出國報告（出國類別：考察）

考察大氣汞監測技術

服務機關：行政院環境保護署

姓名職稱：何璠　　監資處技士
邱富淞　監資處技工
許桂榮　明志大學教授

派赴國家：美國

出國期間：民國 94 年 2 月 21 日至 2 月 27 日

報告日期：民國 94 年 5 月 10 日

行政院及所屬各機關出國報告書提要

公務出國報告提要

頁數：19 頁（未含附錄）

報告名稱：

考察大氣汞監測技術

主辦機關：

行政院環境保護署

出國人員：

何璠　　行政院環境保護署 環境監測及資訊處 技士
邱富淞　行政院環境保護署 環境監測及資訊處 技工
許桂榮　明志大學　教授

出國類別：台美環保技術合作計畫

出國地區：美國

出國期間：民國 94 年 2 月 21 日至 2 月 27 日

報告日期：民國 94 年 4 月 8 日

分類號/目：I5/化學與環境科學

內容摘要：本次出國考察計畫主要觀摩位於夏威夷大島(Big Island)的Mauna Loa 全球背景監測站，藉以瞭解美國目前大氣汞監測技術，作為本署評估鹿林山大氣背景站建置方式與儀器採購規格，明志大學許桂榮教授偕同前往，本計畫之執行可供空氣品質監測業務推動參考，並可增強我國與美國環境保護署之環保合作關係。

一、參訪位於夏威夷希洛（Hilo）之NOAA實驗室：

對於Mauna Loa火山背景測站無法進行即時監測之採樣樣品，均被送至此實驗室進行檢測，無法立即修復的儀器也被送到此實驗室進行維修。

二、參訪美國夏威夷Mauna Loa 火山之監測站：

Mauna Loa全球背景監測站位於夏威夷大島，高度為3397m，最早由美國NOAA於1956年建置， NOAA / CMDL是全球運轉歷史最久，最適合代表北半球背景的觀測地點，目前已有10棟建築物及將近250個監測參數，目前已經有12個參與的單位。

Mouna Loa觀測項目除了一般NOAA長期監測之項目，包括粒狀物、CO2、CO、CFCs、CH4、水汽、Lidar、太陽輻射外，美國環保署亦於近年於該處設置大氣汞監測儀器，以追蹤汞物種之長程傳輸。

目錄

第一章 前言

1. 緣起

近年來亞洲地區大氣污染物對台灣的長程輸送已受到相當廣泛的注意，每當沙塵暴、生質燃燒或酸雨發生時，均受到民眾普遍重視與關切。除了台灣之空氣品質受到衝擊外，亦可能會導致區域環境與氣候衝擊。

台灣正好位於東亞大氣污染物下風處及南亞生質燃燒傳送路徑之下風處，本署於全國設置 74 個採樣之監測站多為代表地區性之特性，目前仍無代表一區域型之觀測地點，因此在若干境外污染物傳送影響之議題上，常受到地區性污染物干擾，採樣分析的結果往往難以量化受境外影響之程度。因此，考量中部高山乃為大氣背景站之絕佳之觀測點，本署已選擇將背景測站設於鹿林山(2862m)上，因該處對於來自上游氣流有較佳之掌握。

此次參訪地點 Mauna Loa 為一相當重要之全球性背景站，在籌設背景站之初期階段亟需相關國際監測經驗，因此藉由此次國際合作是一個與國際接軌之極佳機會。

2. 目的

藉由參與本次出國考察計畫，觀摩美國大氣汞監測技術，以及全球性背景站規劃經驗、儀器採購之種類等，並蒐集大氣汞監測國際合作相關資訊，作為本署大氣汞監測之規劃、未來設置測站及操作運轉方式參考，並可增進我國與美國環保合作關係。

3. 考察行程與出國人員

本次出國參訪自 94 年 2 月 21 日～2 月 27 日，出國期間參訪單位包括 NOAA 位於 Hilo 之實驗室、Mauna Loa 全球背景監測站，以下是本次參與單位人員簡要說明以及詳細參訪行程：

姓名	單位/主管業務或職稱
Mr. Dan Thompson	美國環保署國際合作事務部門/計畫經理
Mr. Robert K. Stevens	佛羅里達環保局/汞監測計畫研究員
Mr. Matthew S. Landis	美國環保署/環境健康研究員
Mr. Christopher Plante	亞洲基金會/環保計畫主持人

表一 參訪行程

日期	地點	工作內容
九十四年二月二十一日（星期一） I	台北 到 夏威夷	起程
九十四年二月二十二日（星期二） II	夏威夷	1. 拜訪美國環保署成員。 2. 拜訪 NOAA 成員，考察 Mauna Loa 實驗室運轉操作情況。 3. Dan Thompson 介紹美國環保署汞監測計畫的目標以及此行台美環保技術合作的目標。 4. TEPA 成員介紹現存的高海拔監測站及大氣汞監測目標。
九十四年二月二十三日（星期三） III	夏威夷	1. 參訪 Mauna Loa 背景測站。 2. Landis 博士介紹汞監測儀器之操作、校正、維護和疑難問題解決方法。
九十四年二月二十四日（星期四） IV	夏威夷	1. Robert Stevens 介紹佛州汞監測研究之歷史，以及最近研究新發現。 2. Landis 博士介紹美國環保署 ORD 大氣汞研究目標。 3. 台美雙邊汞監測技術合作目標討論。
九十四年二月二十五日（星期五） V	夏威夷	1. 前日討論之問題答復。 2. 研擬下階段之合作模式，包括台灣汞監測站之設立、教育訓練、操作維護及數據分析。

九十四年二月二十六日（星期六） Ⅷ	夏威夷--台北	返國
九十四年二月二十七日（星期日） Ⅸ	夏威夷--台北	返國

第二章 NOAA實驗室考察紀要

1.NOAA實驗室簡介

位於Hilo之NOAA實驗室主要提供Mauna Loa 監測站（簡稱MLO）監測成員一個可供儀器維修、資料蒐集及處理，以及樣品分析的空間。它也是MLO運作管理與聯繫的中心。

在Hilo的辦公室以及在部分山上測站的網路已經從較舊的同軸電纜網路提昇至10 base-T的網路。在Hilo辦公室中的區域網路目前已經更新至100 megabits。較多的網路分享器加在不同的觀測位置上，以容納日益增加的網際網路讀取需求。大部分的電腦和網路設備的電源提供都是使用了不斷電系統。

本次行程第一天即安排參訪此實驗室，與負責MLO監測之成員會面，一方面瞭解此實驗室之功能，另一方面則蒐集MLO之運作模式資料。Dr.Landis 並為我們介紹該實驗室中，用於進行大氣汞監測之儀器，包括了氣相汞、二價汞、粒狀汞之監測設備，以及採樣設備之處理。由於大氣中汞的濃度相當低（ng/m^{3}等級），因此在採樣以及操作時均需要接受嚴格的訓練，否則樣品極容易受到污染。除了介紹大氣汞監測儀以外，另外亦介紹離子層析儀（Ion Chromatography），此項設備是用以檢測微量元素離子，經由所檢測得的結果，可判別及確認排放汞的污染源。

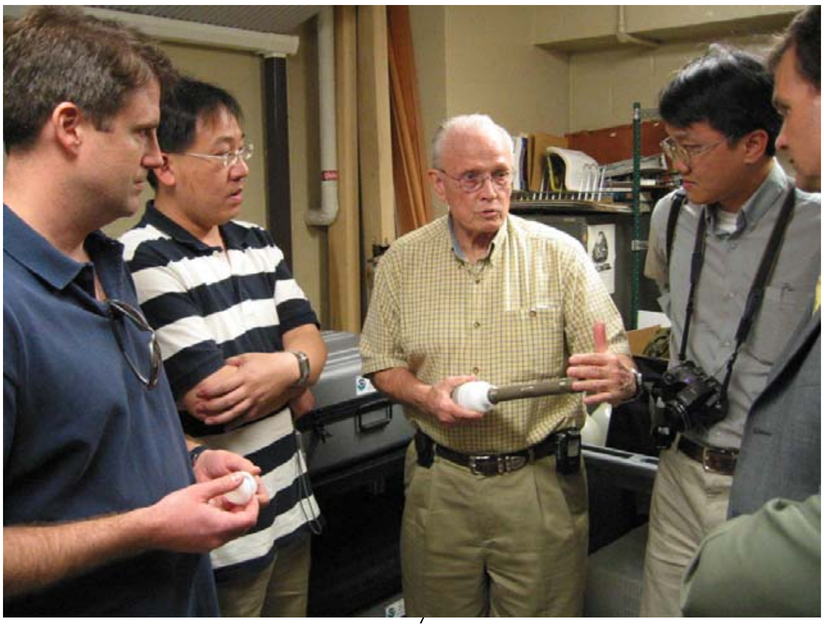


圖 2-1、Mr. Robert K. Stevens 於 NOAA 實驗室介紹運作情況

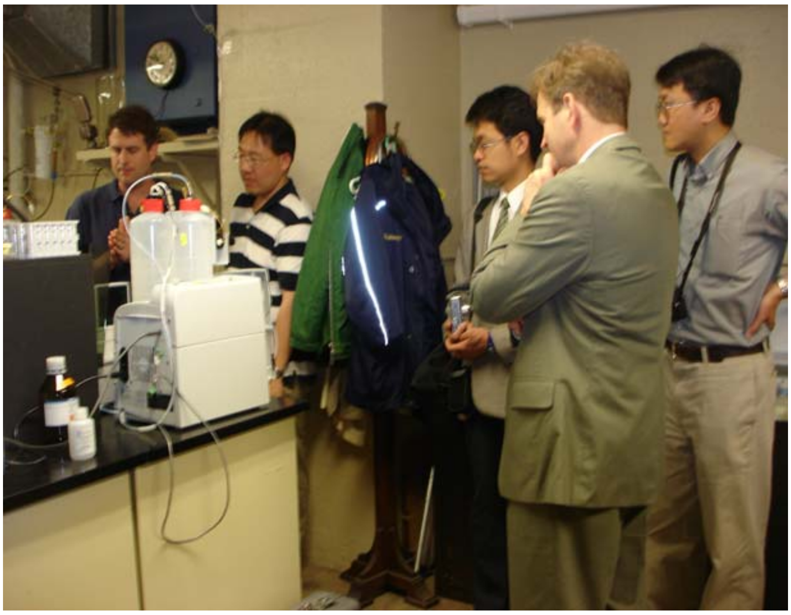


圖 2-2、Mr. Matthew S. Landis 介紹離子層析儀之分析結果

NOAA 實驗室參訪後，美國環保署官員 Mr. Dan Thompson 介紹美國環保署汞監測計畫的目標以及此行台美環保技術合作的目標。

2.美國大氣汞監測發展歷程

歷史上最早紀錄的汞污染事件是發生在日本海濱小鎮水俣因汞污染嚴重，大量海生物窒息死亡，數千人發病，數百人死亡，許多人終生致殘，這就是震驚一時的“水俣病”。就在此事件發生後數十年間，許多國家立法保護居民免於食用受汞金屬污染之魚類，不過大部分的法規是針對含汞污水之直接排放。然而科學家於近年來卻發現大氣沈降是海域河流生態中汞污染最主要的來源。

美國環保署於 1989 年將汞列為危害性空氣污染物。美國國會於 1990 年頒佈的清淨空氣修正法案要求美國環保署（EPA）草擬有關汞之最新發展報告。美國 EPA 則於 1998 年將上述報告完成，報告中首次認為大氣中人為排放的汞與造成魚體中生物累積之甲基汞極有可能具有

