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Natural surface emissions dominate anthropogenic emissions contributions to total gaseous mercury at Canadian rural sites

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Supplement References

S1 PMF sensitivity runs

The model fit results for the final PMF solution are shown in Fig. S1. The source apportionment results for each of the three sites are stable and reliable. The coefficient of determination (r^2) between the PMF modelled and observed TGM concentrations were between 0.43 and 0.75, indicating a good model fit for the variable selection and model parameters chosen in the final run. There is also strong overlap between the modelled and observed time series for 24 h mean TGM, indicating the model adequately captured the daily variability. The most important consideration in deriving the final PMF solution is the justification of the factors and assignment to Hg sources. The sensitivity tests using 5 and 7 factors resulted in factors that were difficult to interpret (Tables S3, S4, and S5). A 5-factor solution results in tracers loading on multiple factors. This leads to a scenario where multiple factors can be assigned to the same source. An ideal PMF solution is one where each factor is assigned to a unique source. A 7-factor solution contains all the results of the 6-factor solution; however, it includes an additional factor that cannot be definitively assigned to a source.

S2 PMF residuals analysis

PMF residuals were analyzed for the final 6-factor solution. The scaled residuals were within the recommended limit of three standard deviations (Fig. S10) and followed a normal distribution (Hopke et al., 2023). This confirms the modeled factors adequately explain the observed TGM data in addition to the good R^2 between modeled and observed TGM concentrations (Fig. S1). The model could not reproduce a few elevated TGM concentrations at KEJ. There was a total of 7 data points (0.22%) out of 3118 in the entire 2005-2016 time series where the scaled residuals were beyond three standard deviations.

S3 Tekran model B and X measurement intercomparison

Hourly TGM differences between Tekran 2537X and 2537B have been assessed and was published along with the quality controlled TGM dataset (ECCC, 2024). The model X and B analyzers at the EGB site operated side by side during Feb-Aug 2017. Model X reported slightly higher TGM than model B with a mean hourly difference of 0.06 ng m^{-3} (3.9%). Monthly mean hourly TGM differences were in the range of 0.02-0.1 ng m^{-3} (1.4-6.3%). Model X and model B analyzers were also operated side by side at the same site during Mar-Jul 2018. Model X reported higher TGM than model B with a mean hourly difference of 0.08 ng m^{-3} (6.4%). Monthly mean hourly TGM differences were in the range of 0.07-0.09 ng m^{-3} (5.4-7.4%). The difference plots are shown in Fig. S11. Considering the differences were not significant and the concentrations showed similar trends, the valid hourly concentrations from the model X and B analyzers were averaged for the PMF dataset and long-term trends analysis.

TGM was measured concurrently at KEJ and KEB from February to June in 2017. Note that KEJ and KEB sites are not co-located. KEJ was operating a model B analyzer; the site was relocated 3 km south of the original site in Feb 2017 (KEB) and the model X analyzer began operating at the new site. TGM was higher at KEB than at KEJ with a mean hourly difference of 0.26 ng m^{-3} (18.8%).

Monthly mean hourly TGM differences were 0.20-0.29 ng m^{-3} (16.6-21.5%). These differences may be due to the different analyzer models and/or relocation of the monitoring site; the exact cause is inconclusive. Given the large TGM differences between KEB and KEJ, our decision was that the data from the two sites should not be combined into a single time series. Therefore, the 2017-2018 data at the new site were not used for PMF modeling and long-term trends analysis.

Table S1: TGM and ancillary data

Measurement	Unit	Data frequency	Network
TGM	ng m^{-3}	hourly	ECCC CAPMoN[1]
SO_2, inorganic ions (Na^+, K^+, Cl^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NH_4^+)	µg m^{-3}	24-h	ECCC CAPMoN[2]
CO	ppm	hourly	ECCC National Air Pollution Surveillance (NAPS) program[3], ECCC Canadian Greenhouse Gas Measurement program[4], USEPA Air Quality System (AQS)[5]
Total carbon	µg m^{-3}	1-in-3 day	Interagency Monitoring of Protected Visual Environments (IMPROVE)[6]
Air temperature	°C	hourly	ECCC Historical Climate Data[7]

[1]Environment and Climate Change Canada (ECCC): Total Gaseous Mercury (TGM), Government of Canada Open Government Portal [dataset], https://doi.org/10.18164/e1df5764-1eec-4a9f-9c03-f515b396b717, 2025.

[2]Environment and Climate Change Canada (ECCC): Major Ions and Acidifying Gases, Government of Canada Open Government Portal [dataset], https://doi.org/10.18164/e73c7f47-df9c-4877-923c-20e09db28176, 2025.

[3]Environment and Climate Change Canada (ECCC): National Air Pollution Surveillance (NAPS) Program, Government of Canada Open Government Portal [dataset], https://data-donnees.az.ec.gc.ca/data/air/monitor/national-air-pollution-surveillance-naps-program/, 2025.

[4]Worthy, D.: Atmospheric CO at Egbert, Environment and Climate Change Canada (ECCC) Canadian Greenhouse Gas Measurement program, World Data Centre for Greenhouse Gases [dataset], https://gaw.kishou.go.jp/, 2025.

[5]United States Environmental Protection Agency (USEPA): Hourly CO, Air Quality System [dataset], https://www.epa.gov/aqs, 2025.

[6]Interagency Monitoring of Protected Visual Environments (IMPROVE): Total Carbon, Federal Land Manager Environmental Database [dataset], https://vista.cira.colostate.edu/Improve/improve-data/, 2025.

