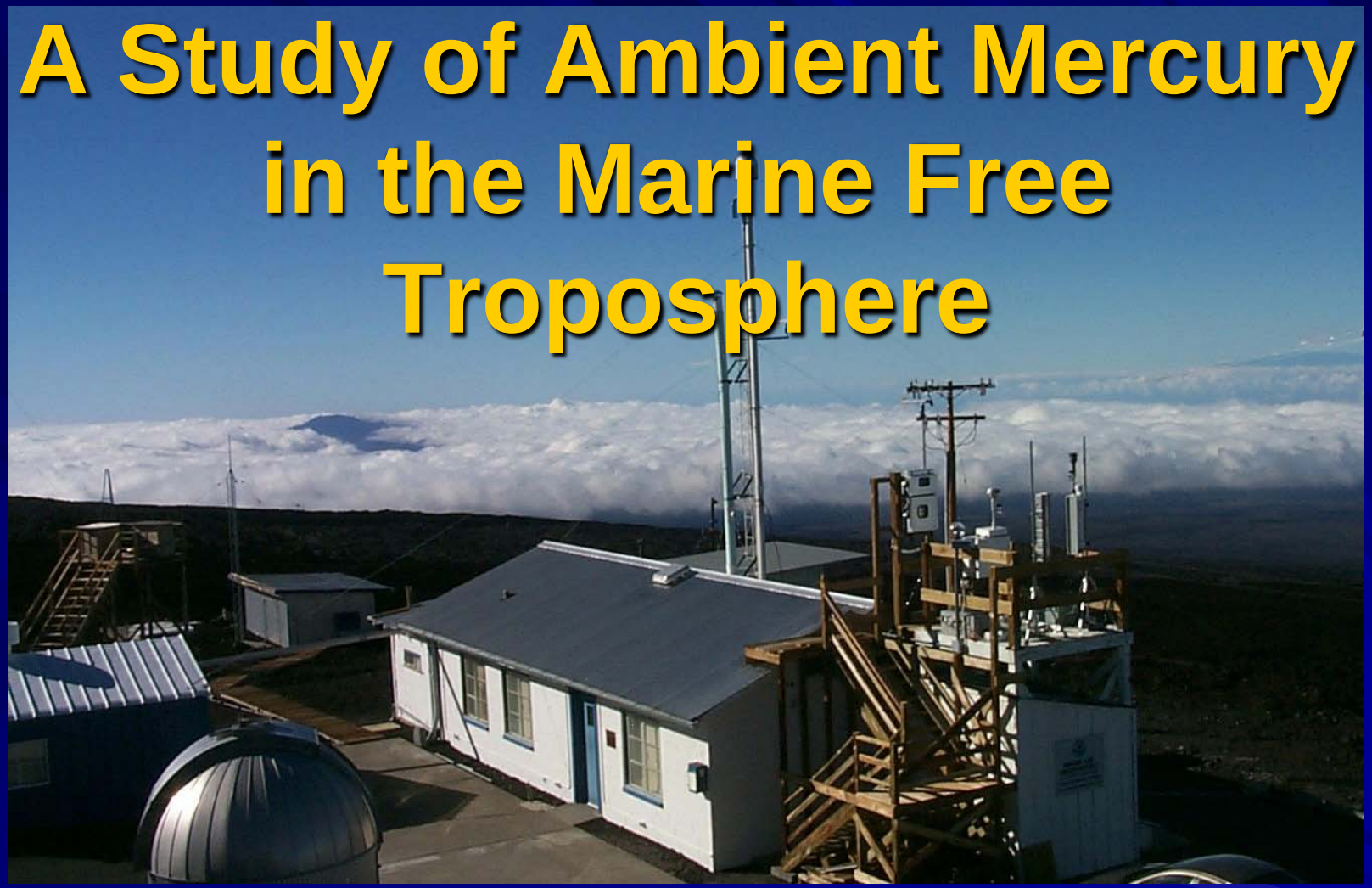
A Study of Ambient Mercury in the Marine Free Troposphere