相關性。美國 EPA 隨即針對鹼氯工廠、醫療及民生廢棄物焚化廠進行立法，藉以削減排放至大氣之汞的量。由於汞排放庫存量、大氣化學和沈降相關參數的不確定性，以致於目前要訂出的汞的濃度模式是一件相當複雜的工作。

美國對於大氣汞的監測實際上已進行了超過 30 年的時間，最初是靠每日人工採集總氣態汞，後來則演進到可以以半連續方式監測三種型態的汞，包括氣態汞、二價汞、粒狀汞。由於二價汞以及粒狀汞的沈降速度較快，因此在局部區域會有乾濕沈降發生。至於氣態汞則會有長程傳輸的情況。近十年來大氣汞監測技術有長足的發展，大氣汞動力學、乾沈降機制均被納入考量，因此，目前亟需建立全球大氣汞監測網路，唯有更多、更廣泛以及具可靠性之監測數據，才可進一步發展大區域的大氣汞模式。

第三章 美國夏威夷全球大氣背景測站（MLO）考察紀要

Mauna Loa 位於夏威夷火山口的北坡，高度為 3397 公尺，最早為美國 NOAA 於 1956 年所建置。目前已經有 10 棟建築物及將近 250 個監測參數，以及 12 個參與的單位。此測站附近全景及空照圖如下。

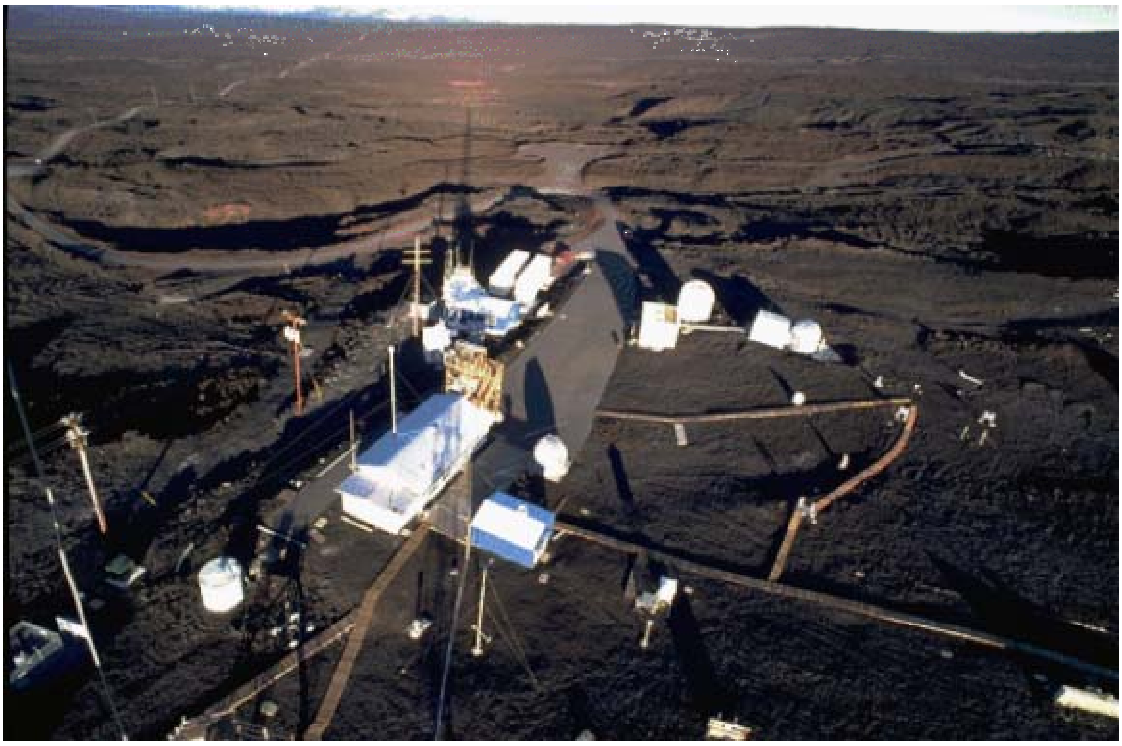


圖 3-1 MLO 全景及空照圖

有關本測站之氣象條件，由於夏威夷緯度較低，雖其高度超過 3,000 公尺，但全年平均溫度仍未到 0 度，年降雨量也僅 457mm，平均溫度較高，為 5m/s，代表風向為東風及東北風。

此次前往該測站，除了參觀美國EPA於該測站架設之大氣汞分析儀即時採樣分析情況外，另外亦參觀該站最出名的CO_2觀測，該項觀測自 1958 年起即開始進行，至今仍持續進行中，由濃度變化趨勢可明顯看出

氣候變遷的軌跡。

另一項參觀的重點為氣膠及微粒之採樣分析，每日所採集之濾紙均被妥善保存以預備作進一步分析。由於該處所在地點具有相當優勢，來此進行短期觀測的國際科學研究單位持續增加，例如許多團體在當地架設儀器來量測不同波段的太陽輻射，另外中研院也於該處架設天文觀測儀器，預備進行天文研究計劃。目前在當地進行的科學計劃詳如下表。

表 3-1 在 Mauna Loa 進行之科學研究計劃

Scientific Programs at MLO			
Carbon Cycle Gases	**Ozone, Water Vapor, & Halocompounds**	**Solar Radiation & Aerosols**	**Miscellaneous**
Carbon Dioxide (CMDL)	Total Ozone & profiles - Dobson (CMDL)	SOLAR RADIATION (CMDL)	METEOROLOGY (CMDL)
Methane (CMDL)	Surface Ozone (CMDL)	UV radiation and NO2 (NIWA)	PRECIPITATION CHEMISTRY (CMDL)
Carbon Monoxide (CMDL)	Ozone profiles-ozonesondes (CMDL)	Aerosol profile - LIDAR (CMDL)	Temperature max/min and precipitation (NOAA National Weather Service)
Carbon 13 (CMDL)	Total Ozone - Brewer (AES)	Aerosol system - PSAP (CMDL)	Radon (Australian Nuclear Science and Technology Organization)
CO_2, N_20, ^{13}C, and O_2 (SCRIPPS Institution of Oceanography)	Stratospheric ozone, aerosol and temperature profiles (JPL)	Condensation Nuclei (CMDL)	SULFUR DIOXIDE (CMDL)
VOLCANIC CO_2 (CMDL)	Stratospheric ozone profiles (Universityof Massachusetts)	Aerosol Light Scattering - Nephelometer (CMDL)	Radio nuclides and precipitation chemistry (U.S. Dept. of Energy)
$^{13}C/^{12}C$ in CO_2, CO , & CH_4 (Commonwealth Scientific & Industrial Research organization, Australia)	FTIR, HNO3, O3, HCl (University of Denver)	Aerosol Light Absorption-Aethalometer (CMDL)	Cosmic Dust collection (Caltech)

CO isotope (Marine Science Research Center)	Stratospheric water vapor profiles (NRL)	AERONET sunphotometers, (NASA GSFC)	National Satellite Test bed (FAA)
	HALOCOMPOUNDS & other trace species (CMDL)	Sulfates, nitrate aerosols, nitric acid vapor (University Of Hawaii)	Earthquake Seismometer (HVO)
		Aerosol chemistry (University of California, Davis)	**Elemental, gaseous, and particulate Mercury** (EPA)
		UVB (Colorado State University)	**Ground Winds** (University of New Hampshire)

圖 3-2　於 MLO 聽取光達觀測情況

圖 3-3 於 MLO 參觀各項研究計畫之設備

第四章 美國大氣汞監測技術介紹

1.各物種特性簡介

汞物種共包括氣態汞、二價汞、粒狀汞三類。三類物種的物性及化性都有其獨特性。氣態汞的蒸氣壓最高，水中溶解度最低（$4.9\times10^{-5}gL^{-1}$），沈降速度也最低（0.05～0.1cm s^{-1}）。因此氣態汞的半生期較長（數周到數個月），且會經由長程傳輸，使另一區域受到影響。二價汞的蒸氣壓則較低，且為水溶性（66 gL^{-1}），其沈降速度為 1～5cm s^{-1}。粒狀汞的沈降速度則由粒徑大小決定，大致上介於 0.1～1cm s^{-1}。雖然大氣中二價汞及粒狀汞的濃度比氣態汞小了 1,000 倍，但是它們沈降速度較大，所以其乾濕沈降會造成區域性受到污染。

2.氣態汞監測

長久以來，氣態汞的採樣與分析是先利用金與其化合成汞齊，然後再加熱脫附後分析濃度。不過樣品與金化合之前需先通過一特殊之過濾裝置，以預防氣膠的進入。隨後加熱吸附管柱至 500℃使氣態汞脫附，再以冷蒸氣原子螢光光譜法（cold vapor atomic fluorescence spectroscopy，簡稱CVAFS）或冷蒸氣原子吸收光譜法（cold vapor atomic absorption spectroscopy，簡稱CVAAS）分析。使用以上兩種方式分析的儀器大致上都可提供每 5 分鐘一筆數據，且偵測極限可到達 0.1 ng m^{-3}。

3. 二價汞監測

美國在 1995 年左右針對全美的醫療廢棄物焚化爐、一般廢棄物焚化爐以及燃煤設施進行排放汞檢測，結果發現總汞中所含二價汞的比例分別為 95±5％、78±8％、67±27％。隨後在密西根湖進行的一項模式研究發現，二價汞在乾沈降中佔多數，且大氣沈降中約 40％為二價汞。由於大氣中二價汞的濃度範圍為 1～100pg m^{-3}，因此找到一個可靠的量化方法是一件相當具有挑戰的工作。過去 5 年來在二價汞的採樣與分析已經有了長足的發展，現在使用的方法包括了下列三種：陽離子交換薄膜(Cation-exchange membranes)、逆向霧艙(Refluxing mist chambers)以及氯化鉀被覆環狀剝離管(KCl-coated annular denuders)，以下僅針對第三種方法詳述。

氯化鉀被覆環狀剝離管

環狀剝離管最早是用來移除氣態氨，防止其和細微（粒徑小於 2.5um）的酸性氣膠產生中和作用。氯化鉀被覆環狀剝離管則最早是用於測量焚化爐煙囪的二價汞濃度，後來才被改良成用於大氣中二價汞的檢測。以此方式的流速限制為低流速(約每分鐘一公升)，需使用酸性溶液將二價汞萃取出來，後使用$SnCl_2$將二價汞還原成氣態汞，隨後導入金圈再進行分析。目前氯化鉀被覆石英環狀剝離管法是最常被使用，也是最適當被用來收集二價汞的方法。

4. 粒狀汞監測

大氣中粒狀汞的採樣量化需先將其收集至石英濾片上，然後再用CVAFS或CVAAS分析。石英濾片上所採集的樣品可用硝酸溶液中微波吸收的方式萃取，隨後以BrCl氧化，並以$SnCl_2$還原，最後再通過金圈；亦可使用先熱分解，然後再通過金圈的方式。其實在過去十年來大家對粒狀汞的採樣造成的誤差有許多爭論，一方面是正誤差（二價汞吸附至粒狀汞上），另一方面則是負誤差（粒狀汞揮發）。若在採集粒狀汞之前先使用氯化鉀被覆環狀剝離管，可有效將正誤差降低。研究顯示，較長時間的採樣與短時間採樣相比較，較易發生負誤差的狀況。