[7]Environment and Climate Change Canada (ECCC): Historical Climate Data, Government of Canada [dataset], https://climate.weather.gc.ca/, 2025.

Table S2: Descriptive statistics of 24-h average TGM concentrations (ng m^{-3}) at Egbert (EGB), Kejimkujik (KEJ) and Saturna (SAT). P denotes percentile.

Site	Year	N	Mean	Median	StdDev	P5	P25	P75	P95	Min	Max
EGB	2005	344	1.60	1.57	0.21	1.33	1.45	1.66	2.05	1.19	2.53
EGB	2006	335	1.64	1.63	0.18	1.36	1.52	1.75	1.95	1.25	2.30
EGB	2007	301	1.54	1.55	0.20	1.19	1.41	1.66	1.85	1.08	2.36
EGB	2008	345	1.46	1.45	0.14	1.23	1.36	1.56	1.68	1.10	1.85
EGB	2009	358	1.41	1.43	0.15	1.14	1.30	1.51	1.62	0.92	1.76
EGB	2010	340	1.39	1.39	0.19	1.09	1.25	1.53	1.69	0.97	1.88
EGB	2011	104	1.27	1.25	0.16	1.06	1.17	1.37	1.57	0.97	1.84
EGB	2012	272	1.19	1.16	0.15	1.00	1.11	1.27	1.47	0.92	1.81
EGB	2013	305	1.09	1.06	0.16	0.87	0.97	1.17	1.35	0.80	1.68
EGB	2014	341	1.28	1.31	0.23	0.90	1.06	1.46	1.60	0.84	1.80
EGB	2015	344	1.30	1.32	0.14	1.06	1.20	1.41	1.52	0.96	1.70
EGB	2016	356	1.28	1.28	0.16	1.03	1.17	1.41	1.52	0.82	1.69
EGB	2017	386	1.36	1.37	0.16	1.09	1.23	1.49	1.58	1.00	1.77
EGB	2018	485	1.25	1.25	0.13	1.05	1.17	1.34	1.44	0.85	1.75
KEJ	2005	332	1.73	1.53	0.75	1.12	1.32	1.82	3.19	0.99	6.87
KEJ	2006	342	1.10	1.09	0.21	0.79	0.93	1.28	1.43	0.65	1.62
KEJ	2007	312	1.16	1.15	0.15	0.94	1.05	1.27	1.40	0.71	1.52
KEJ	2008	307	1.32	1.32	0.16	1.06	1.20	1.44	1.58	0.95	1.72
KEJ	2009	341	1.27	1.27	0.17	1.01	1.15	1.40	1.48	0.83	2.38
KEJ	2010	354	1.34	1.36	0.15	1.09	1.23	1.44	1.57	0.84	1.79
KEJ	2011	346	1.37	1.41	0.17	1.05	1.24	1.50	1.57	0.97	1.62
KEJ	2012	349	1.36	1.37	0.16	1.10	1.23	1.50	1.61	0.98	1.67
KEJ	2013	345	1.30	1.33	0.16	1.01	1.19	1.44	1.51	0.79	1.67
KEJ	2014	336	1.30	1.30	0.16	1.02	1.18	1.44	1.53	0.91	1.61
KEJ	2015	350	1.19	1.21	0.16	0.91	1.06	1.33	1.39	0.74	1.53
KEJ	2016	312	1.14	1.12	0.16	0.91	1.01	1.28	1.38	0.82	1.50
KEJ	2017	140	1.17	1.21	0.11	0.92	1.12	1.25	1.28	0.83	1.34
SAT	2009	274	1.36	1.35	0.21	1.06	1.20	1.52	1.73	0.94	2.01
SAT	2010	266	1.50	1.51	0.17	1.24	1.39	1.61	1.75	1.14	2.53
SAT	2011	302	1.35	1.36	0.13	1.15	1.25	1.43	1.55	0.83	1.75
SAT	2012	334	1.22	1.24	0.12	1.01	1.14	1.31	1.40	0.91	1.54
SAT	2013	287	1.33	1.33	0.12	1.13	1.25	1.43	1.51	0.90	1.61
SAT	2014	333	1.26	1.27	0.10	1.10	1.20	1.33	1.41	1.00	1.53
SAT	2015	263	1.16	1.16	0.11	0.99	1.09	1.22	1.31	0.76	1.61
SAT	2016	153	1.37	1.38	0.07	1.23	1.33	1.42	1.49	1.18	1.57
SAT	2018	314	1.38	1.38	0.11	1.19	1.32	1.44	1.54	1.08	1.97

Table S3: Factor profiles (species percentages) for SAT using 5 to 7 factors. In the 5 factor sensitivity run, two factors can be assigned to secondary sulfate; aged sea-salt factor was not extracted.