L. Krnavek[1], M. S. Landis[1], A. Colton[2], D. Kuniyuki[2]
[1]US EPA Office of Research and Development
[2]US NOAA Earth System Research Laboratory
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Ambient Mercury Chemistry Terminology

Anthropogenic

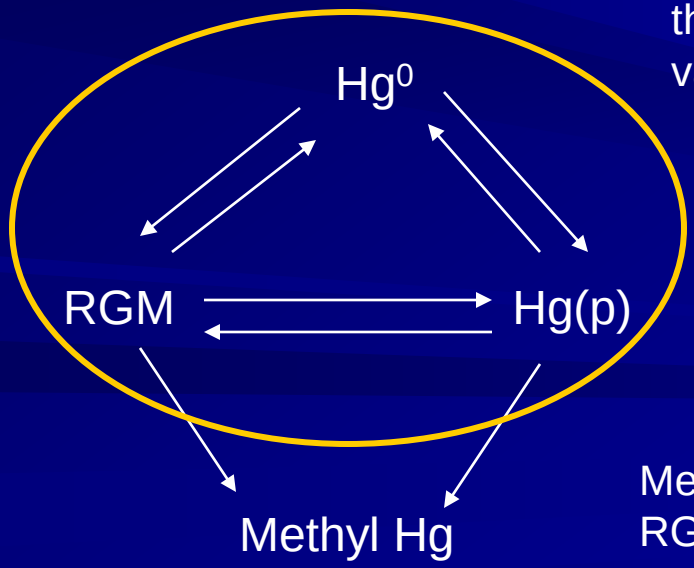
Natural, volcanic

→ Hg^0 – Elemental Hg → Stable gas specie, long residence lifetime, long distance transport

→ RGM – Reactive gaseous Hg → Reactive species, oxidation state is +2, water soluble, shorter residence lifetime, found closer to source

→ Hg(p) – particulate Hg → Reactive species, oxidation state is +2, water soluble, shorter residence lifetime, found closer to source

RGM = any gas species with HgII. Hg^0 its oxidized to +2 in the gas phase however its counter ion combinations can be variable



Hg(p) = Hg^0 its oxidized to RGM and aerosol particles scavenge the +2 species

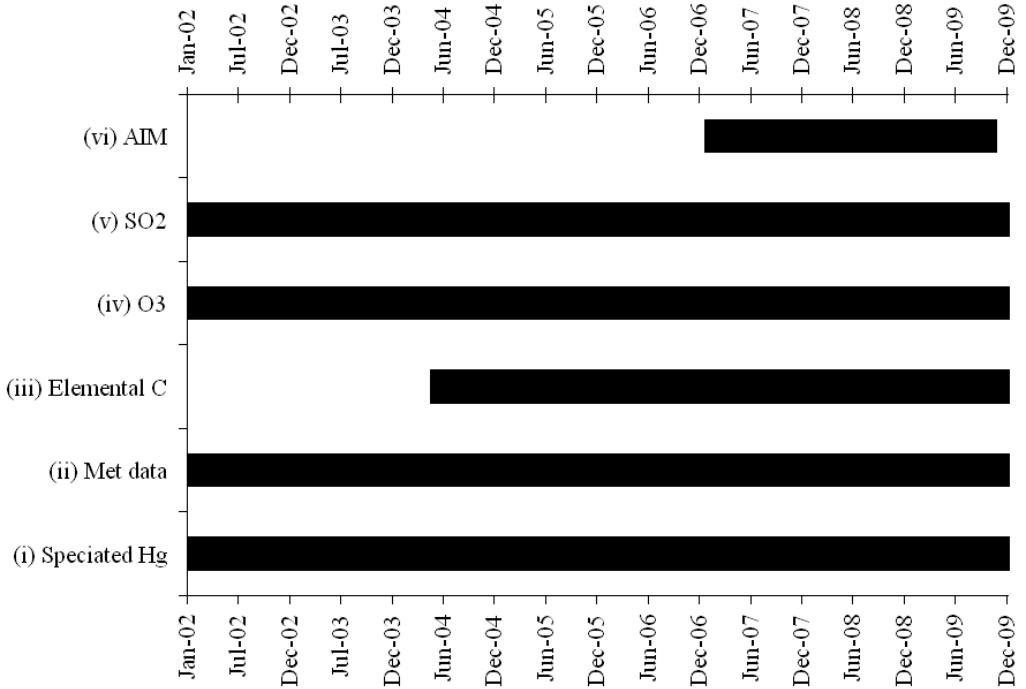
Methyl Hg = when assimilated by living organisms is toxic, RGM and Hg(p) are precursors of methyl Hg,

