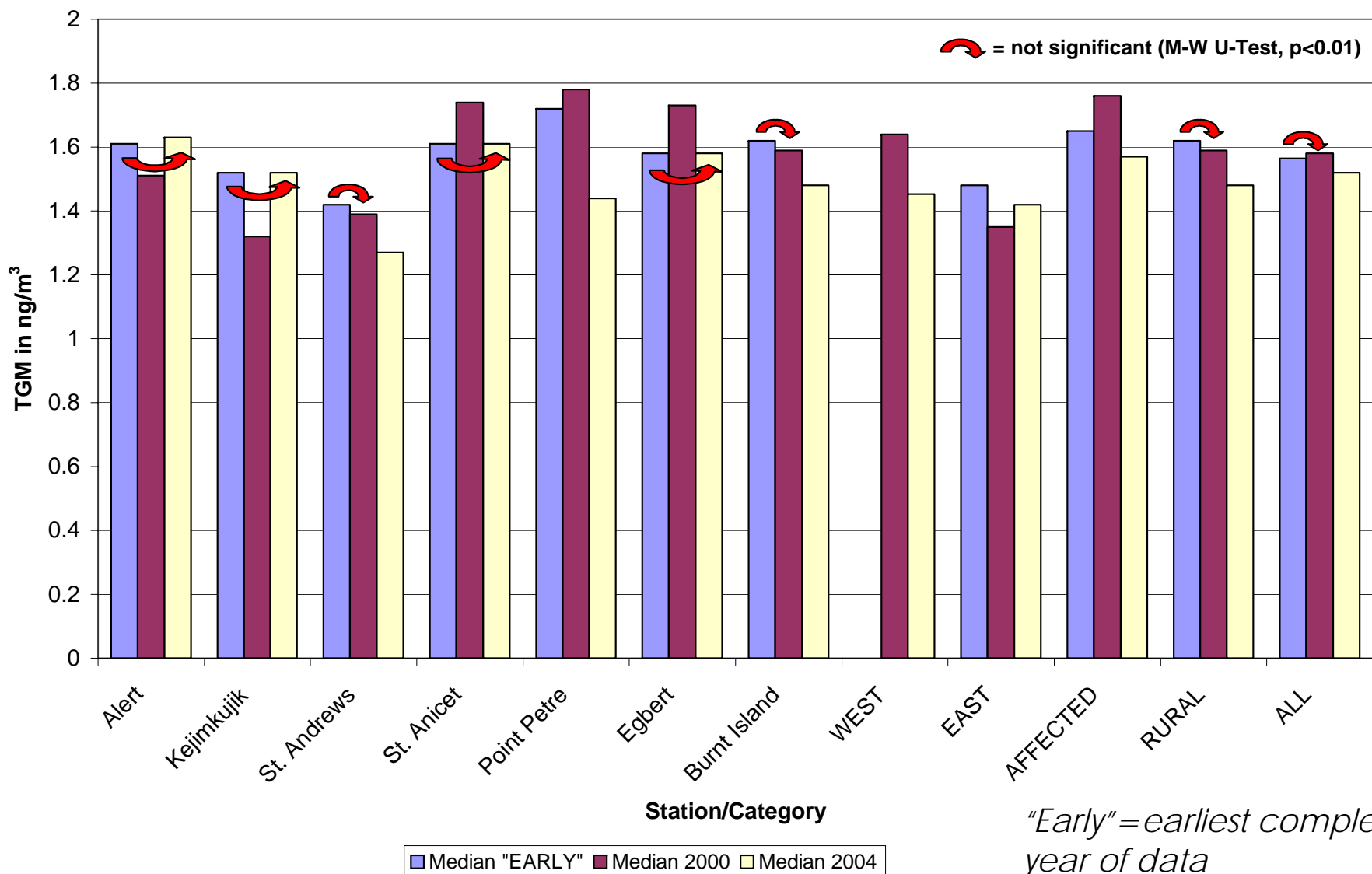
Source: Toxics Release Inventory of US EPA

electric utilities all industries

Canadian atmospheric Hg emissions



Median TGM concentrations over time at selected CAMNet stations/categories



"Early" = earliest complete year of data