5 factor sensitivity run	Fresh sea-salt	GEM re-emissions/biomass burning	Sulfate	Local combustion or sulfate (no Hg)	Hg pool
SO4	4.26	9.55	70.93	15.26	0.00
NH4	0.00	0.00	49.48	40.33	10.18
Cl	93.88	0.00	0.00	1.30	4.81
Ca	37.17	31.21	12.45	14.56	4.61
Mg	79.07	11.38	9.55	0.00	0.00
Na	82.41	6.13	9.93	0.68	0.85
K	41.75	15.07	16.26	12.04	14.88
SO2	5.65	3.49	0.00	90.86	0.00
TGM	7.86	31.92	10.99	0.00	49.23
Temperature	0.00	100.00	0.00	0.00	0.00
CO	3.59	16.26	9.59	13.78	56.78
Total carbon	0.00	51.35	18.35	8.75	21.55

6 factor final run	GEM re-emissions/biomass burning	Fresh sea-salt	Sulfate (no Hg)	Local combustion	Hg pool	Aged sea-salt
SO4	0.00	0.00	31.30	0.00	0.00	68.70
NH4	0.00	0.00	73.09	5.00	8.97	12.94
Cl	0.00	95.72	3.00	1.28	0.00	0.00
Ca	24.35	32.49	4.46	14.43	5.31	18.96
Mg	4.42	74.59	0.00	0.00	0.00	20.98
Na	0.00	77.11	0.00	1.61	0.59	20.70
K	13.81	40.26	12.45	6.56	13.80	13.12
SO2	6.01	0.00	0.00	87.69	0.00	6.30
TGM	29.64	6.33	0.00	3.32	50.35	10.36
Temperature	100.00	0.00	0.00	0.00	0.00	0.00
CO	17.87	3.63	11.66	11.44	55.40	0.00
Total carbon	53.16	0.00	18.97	0.00	20.57	7.30

7 factor sensitivity run	Local combustion (no Hg)	Aged sea-salt	GEM re-emissions/biomass burning	?	Hg pool	Sulfate (no Hg)	Fresh sea-salt
SO4	0.00	59.26	6.89	0.00	0.00	33.85	0.00
NH4	4.68	0.00	0.00	11.11	8.66	74.60	0.96
Cl	1.72	0.00	0.00	0.00	1.41	2.85	94.02
Ca	12.78	17.11	11.71	25.18	1.43	1.71	30.08
Mg	0.00	20.11	3.83	3.62	0.00	0.00	72.44
Na	1.51	19.65	0.00	3.05	0.86	0.00	74.92

K	5.48	11.29	2.99	20.86	12.71	9.68	36.99
SO2	87.00	5.52	6.77	0.70	0.00	0.00	0.00
TGM	0.00	11.66	31.83	0.00	53.79	0.00	2.73
Temperature	0.00	0.00	100.00	0.00	0.00	0.00	0.00
CO	8.16	0.00	12.86	11.94	57.44	9.60	0.00
Total carbon	0.05	0.00	0.00	90.87	0.00	9.09	0.00

Table S4: Factor profiles (species percentages) for EGB using 5 to 7 factors. In the 5 factor sensitivity run, two factors can be assigned to local combustion, secondary sulfate, and crustal/soil emissions.

5 factor sensitivity run	Road salt	Hg pool or sulfate	Local combustion or sulfate (no Hg)	Crustal/soil or local combustion	GEM re-emissions/biomass burning or crustal/soil
SO4	0.11	19.48	70.51	3.72	6.19
NH4	0.00	19.07	76.11	0.00	4.83
Cl	85.78	9.84	0.67	3.71	0.00
Ca	3.63	0.00	0.05	79.65	16.68
Mg	4.76	1.89	0.00	75.67	17.68
Na	81.13	11.12	1.78	5.23	0.75
K	4.27	17.60	29.76	9.96	38.41
SO2	0.00	0.00	71.59	28.41	0.00
TGM	0.86	80.69	0.00	16.75	1.70
Temperature	0.00	0.00	0.00	0.00	100.00
CO	1.50	79.52	1.61	17.37	0.00
Total carbon	2.09	46.43	9.30	4.45	37.74

6 factor final run	Road salt	GEM re-emissions/biomass burning	Sulfate (no Hg)	Hg pool	Local combustion	Crustal/soil
SO4	0.76	0.97	78.12	9.01	5.72	5.42
NH4	1.02	0.01	84.36	9.10	4.38	1.13
Cl	88.15	4.59	0.03	4.55	0.44	2.23
Ca	2.25	0.00	2.25	3.44	0.00	92.05
Mg	3.16	3.31	0.54	4.82	1.82	86.36
Na	83.20	5.22	0.93	5.69	1.38	3.57
K	4.39	32.62	36.41	9.48	3.49	13.61
SO2	0.73	5.42	0.07	3.51	88.38	1.91
TGM	2.42	23.89	0.00	67.19	1.59	4.91
Temperature	0.00	100.00	0.00	0.00	0.00	0.00
CO	3.06	20.89	2.82	65.83	1.24	6.16
Total carbon	3.08	46.74	14.03	36.15	0.00	0.00

7 factor sensitivity run	Sulfate (no Hg)	?	Crustal/soil	GEM re-emissions/biomass burning	Road salt (no Hg)	Local combustion	Hg pool
SO4	75.13	0.00	9.72	0.00	1.16	3.80	10.19
NH4	71.73	24.21	0.00	0.00	0.00	4.06	0.00
Cl	0.00	28.88	0.00	0.00	71.12	0.00	0.00
Ca	0.58	5.04	91.63	2.75	0.00	0.00	0.00
Mg	0.00	3.35	86.06	5.00	1.24	1.67	2.68
Na	2.14	0.00	6.06	0.42	77.45	0.42	13.51
K	21.15	28.66	9.92	33.98	1.10	4.72	0.47
SO2	0.00	3.15	2.37	2.69	0.08	85.52	6.20
TGM	0.00	13.63	5.15	6.02	0.00	0.56	74.64
Temperature	0.00	0.00	0.00	100.00	0.00	0.00	0.00
CO	1.86	16.00	5.99	4.20	0.36	0.16	71.45
Total carbon	10.93	11.46	0.00	38.11	1.28	0.00	38.22

Table S5: Factor profiles (species percentages) for KEJ using 5 to 7 factors. In the 5 factor sensitivity run, aged sea-salt factor was not extracted.