Why Mauna Loa?

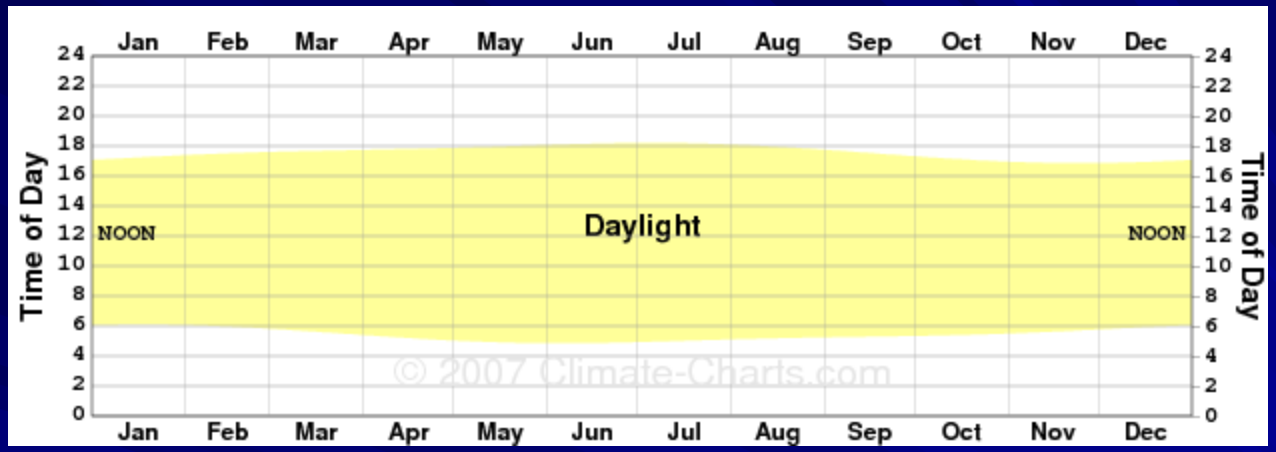
- A collaborative aircraft study profiling speciated mercury from 60 - 3650 m found high concentrations of RGM in the marine free troposphere suggesting:
  - anthropogenically produced RGM was being transported up to that altitude or,
  - homogeneous and/or heterogeneous formation of RGM aloft in the marine free troposphere
- Mauna Loa Obs. its found at 3397 m (~3.4 km) high and its location in the remote marine free troposphere are ideal for this study.