5. 大氣汞監測系統介紹

此次學習之旅，從美國大氣汞監測專家得知，目前具備大氣汞監測能力之廠牌，唯有加拿大 Tekran 這家儀器商。該儀器原本僅能進行半連續性（Semi-Continuous）採樣分析，後來由於美國環保署的監測需求，目前已演進至可以自動連續採樣，只是由於它的監測極限極低，因此操作上需經過相當嚴格的訓練，對此美方也表示會盡力協助本署進行操作維護訓練，務必使所蒐集的資料具有相當可靠性，如此數據才能與國際接軌。

Tekran 物種分析系統

以上所提之Tekran 1130/1135/2537A物種分析系統是目前可用於進行大氣汞分析研究之唯一一套系統。Model 2537A為分析主機，可分析氣態汞，其監測極限可達 0.1 ng/m^{3}以下，另外Model 1130 為選配儀器，可用於分析二價汞（即所謂的物種分析部分），其監測極限可達 3 pg/m^{3}以下。另外Model 1135 則為粒狀汞分析模組。此套儀器之概略圖示詳見下圖。

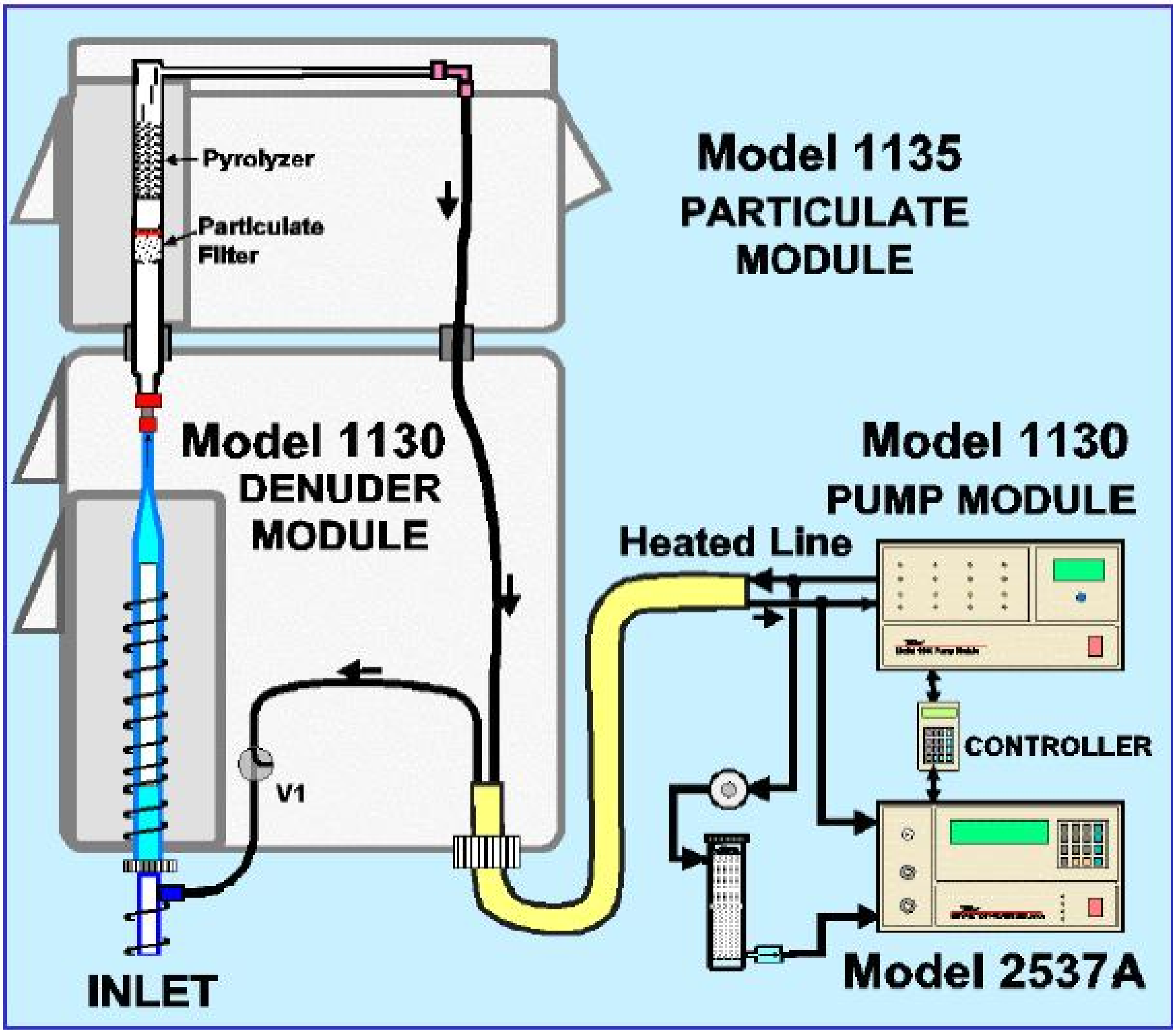


圖 4-1 Tekran 1130/1135/2537A 大氣汞物種分析系統簡略圖示

此套系統的操作溫度範圍相當廣（-40℃～50℃），也可依使用者設定成每小時採樣一次。有關它的採樣分析流程簡述如下：採樣入口(Inlet)須經預熱，採樣流速則為 10L/min^{-1}，接著通過加熱至 50℃的氯化鉀被覆環狀剝

離管，在此管內收集二價汞，接下來通過微粒過濾器單元，收集粒徑大於2.5um之粒狀汞，之後再通過一條加熱線路至Model 2537A來收集並分析氣態汞。建議最短之採樣時間訂於1小時，如此才可同時完成二價汞及粒狀汞的收集。在採樣的同時，Tekran 2537A可每5分鐘進行採樣及分析。待採樣完畢後，分別將過濾器以及剝離管加熱至800℃及500℃，如此可將粒狀汞及二價汞脫附，兩者加熱分解後，最後都會變成氣態汞，而再以Model 2537A分析。完成一個採樣循環後，系統先冷卻10分鐘，然後再進行另一個採樣分析循環。

此套分析分析方法以目前來說是最為先進的技術，它可分析大氣中3種最重要的汞物種，在全球的所有的NOAA背景站均放置此套儀器進行長期監測。

第五章 後續合作及考察心得

本署自 93 年度即著手規劃背景測站之設立，目前已規劃將背景測站設立於海拔約 2800 公尺之鹿林山上。因目前仍於規劃階段，此次行程的重要性就顯的相當大了。美國 NOAA/CMDL 已在全球設立多站背景測站，包含此次參觀的 Mauna Loa 背景測站，另美國 EPA 有鑑於大陸工業急速發展，其所製造的污染物有可能隨著氣流飄至台灣，甚至其他更遠的區域，因此美方對本署即將設置之背景測站抱持相當大的期待，因為若能建立一個更為完整的國際監測網路，對於將來污染物長程傳輸路徑的掌握一定更有信心，且能夠進一步研究污染物對於人體健康及生態的影響。對於這次的參訪主題：大氣汞監測技術，美國也是在近十多年才開始重視，許多重要的發現已是在這十年內得到，因此此次向他們學習是一個非常好的機會。

至於後續與美方的合作事項，也是在此次參訪中一個相當重要的議題，在夏威夷討論過後所預擬的期程安排詳如表 5-1。

此次參訪僅 7 天，茲依據心得提供幾點建議，以提供空氣監測規劃參考。

一、 美國的實驗室人員在儀器操作上完全遵照 SOP 進行，且維護同仁均具備儀器維護能力，如此可縮短儀器故障送修所須時間，增加數據可用率。

二、 美國 EPA 空品測站儀器的 QA/QC 是以多重稽核的方式進行，譬如說，由政府委辦進行儀器 QA/QC 的業者，同樣會有另一家廠商對其進行稽核，如此多重稽核的方式對於儀器數據品質的保障應有提昇。

三、 經與美方查詢，發現本署在空品監測所採購的儀器已算相當豐富，將來在本署的善加利用下一定可以逐步蒐集多項數據。

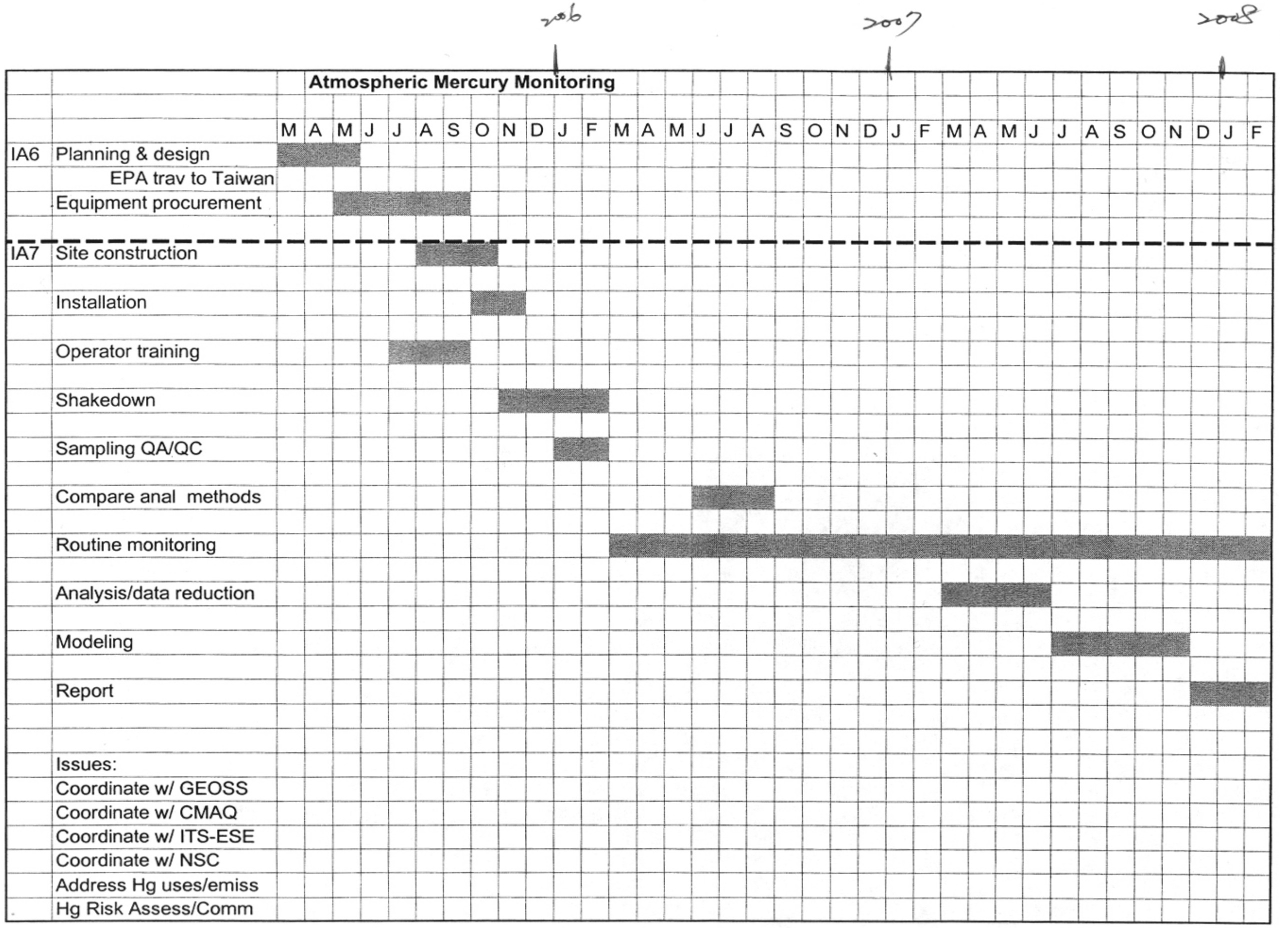


表 5-1 台美大氣汞監測技術合作預擬時程

附錄一

US International Mercury Initiative 2005

US International Mercury Initiative 2005

Background

- Responding to concerns that national and regional action was not sufficient to address mercury pollution, UNEP's Governing Council initiated the Global Mercury Assessment in February 2001.
- Summary of current science and other topics relevant to mercury
- Called for submissions from governments, IOs, NGOs, and industry
- Established open-ended working group to finalize report

http://chem.unep.ch/mercury

Key findings

- Hg is persistent and cycles globally
- Due to long-range transport, even nationsl with minimal Hg emissions and use and areas remote from industry can be affected
- Due to the contamination of fish, many humans and animals are at risk
- H2 may becoming more problemmatic in less developed regions
- Uses phased out in developed countries still are ongoing in developing countries
- Important sources of concern include: energy sector, waste treatment, and artisinal gold mining