5 factor sensitivity run	Fresh sea-salt	Sulfate (no Hg)	GEM re-emissions/biomass burning	Hg pool	Local combustion (no Hg)
SO4	1.52	86.17	8.79	0.92	2.61
NH4	0.00	88.17	11.83	0.00	0.00
Cl	99.74	0.00	0.26	0.00	0.00
Ca	36.94	35.48	14.92	8.54	4.12
Mg	79.76	13.05	3.92	2.86	0.41
Na	85.92	8.46	0.00	5.27	0.36
K	36.10	31.64	25.57	4.79	1.89
SO2	1.34	0.00	4.97	3.14	90.55
TGM	6.64	0.00	27.35	66.02	0.00
Temperature	0.00	0.00	100.00	0.00	0.00
CO	4.68	3.95	28.17	62.26	0.95
Total carbon	0.00	5.48	46.72	42.42	5.39

6 factor final run	Fresh sea-salt	Local combustion (no Hg)	Sulfate (no Hg)	GEM re-emissions/biomass burning (no Hg)	Hg pool	Aged sea-salt
SO4	0.00	0.84	74.61	0.00	0.99	23.56
NH4	3.02	0.17	93.63	3.18	0.00	0.00
Cl	94.46	0.27	0.75	0.00	4.51	0.00
Ca	29.46	3.38	22.61	9.70	8.85	26.00

Mg	62.27	0.00	2.06	5.11	0.00	30.56
Na	67.06	0.34	0.00	1.65	1.43	29.52
K	31.00	1.47	25.45	21.20	5.82	15.07
SO2	0.00	90.34	0.00	0.14	5.70	3.82
TGM	7.90	0.00	0.00	0.00	81.52	10.58
Temperature	0.00	0.00	0.00	100.00	0.00	0.00
CO	6.27	1.01	4.05	1.79	77.11	9.77
Total carbon	2.74	5.79	11.30	27.31	52.87	0.00

7 factor sensitivity run	Aged sea-salt	?	GEM re-emissions/biomass burning (no Hg)	Sulfate (no Hg)	Fresh sea-salt	Hg pool	Local combustion (no Hg)
SO4	25.60	0.00	0.00	71.89	0.00	0.00	2.51
NH4	0.00	16.96	0.00	83.04	0.00	0.00	0.00
Cl	0.00	0.34	0.00	0.63	91.83	7.20	0.00
Ca	0.00	94.62	0.00	0.00	5.38	0.00	0.00
Mg	25.99	11.42	4.09	0.62	57.88	0.00	0.00
Na	28.77	0.00	3.00	0.00	65.48	1.55	1.20
K	11.05	19.39	17.91	19.17	25.25	6.35	0.88
SO2	2.07	0.30	1.80	0.54	0.47	6.24	88.58
TGM	10.09	0.01	0.00	0.00	3.40	86.51	0.00
Temperature	0.00	0.00	100.00	0.00	0.00	0.00	0.00
CO	9.20	0.00	1.81	3.86	2.12	81.95	1.06
Total carbon	0.00	0.00	27.08	10.62	0.00	56.61	5.69