Measurements at MLO

Instruments platform in MLO



Downslope Data

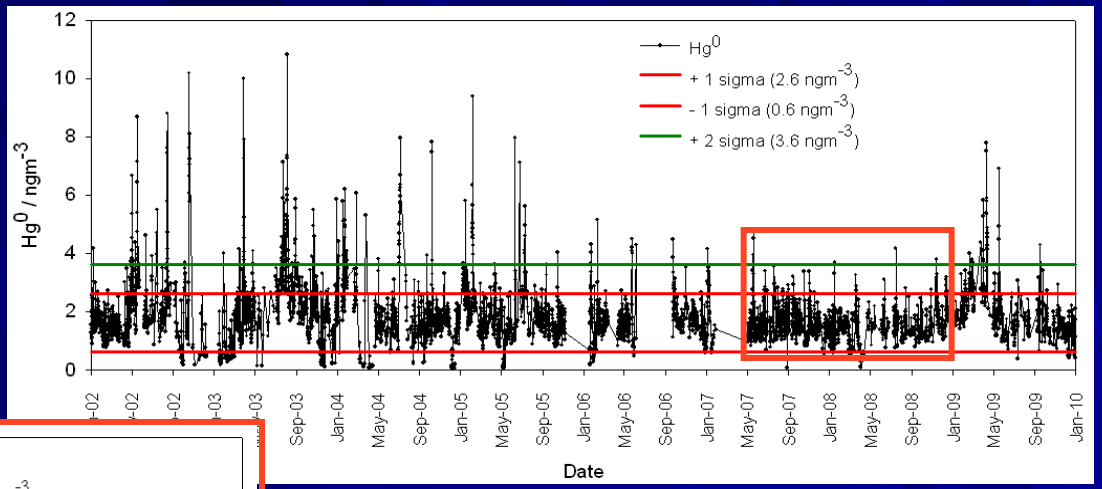


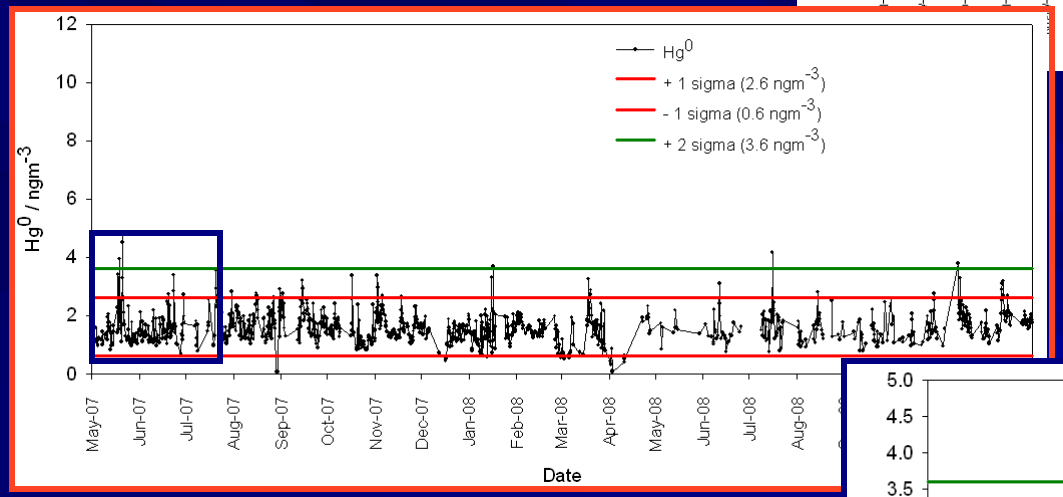
- We selected only downslope data to work with at this time
  - Downslope = 18:00 to 6:00
  - This time range is during the nighttime to minimize influences from low troposphere that occurs during the day due to convection.
- The picture above was taken from Mauna Loa Slope Observatory Climate Research webpage.
  - It shows clearly that our downslope data is during the dark.