Conclusions

There is sufficient evidence of significant global impact to warrant further international action

Better understanding is important but not necessary to start initiating action

The Governing Council:

- Urged all countries to adopt goals and take actions to identify exposed populations and reduce Hg releases
- Requested UNEP to facilitate technical assistance and capacity building
- Encouraged governments, IOs, and other partners to mobilize resources to support national, regional and global efforts and capacity building
- Agreed to continue discussions on need for further actions at 2005 session, including legally binding agreement, non-binding agreement, or other actions
- Agreed to consider what further action to take with regard to other heavy metals

UNEP Mercury Program 2003-2004

Focus on assisting countries ot understand and address Hg

- Building inventories of uses and releases
- Indentifying populations at risk
- Developing risk communication and outreach
- Initiating actions to reduce uses and releases, including promoting mercury-free products, technologies and processes and using environmentally friendly alternatives

Organize awareness raising workshops in Argentina, Lebanon, Senegal, South Africa, Thailand, Trinidad and Tobago, and Ukraine. Serve as an information clearinghouse.

Produce guidance materials for:

- Developing inventories of Hg releases
- Identifying populations at risk
- Risk communication
- Options to reduce Hg releases

In longer term:
- National and regional aciton plans
- Mobilize technical and financial resources

Future Challenges:
- Coordinate and cooperate with related programs: UNIDO, WHO, ILO, FAO, Convention Secretariats
- Promote consensus on global measures needed

The Future is here: 22nd Session of the UNEP Governing Council, February 2005, Nairobi

- The United States is encouraging UNEP to complete the uses and inventory guidance and to work with North American Commission for Environmental Cooperation (CEC) and the UNECE to compile an international mercury clearinghouse.

- Building on the foundation established by the UNEP Mercury Program, the U.S. calls on all stakeholders to support a series of activities to reduce mercury uses and releases.

- Action should be taken now to develop and implement a multi-stakeholder partnership to launch field activities to bring about effective mercury reductions. (This approach is envisioned as being similar to the "Partnership for Clean Fuels and Vehicles" that was launched at the WSSD.)

- Focusing on key sectors may bring about the greatest reductions in the shortest time. The U.S. proposes giving immediate attention to coal combustion, chlor-alkali, artisinal gold mining, products, as well as continuing research.

Chlor-alkali

- Develop best management practices for operation of mercury cell facilities building upon the World Chlorine Council Stewardship Seminars
- Encourage the use of secondary (recycled) mercury for replenishment
- Adopt suitable national policies for facilities
- Annual reporting of mercury consumption by facilities
- Develop guidelines for calculating mercury consumption
- Reach agreement on reporting methodology and timeframe
- Hold workshop within 12 months to share best practices

Products

- Reduce mercury releases from use in manufacturing processes, during the recycling or disposal of mercury-containing products and wastes
- Promote effective mercury-free alternatives
- Share information on
    - Alternative batteries and other products
    - Use inventories
    - Export and import data on commodity-grade mercury
- Facilitate successful approaches to reduce mercury use and waste in the health care sector
- Share regulatory experience

Artisinal Gold Mining

- Support the efforts under the UNEP Global Mercury Project
- Tailored community outreach and education on risk
- Reduce occupational exposures
- Information sharing
- Develop plan of action for regional cooperation on mercury contamination in the Amazon Basin

- Improve emissions monitoring, data collection, and reporting
- Transfer best practices and demonstrate appropriate technologies
- Provide technical support for voluntary cost-effective operational practices aimed at reduce air emissions of mercury

Coal-fired Power Sector

- Share information and experience and assist countries in evaluating and addressing mercury emissions from coal combustion sources
- Conduct workshops
- Evaluate and demonstrate technologies
- Improve understanding of magnitude, nature (speciation) and impact of mercury emissions from coal-fired power plants
- Support measuring and monitoring programs
- Assist with inventory development
- Because reducing other air pollutants (PM, SO2, Nox) can have co-benefit of reducing mercury, increase knowledge of cost-effective multi-pollutant approaches
- Provide information on applicability, effectiveness, and cost of emerging mercury specific technologies for various coal types and facility configurations

Research

- Structured and collaborative approach to fate and transport research
- Accelerate the development of knowledge and its dissemination between scientists and policy makers
- Reduce uncertainty over the global cycling of mercury
- Increase number of national release inventories
- Standardize/harmonize methods of measurement to increase accuracy of modeling
- Coordinate with Global Earth Observation System of Systems

- Joint field work, inter-laboratory exchanges of personnel, promote face-to-face meetings of scientists and policy-makers
- Host workshops, set up a clearinghouse for monitoring and modeling activities
- Facilitate inter-calibration activities (QA/QC)

Call for partnership

- A partner is any entity who indicates a willingness to contribute either time, resources, and/or experience to implement the objectives of the partnership to achieve concrete reductions in the uses and releases of mercury
- the US is prepared to commit to providing more than $1 million for these efforts in 2005

Addendum

- the US is supportive of further guidance on mercury reduction from waste incineration should other governments be interested
- the US encourages governments and stakeholders to call upon the WHO-FAO to promote and improve the evaluation methods and public health messages that enable citizens to make health-protective dietary choices concerning fish consumption

This Week's Discussion

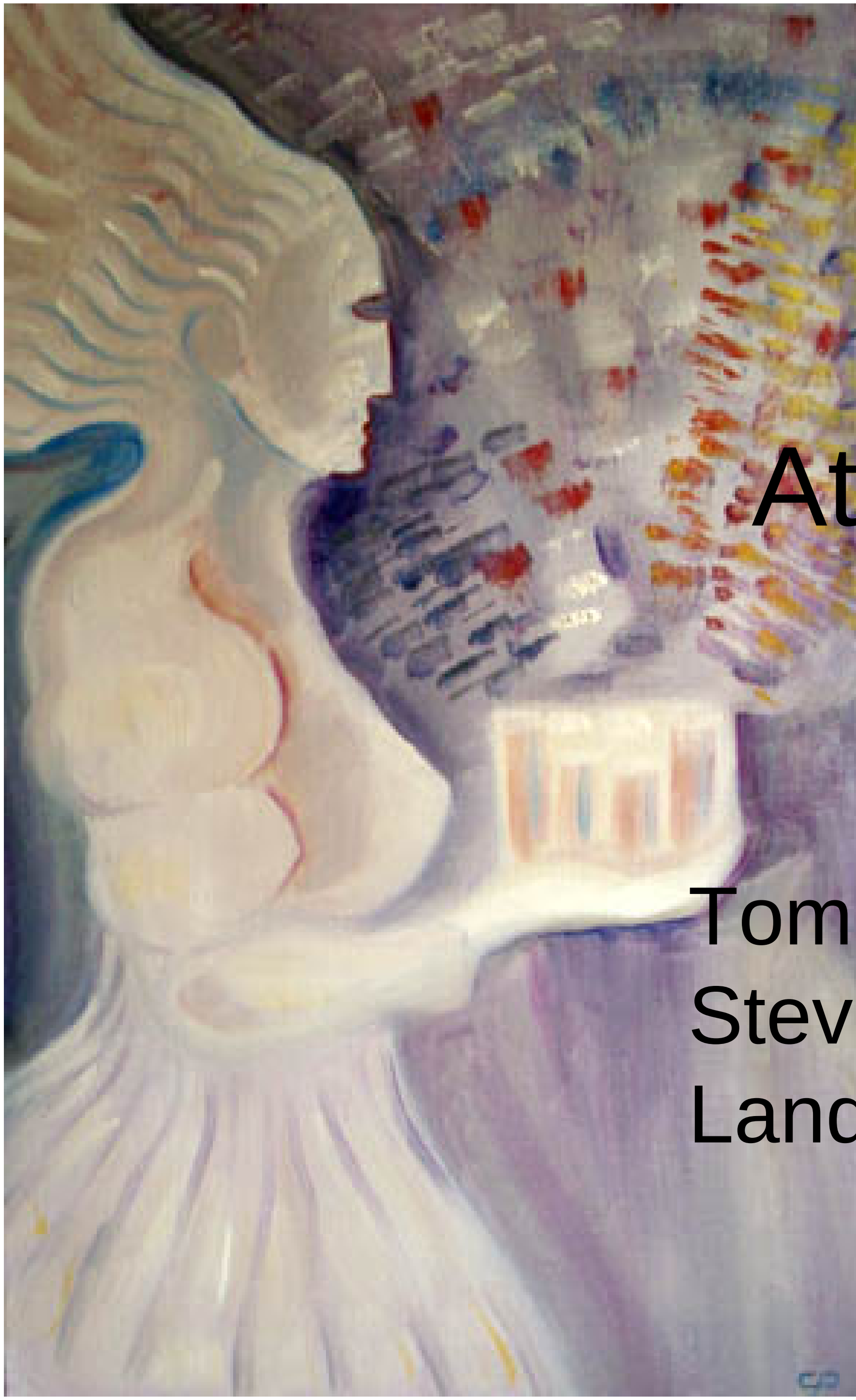
U.S. EPA – EPA Taiwan Cooperation

rstevens4 @ nc.rr.com
stevens.robert-R @ epa.com

附錄二

Atmospheric Mercury: Pandora's Box?

Department of Environmental Protection
Florida



Atmospheric Mercury: Pandora's Box ?