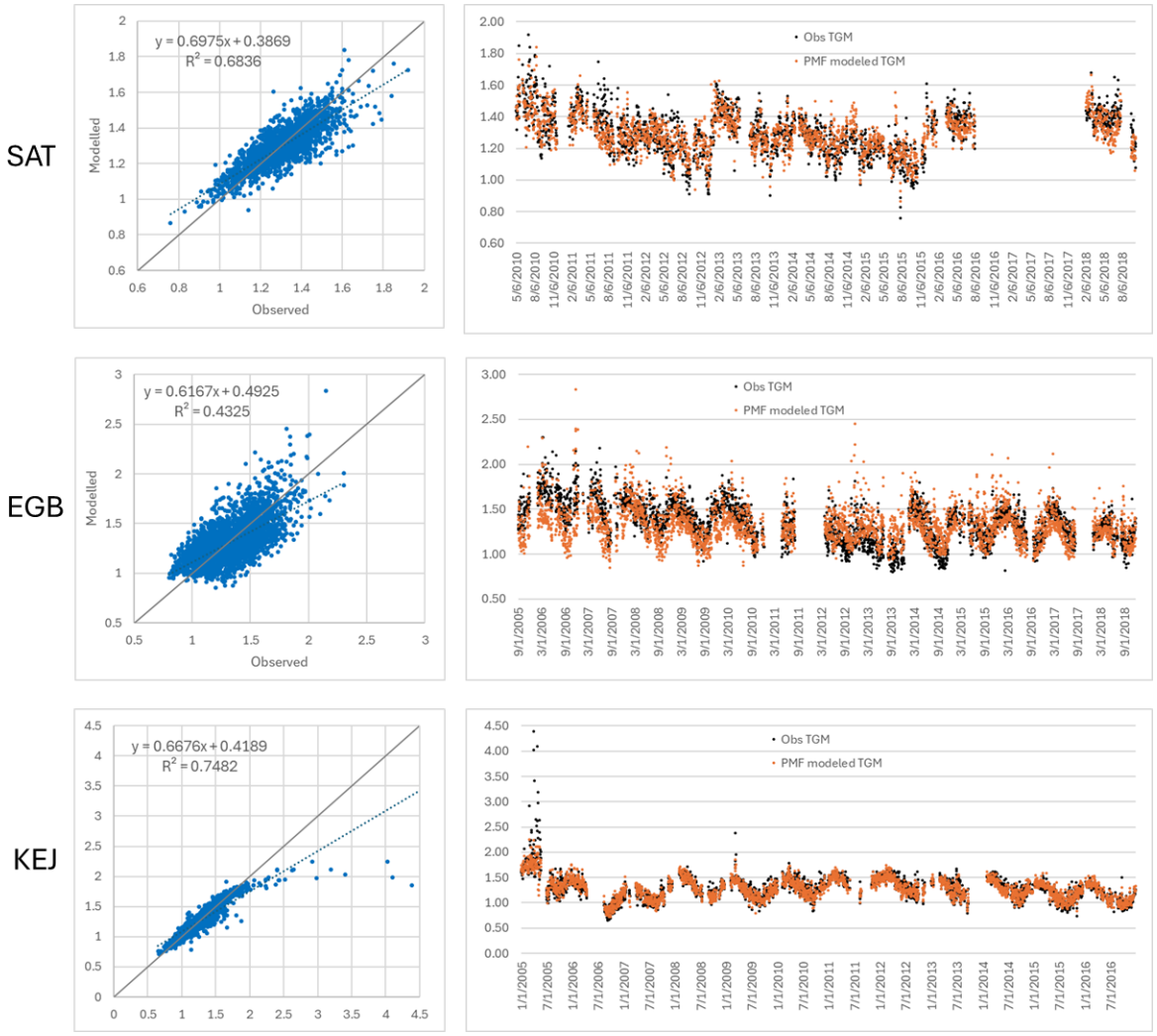


Figure S1: Comparison of PMF modelled and observed 24-h TGM (ng m^{-3}) using regression analysis (left) and time-series analysis (right)

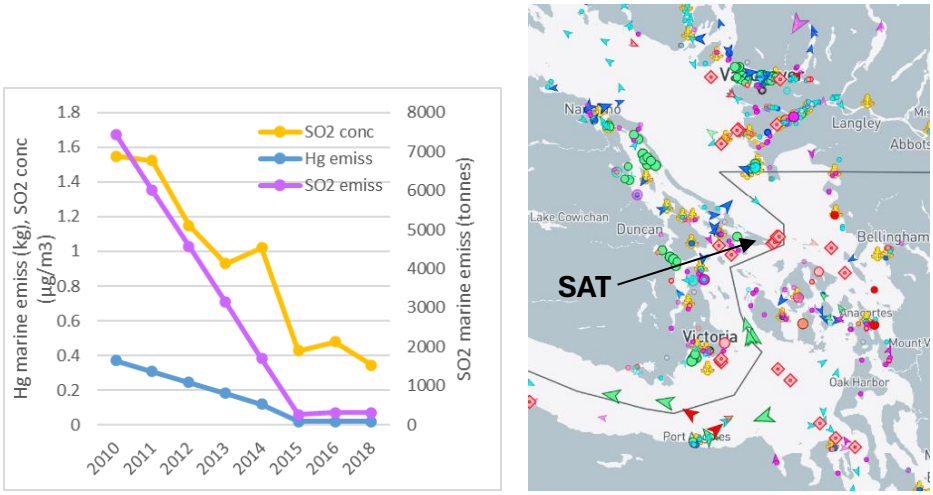


Figure S2: Left - Annual emissions of SO_2 and Hg from marine transportation reported for British Columbia (ECCC APEI, 2023). SO_2 ambient concentrations measured at SAT are also plotted. Right – Symbols represent ship traffic along the Strait of Georgia (http://www.shiptraffic.net/marine-traffic/straits/Strait_of_Georgia).

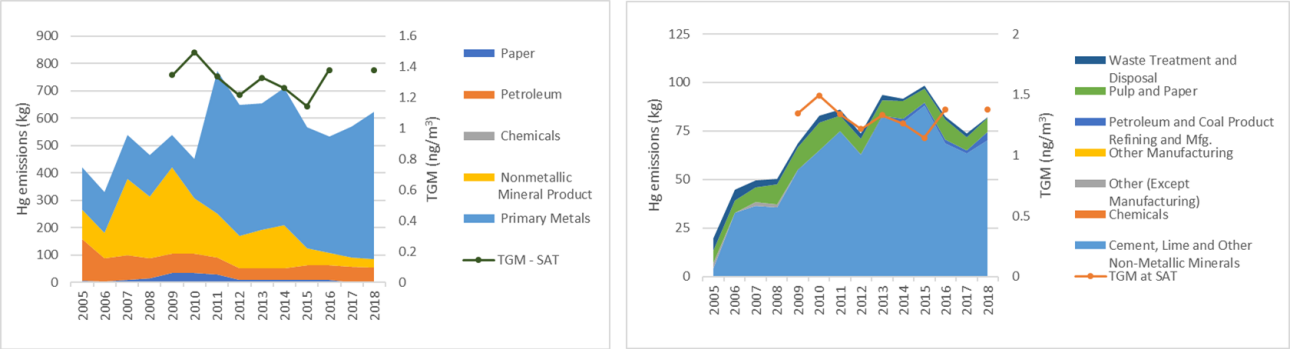


Figure S3: Hg emission sources within 150 km of SAT. Left: Washington State emissions (USEPA TRI, 2023); right: British Columbia emissions (ECCC NPRI, 2023)