Variability in Hg^0 Concentration: 2 Hour Set

High resolution data findings so far:

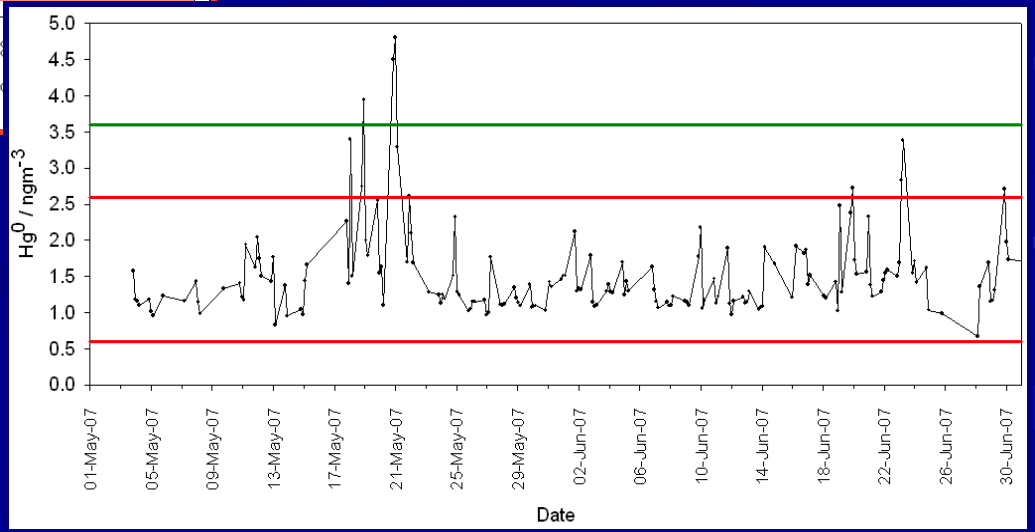
1. High variability in Hg^0 concentration
2. High variability in $[Hg^0]$ indicates active Red-Ox chemistry or changing transportation patterns.





3. If we are to use high resolution data for a long period of time is best to zoom in for a max of 3 months at a time. If interested in long term patters use running averages.

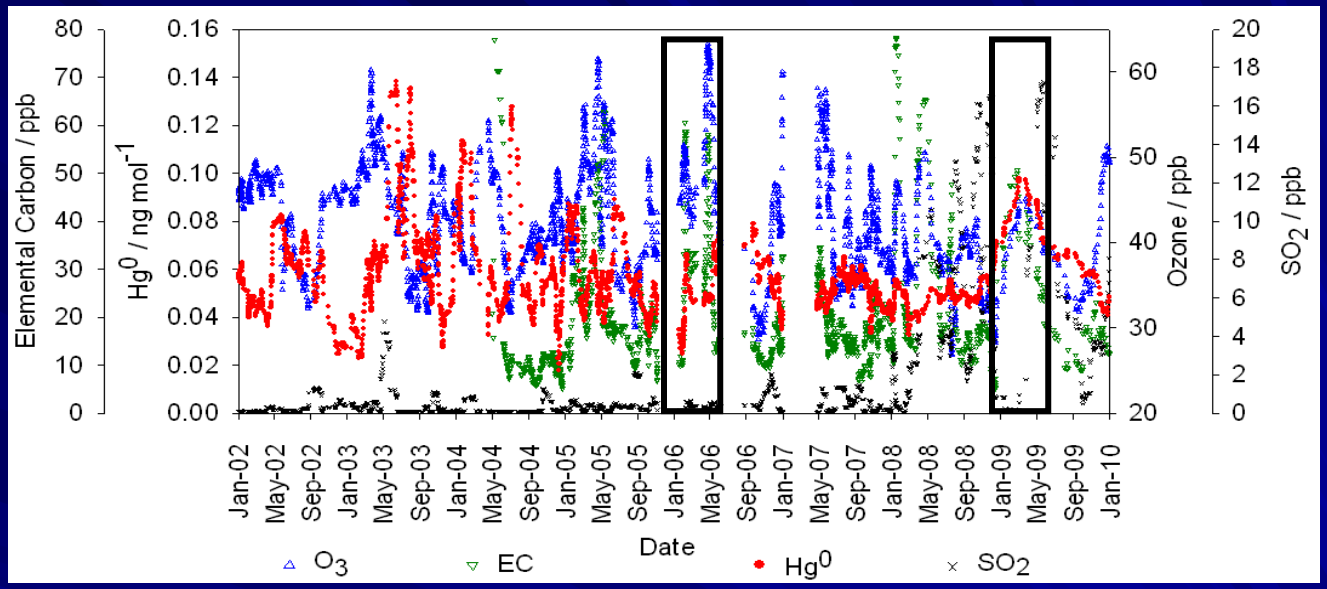
4. Zooms of the data provide visual evidence of how many actual values (dots) are present when observing spikes and drops specially for extreme values.