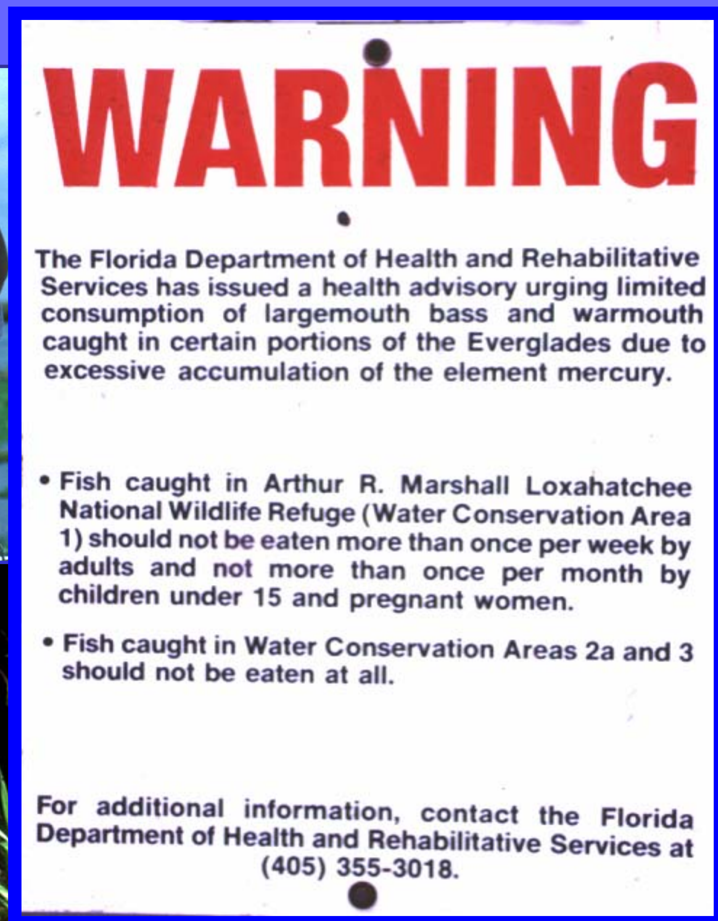
Tom Atkeson, Robert K. Stevens(FLDEP) & Matt Landis(USEPA)

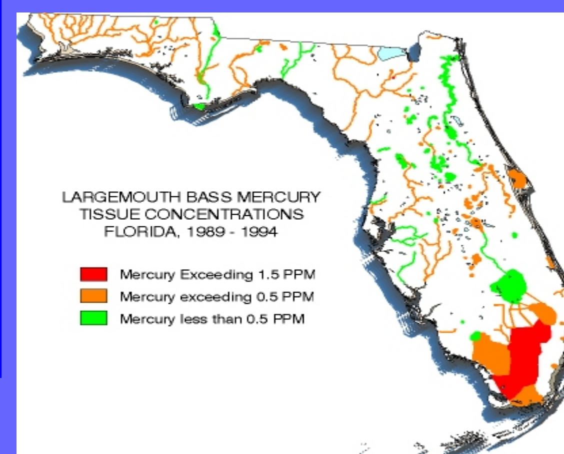
‘It is the hottest, the coldest, a true healer, a wicked murder, a precious medicine and a deadly poison, a friend that can flatter and lie.’

Woodall, J. 1639. *The Surgeon’s Mate, or Military and Domestic Surgery.* London


Hg
Hg
Hg

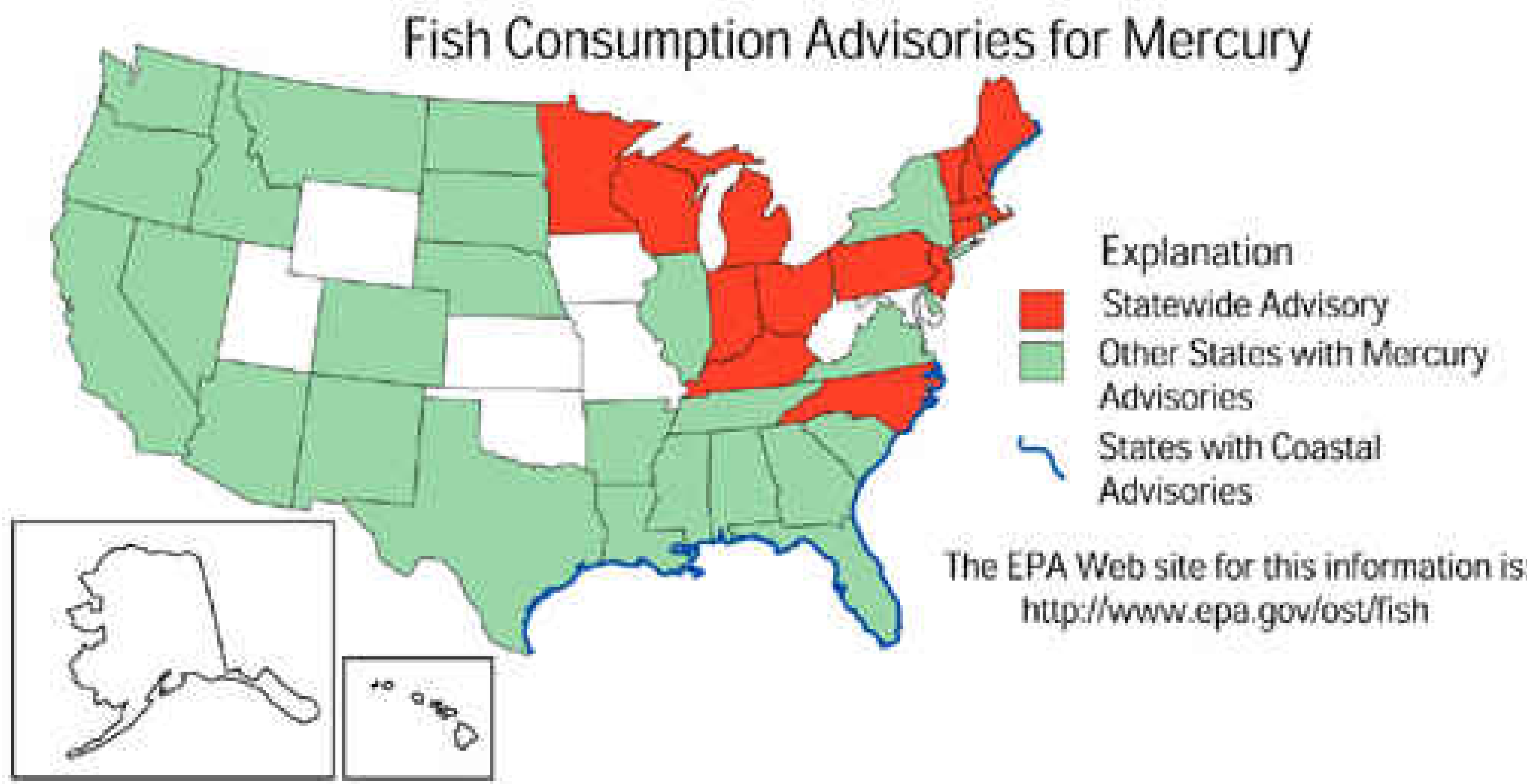
MERCURY The Problem





MERCURY

Health Advisory Status



S. Fla. Mercury Science Program

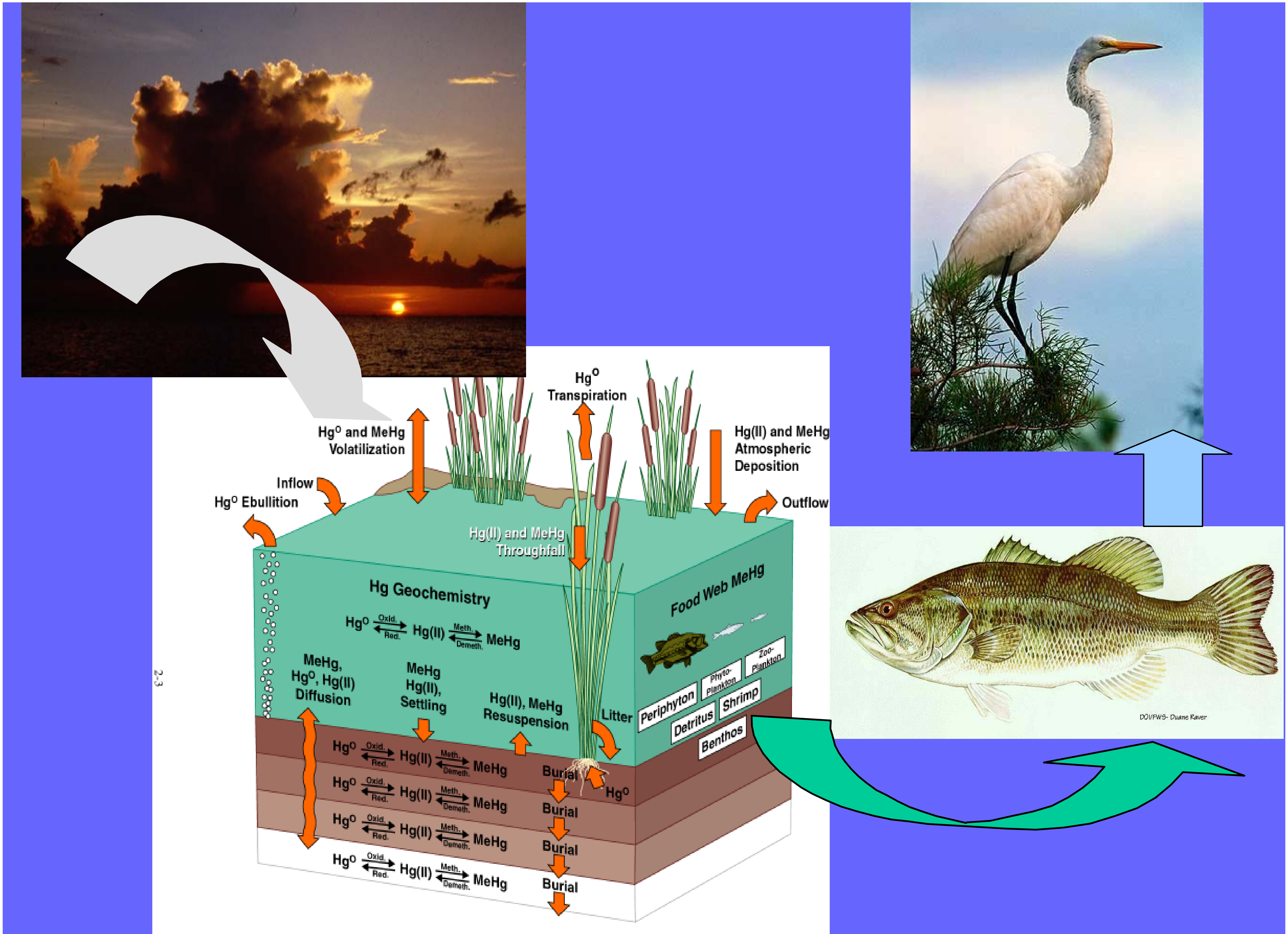
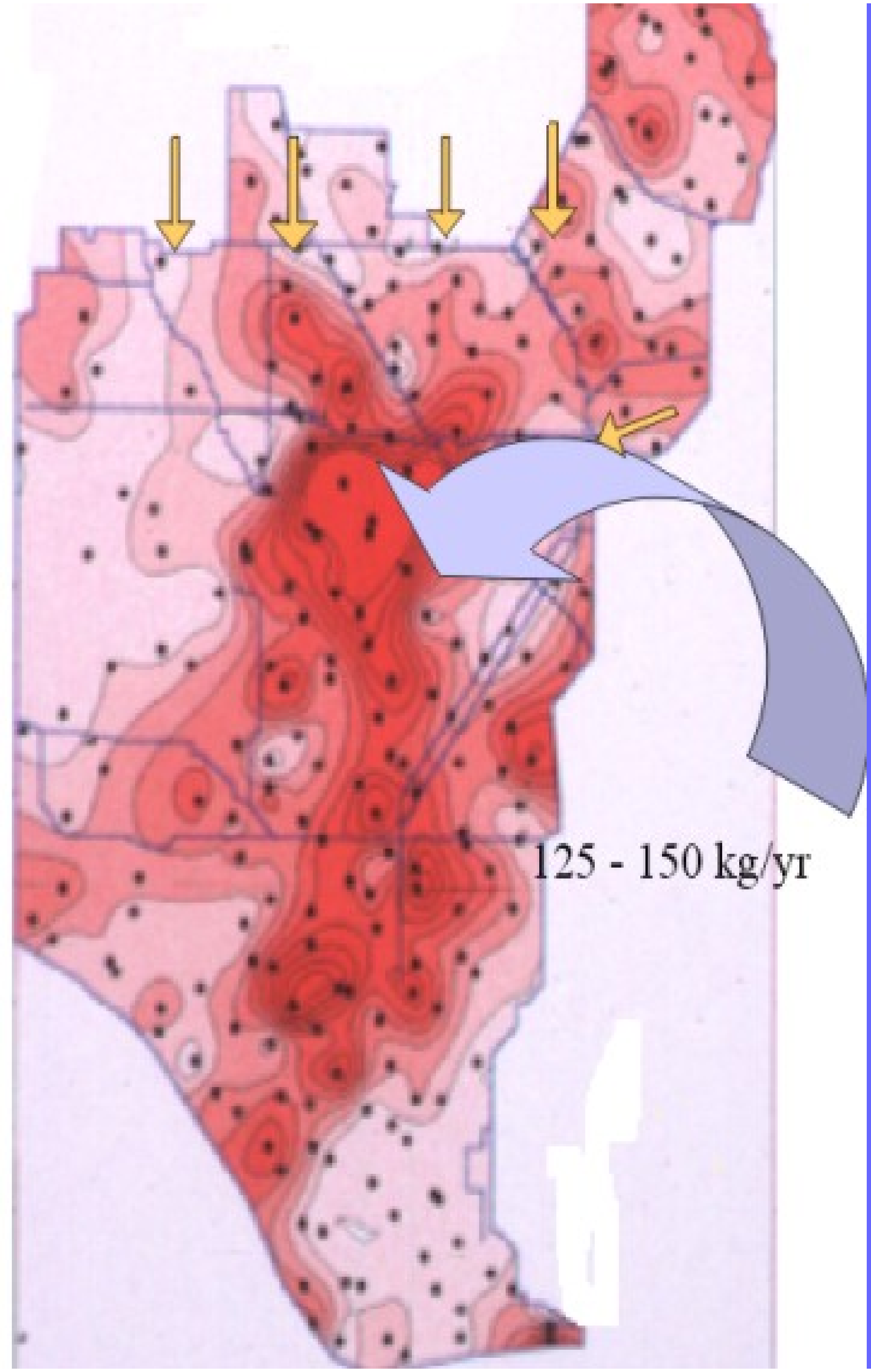