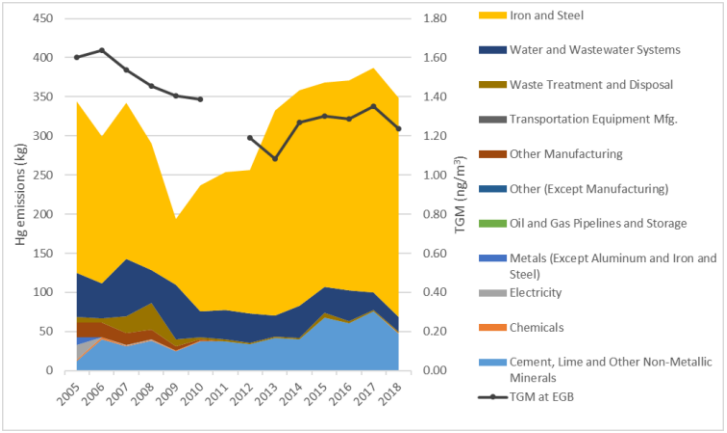
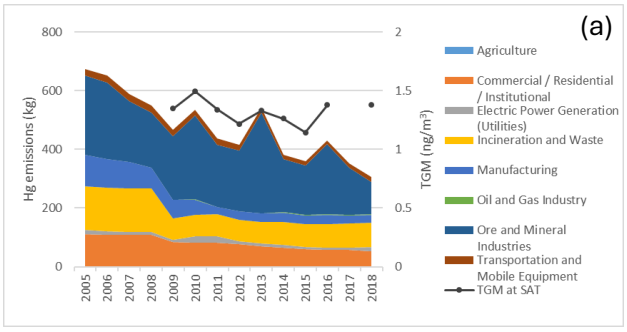
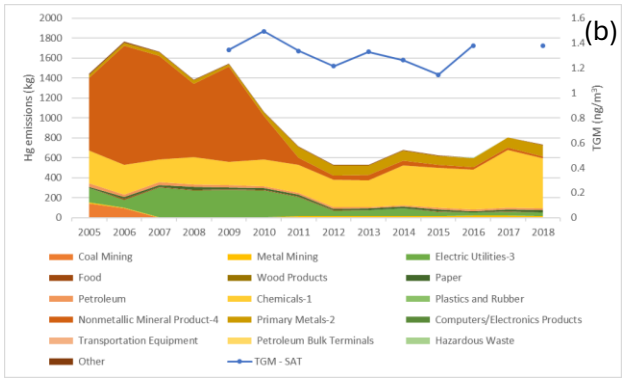
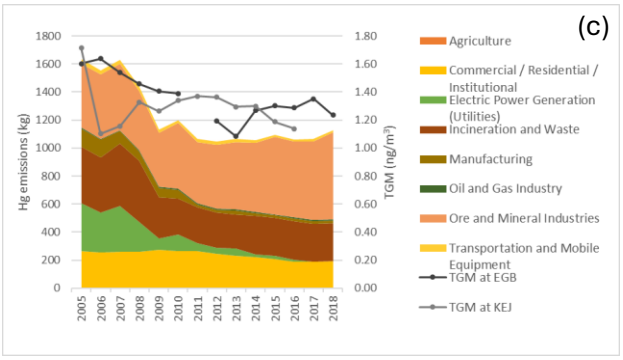
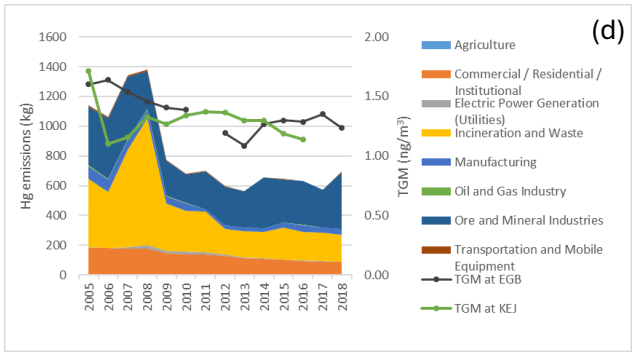


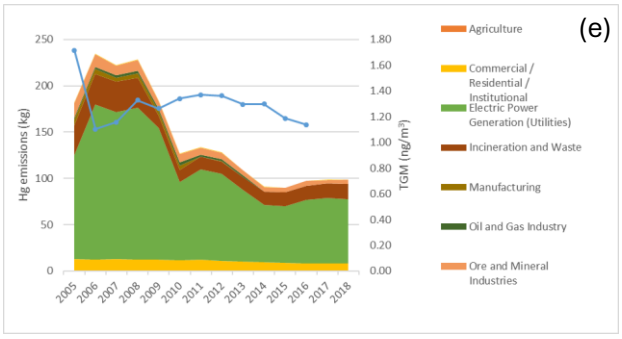
Figure S4: Hg emission sources within 150 km of EGB in Province of Ontario (ECCC NPRI, 2023)