Air Masses Into MLO Free Troposphere

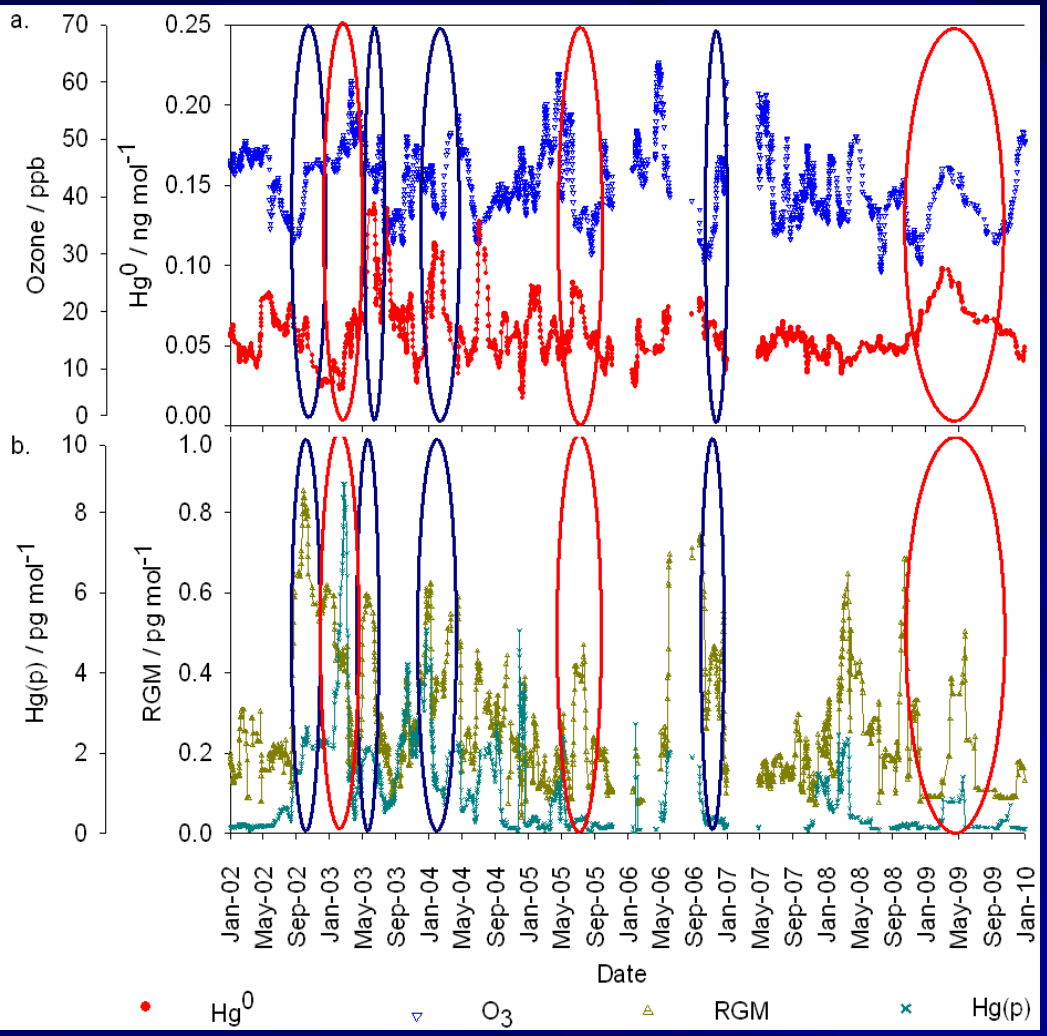
5-day running average

Subset → Rel Hum values between 20 – 65 %



- Periods of time when SO_2 levels are > 1ppb indicate volcanic influences.
  - During these periods SO_2 and EC show negative correlations, suggesting these air masses are influenced by volcanic emissions and not anthropogenic.
- O_3 and Hg^0 show no correlation or negative correlation the majority of time with two notorious exceptions
  - First episode SO_2 levels were <1 ppb and O_3, Hg^0 and EC were positively correlated
  - Second episode SO_2 levels dropped to < 1 ppb and EC levels spiked to some of the largest levels of EC (50 ppb), Hg^0, O_3 and EC show a positive correlation
  - Both episodes indicate anthropogenic influences.
  - It appears that O_3 is a potential Hg^0 oxidizer for air masses with anthropogenic influences, while for air masses with natural influences O_3 is not the main Hg^0 oxidizer

Free Troposphere Mercury Chemistry



Air masses under volcanic influences:

-SO_2 > 1 ppb → blue ovals

- 1st and 2nd blue oval → ambient Hg spike together → redox rxns + addition of external Hg source → volcanic emissions Hg.

- 3rd and 4th blue ovals → RGM ↑, Hg^0 ↓ while low levels of Hg(p) →Hg^0 and Hg(p) are transformed to RGM → SO_2 can participate in RGM reduction.

Air masses under anthropogenic influences

-SO_2 < 1 ppb and EC spikes → red ovals

- 1st red oval →RGM ↓, O_3 ↑, Hg^0 ↑ and Hg(p) ↑ → Hg^0 is oxidized and RGM is rapidly scavenged by particulate → heterogeneous chemistry

- 2nd red oval →RGM, Hg^0 and O_3 peaking at the same time while low levels of Hg(p) → No heterogeneous chemistry

- 3rd red oval → O_3 and ambient Hg peak together →redox rxns + addition of Hg from anthropogenic sources.

Seasonal Analysis

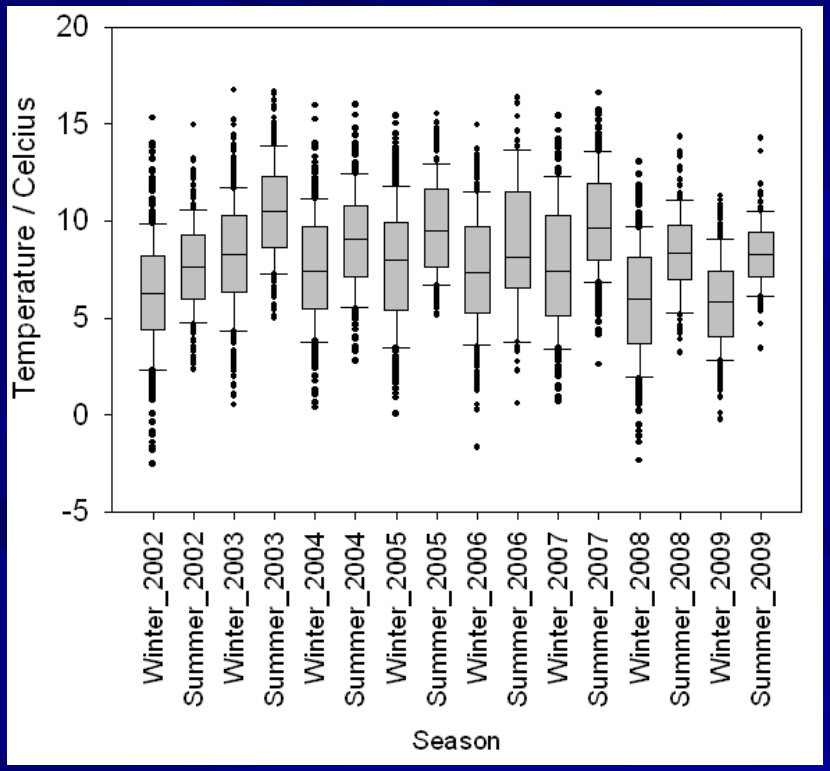
Season definition → Two seasons = Winter and summer → Hawaii's weather is dominated by westerly winds during the summer and some variability during the winter, but changes in temperature define seasonal changes