Figure 1. Conceptual model of Hg cycle in Everglades Hg Model

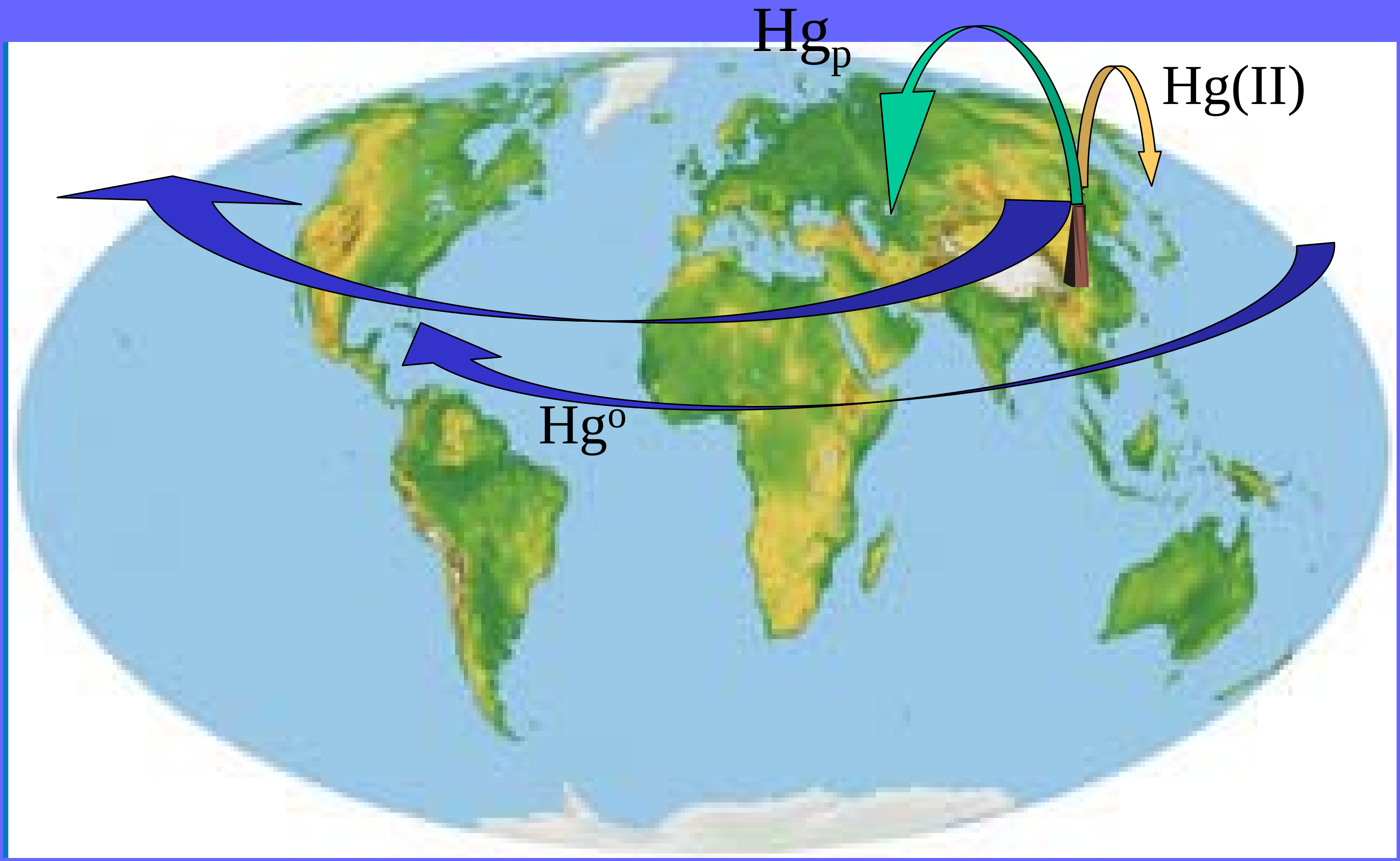


~ 98 %
Atmospheric

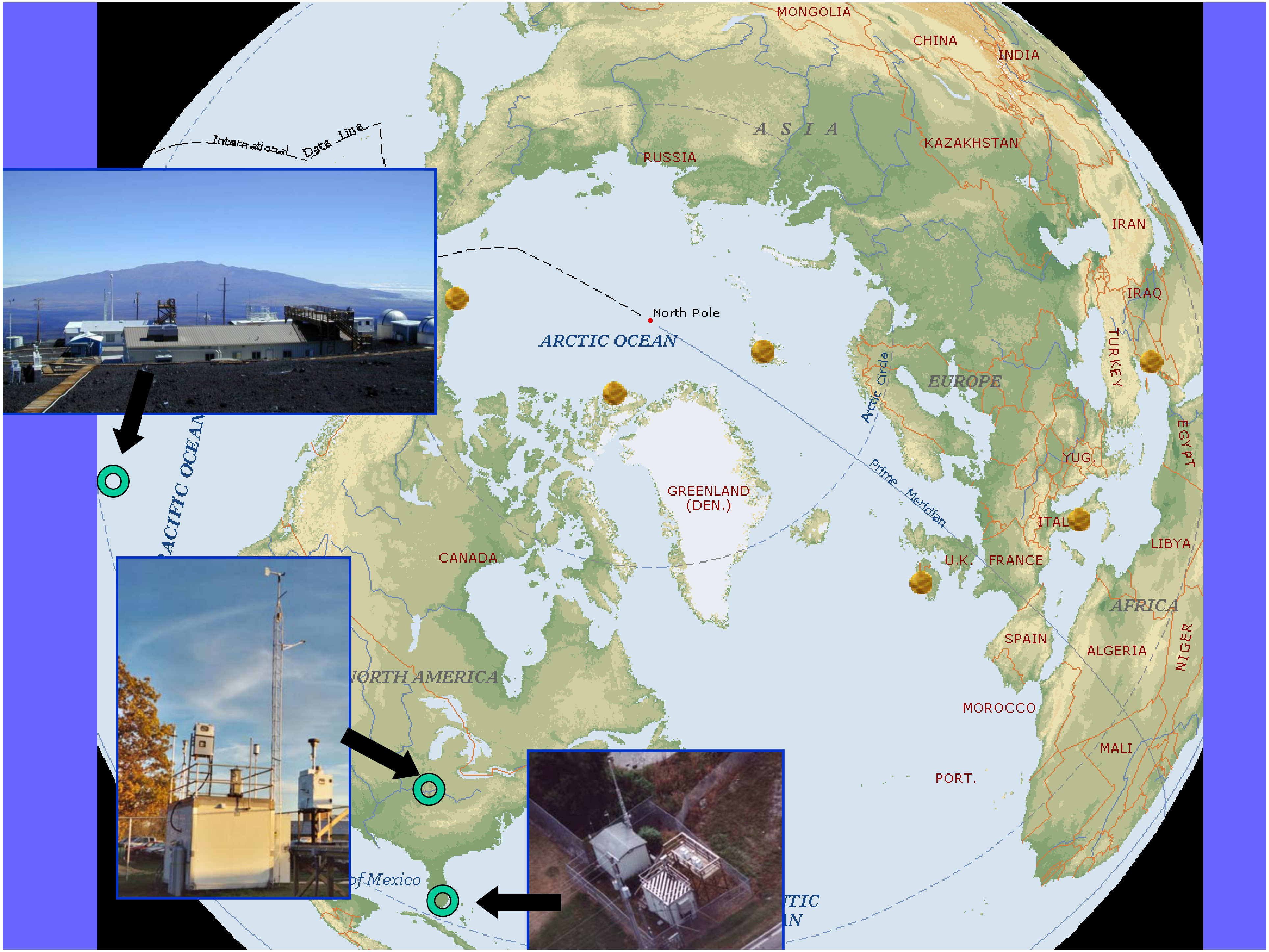
Where does the mercury come from?