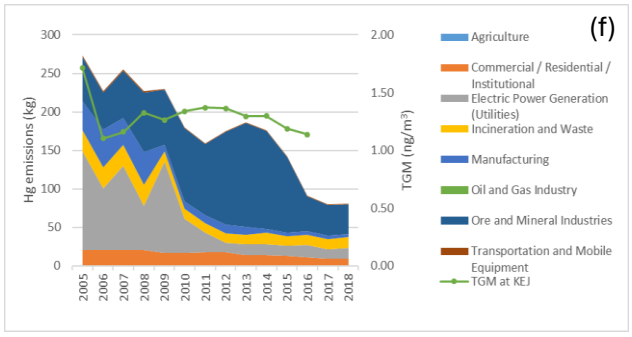












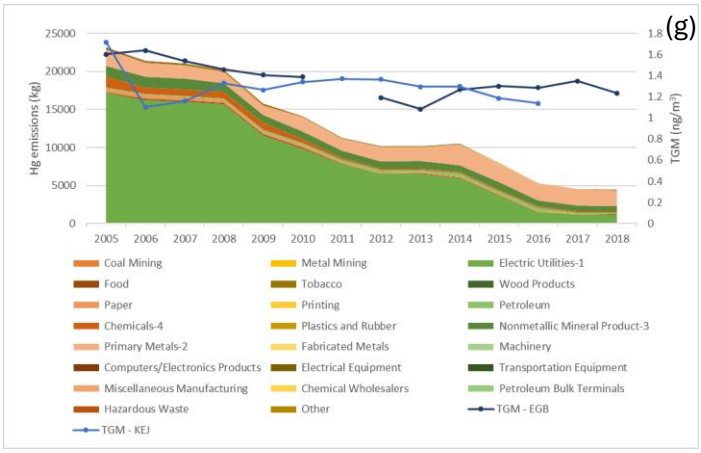


Figure S5: Regional Hg emission sources around SAT, EGB and KEJ. Emissions data for (a) British Columbia, (b) Northwestern U.S., (c) Ontario, (d) Quebec, (e) Nova Scotia, (f) New Brunswick, (g) Northeastern and midwestern U.S. Data sources: ECCC APEI (2023) for Canadian emissions, USEPA TRI (2023) for U.S. emissions.

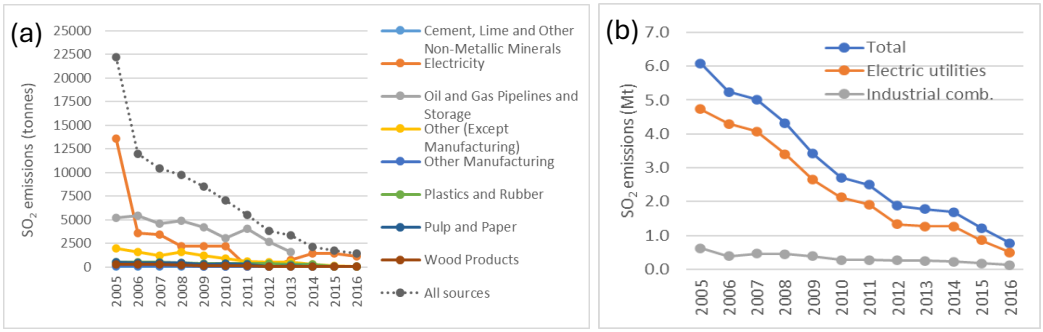


Figure S6: SO_2 emissions (a) local, within 150 km of KEJ (ECCC NPRI, 2023) and (b) regional, U.S. northeast and Midwest regions (USEPA NEI, 2023)

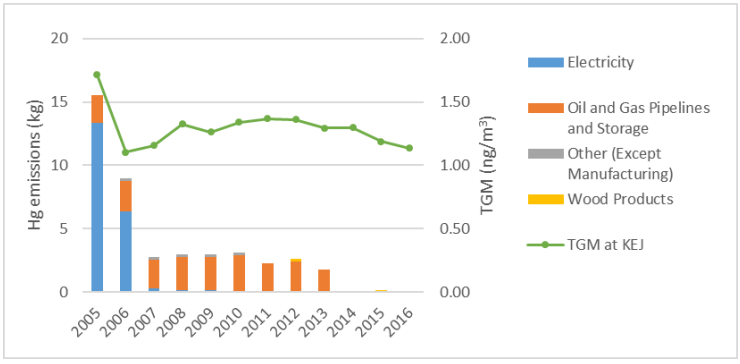


Figure S7: Hg emission sources within 150 km of KEJ in Provinces of Nova Scotia and New Brunswick (ECCC NPRI, 2023)

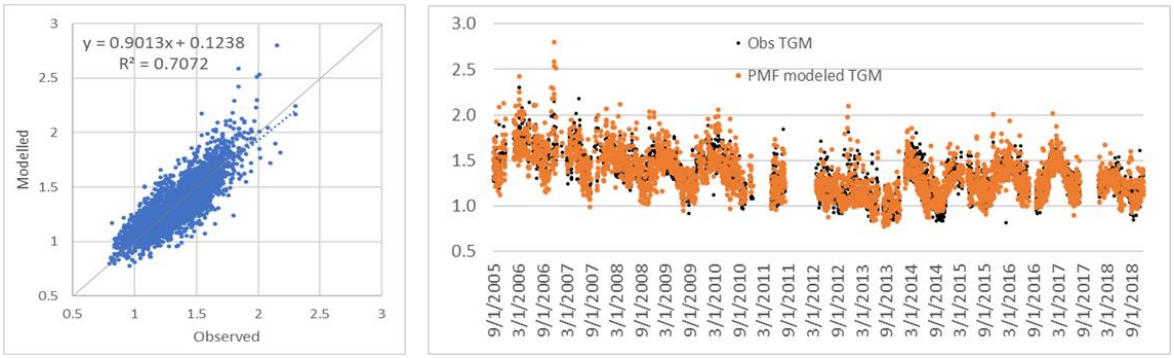


Figure S8: Comparison of PMF modelled and observed 24-h TGM (ng m^{-3}) for EGB using regression analysis (left) and time series analysis (right). PMF modelled TGM are based on yearly runs across the time series.