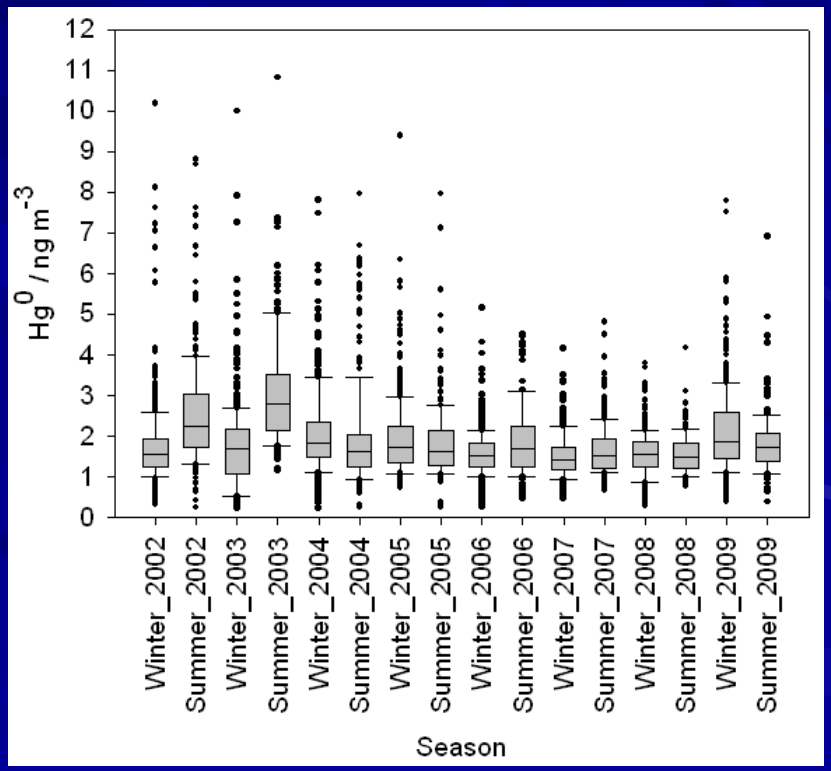
Winter = October to April

Summer = May to September

An Anova test for all speciated Hg showed that there is no significant difference between winter and summer seasons over the years for speciated Hg concentrations, suggesting:

- Speciated Hg concentrations are determined by the red-ox chemistry and re-emission from oceans and surfaces, and not by source increase or decrease at the altitude this experiment was done.





So What Have We Learned?

- Collection of high-time resolution assisted in finding high temporal variability in Hg^0
- Classification of the downslope data into atmospheric layers using RH and comparison of EC and SO_2 helped to identify air masses with anthropogenic and natural influences (volcanic) into MLO and identify free troposphere Hg chemistry occurrences.
- Lack of correlation or negative correlation between O_3 and Hg^0 indicates that O_3 may not be the main Hg^0 oxidant.
- Lack of overall trend and seasonal patters for ambient mercury suggest its concentration is determined by chemical transformations and re-emission and not by source concentration changes in the high free troposphere.
- Correlations and anti-correlations among ambient Hg and the collected species indicate that oxidation/reduction of ambient Hg occurs in the free troposphere, and that when PM is present heterogeneous chemistry occurs as well.