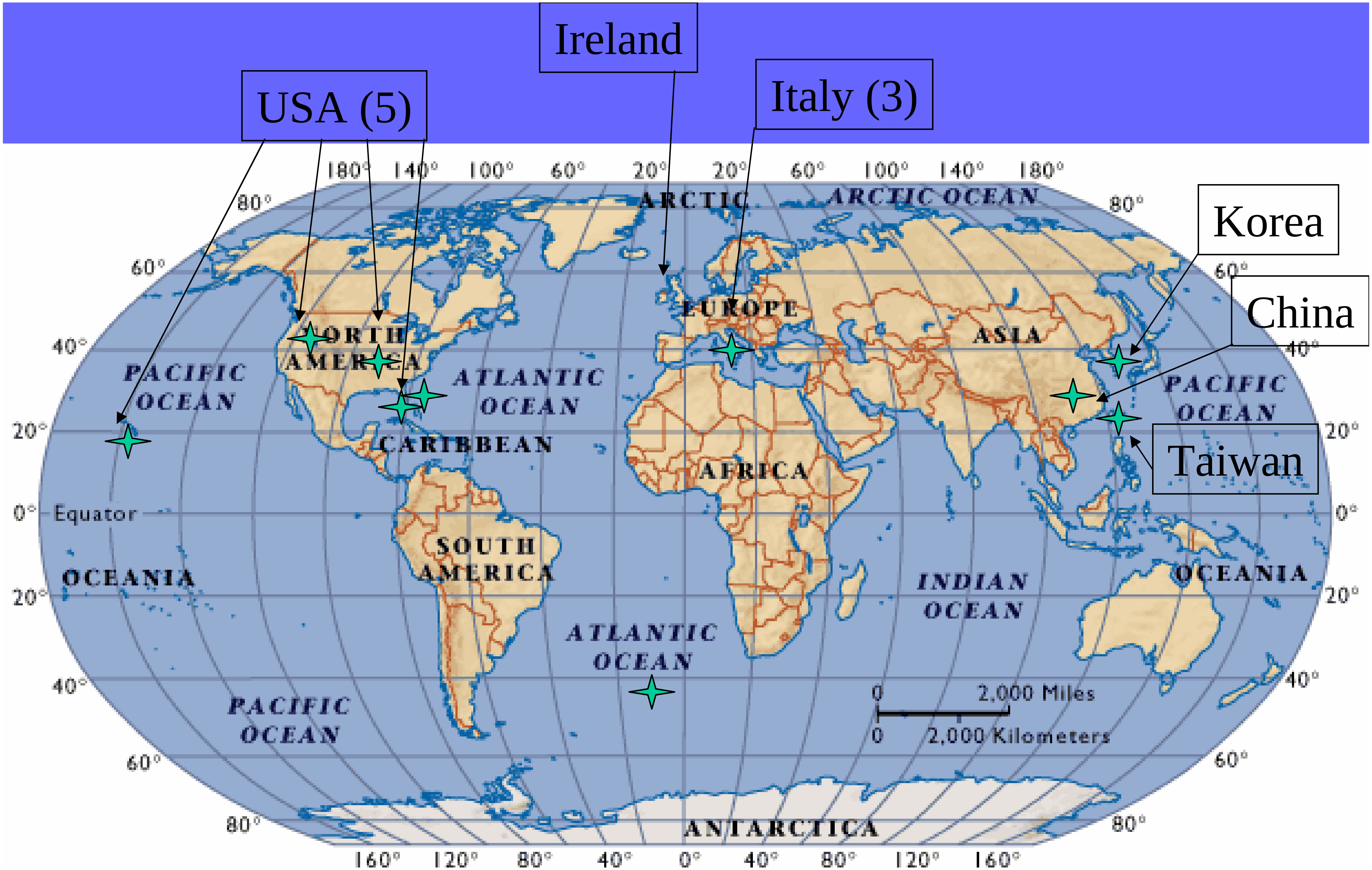
What we think we know about the ‘Global’ Cycle?

Atmospheric Mercury Cycle - 3 Spatial Scales



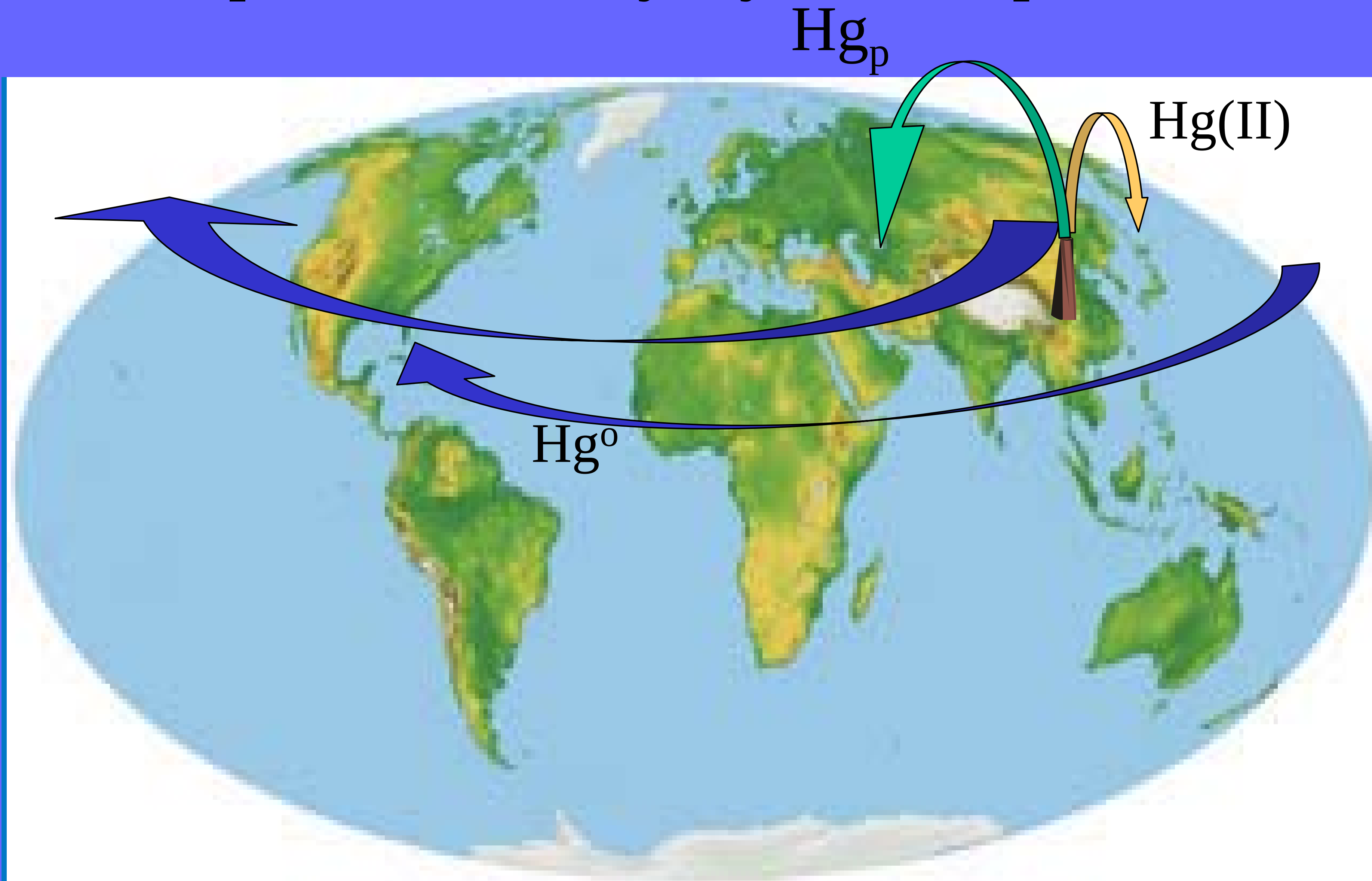
Global - Regional - Local


MONGOLIA
CHINA
INDIA
International Date Line
A S I A
KAZAKHSTAN
RUSSIA
IRAN
IRAQ
North Pole
ARCTIC OCEAN
TURKEY
Arctic Circle
EUROPE
EGYPT
PACIFIC OCEAN
YUG.
Prime Meridian
GREENLAND
(DEN.)
ITALY
LIBYA
CANADA
U.K.
FRANCE
AFRICA
SPAIN
ALGERIA
NIGER
NORTH AMERICA
MOROCCO
MALI
PORT.
Gulf of Mexico
ATLANTIC OCEAN



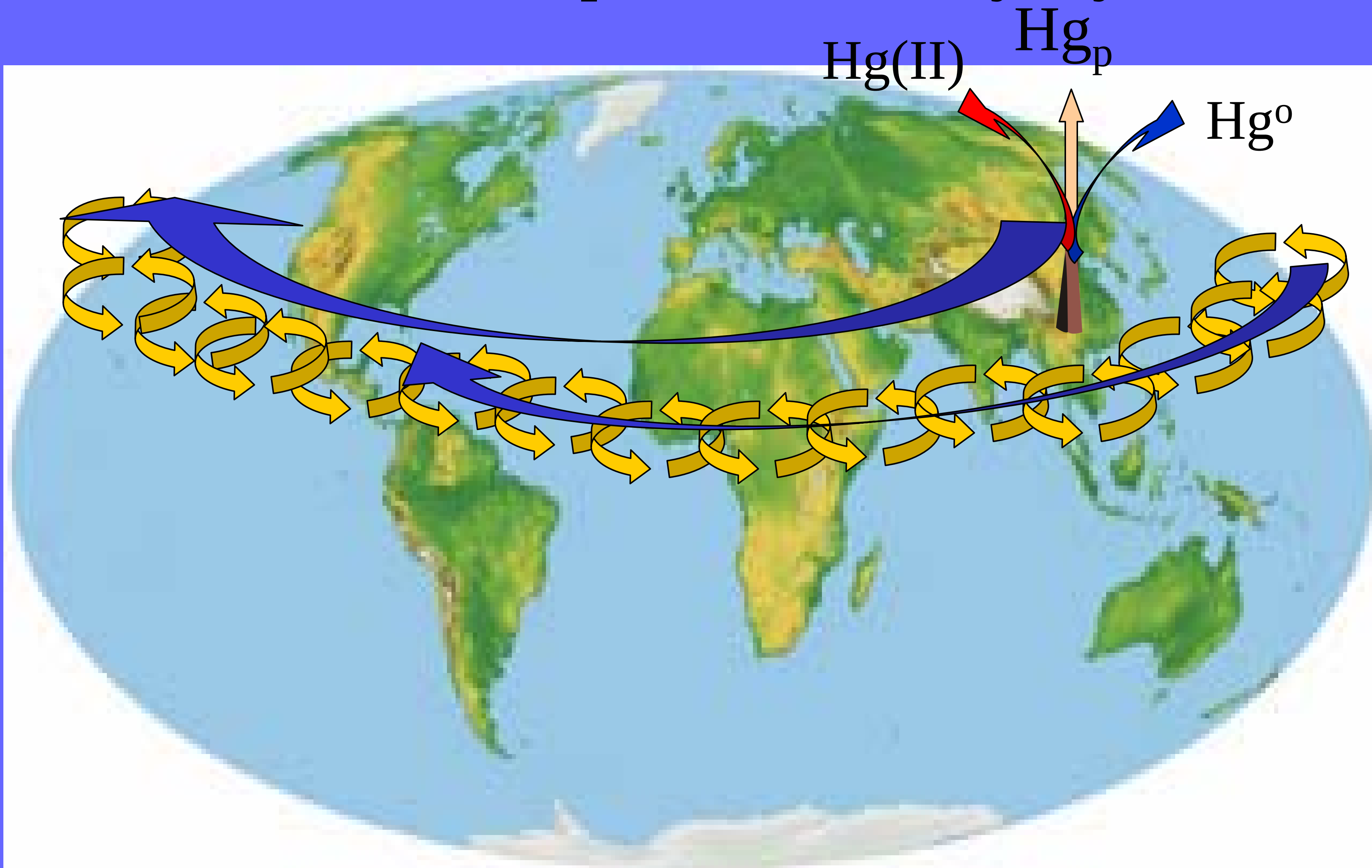
Nascent Global Network of Mercury Super Sites