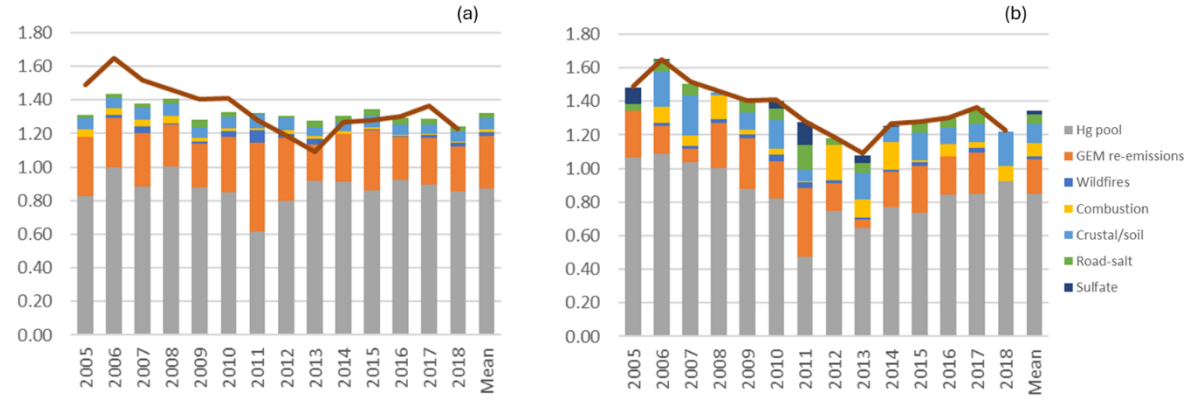


Figure S9: TGM annual source contributions (ng m^{-3}) at EGB for (a) single run and (b) yearly runs for 2005-2018. Bar graphs: PMF modelled TGM; red line: mean observed TGM.

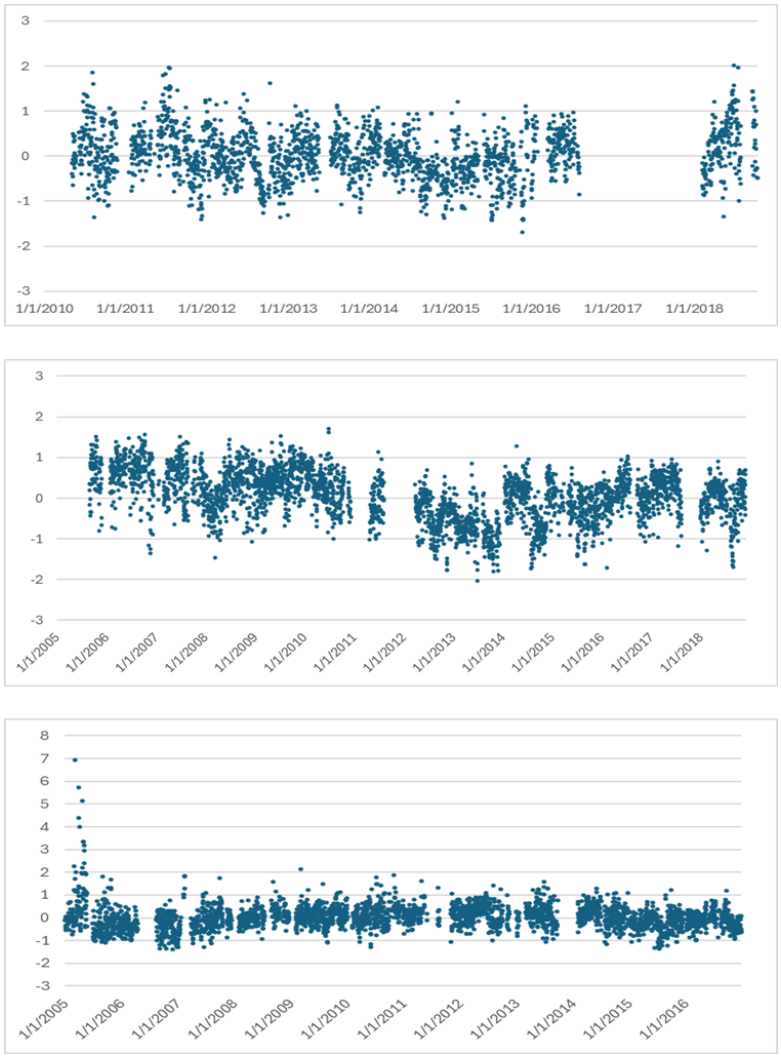


Figure S10: Time series of uncertainty scaled residuals for TGM at SAT (top), EGB (middle), and KEJ (bottom) for the final 6-factor solution

Figure S11: Intercomparison between Tekran model X and B measurements for EGB (top) and KEJ/KEB (bottom). Absolute and relative differences for hourly measurements are plotted.

Supplement References

Environment and Climate Change Canada (ECCC): Canadian Air and Precipitation Monitoring Network (CAPMoN), Toronto, Ontario, Canada, Data files: AtmosphericGases-TGM-CAPMoN-AllSites-2017.csv, AtmosphericGases-TGM-CAPMoN-AllSites-2018.csv; doi:10.18164/e1df5764-1eec-4a9f-9c03-f515b396b717, 2024.

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ECCC NPRI: National Pollutant Release Inventory, https://www.canada.ca/en/services/environment/pollution-waste-management/national-pollutant-release-inventory.html, 2023.

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USEPA NEI: Air Emissions Inventory, https://www.epa.gov/air-emissions-inventories, 2023.

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