Atmospheric Mercury Cycle - 3 Spatial Scales



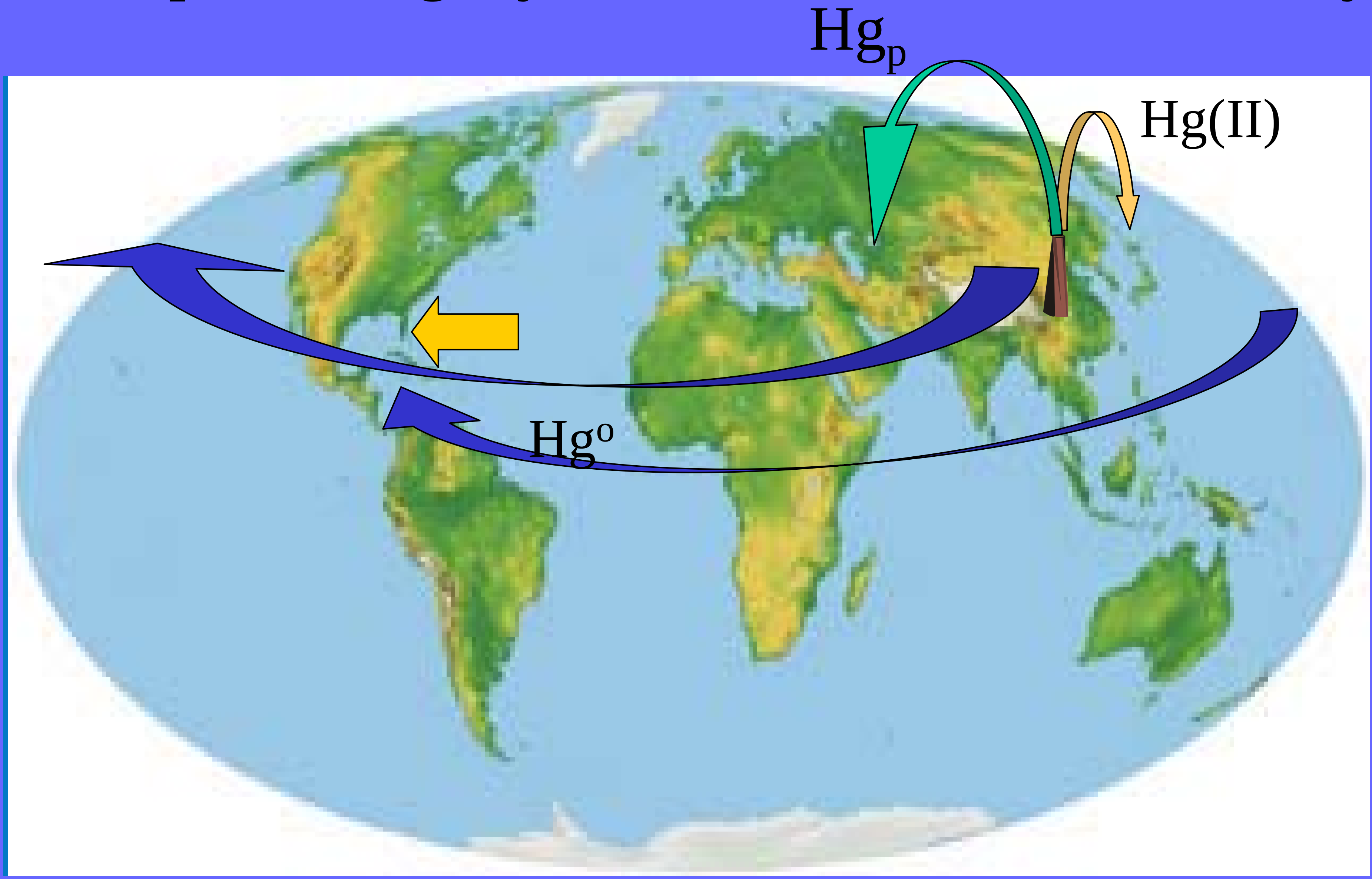
Global - Regional - Local

Global Atmospheric Mercury Cycle ?



Rapid Oxidation, Deposition, Evasion, ad infinitum ?

Atmospheric Hg Cycle – Marine Photochemistry

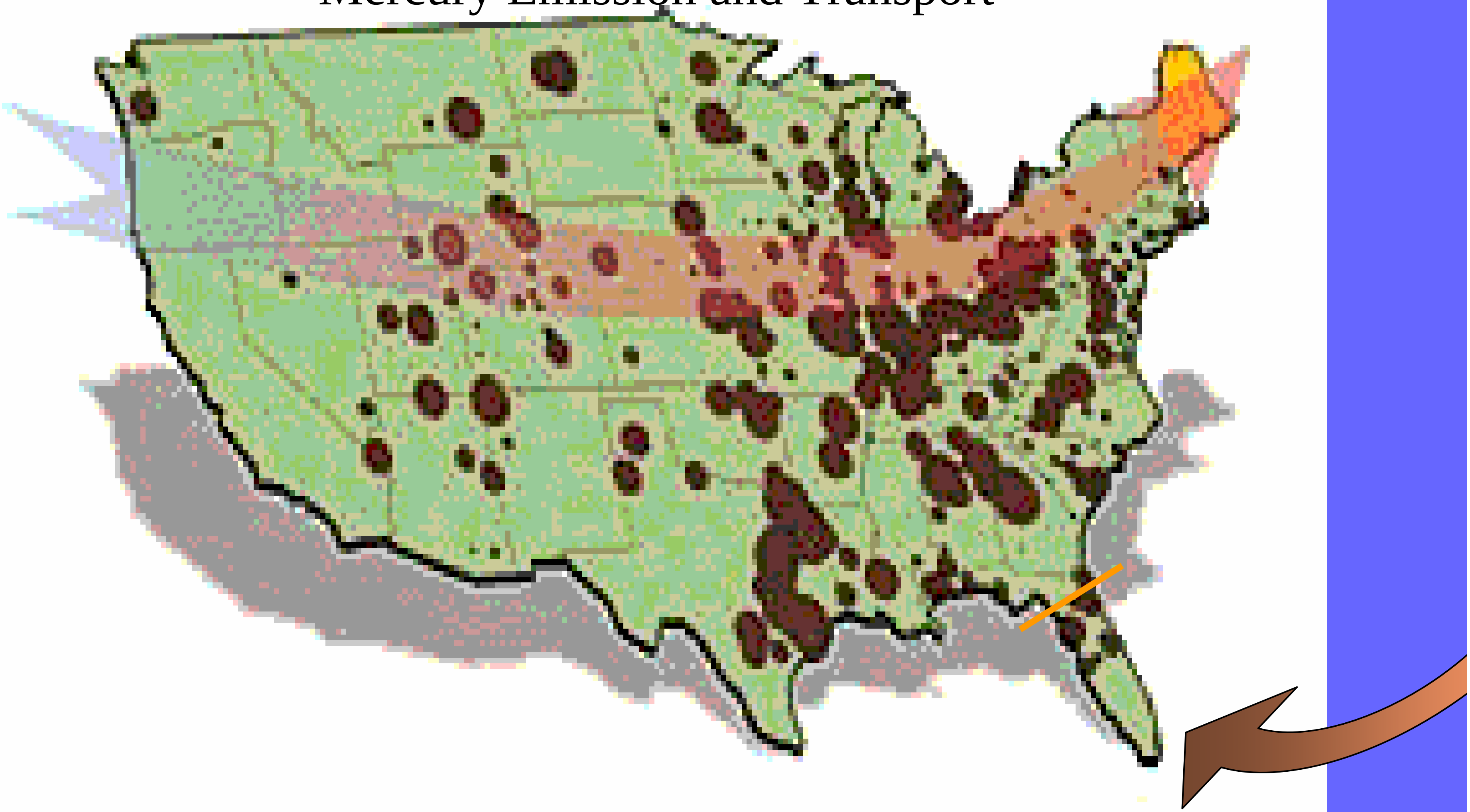


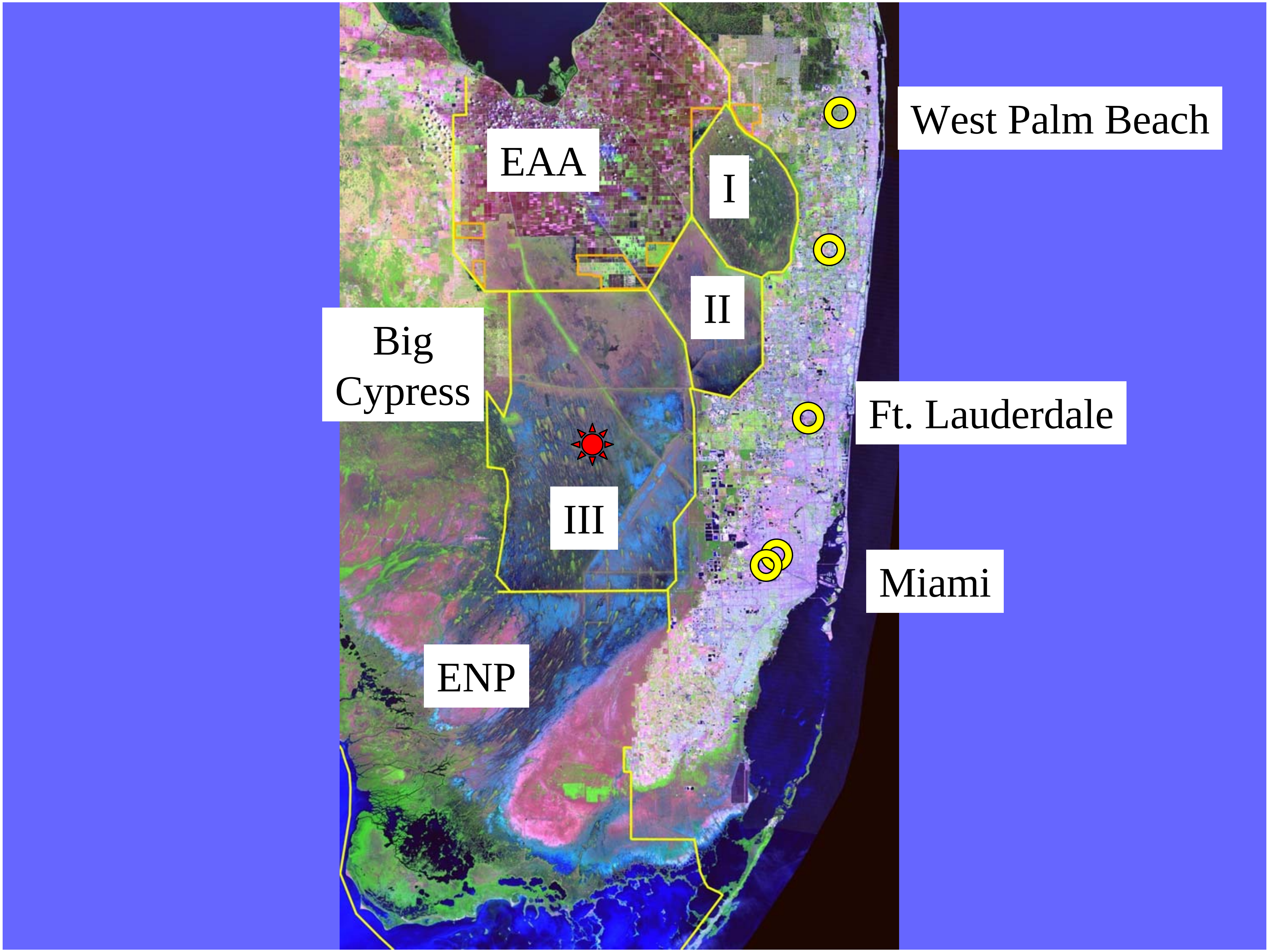
RGM Production: Marine Boundary Layer??

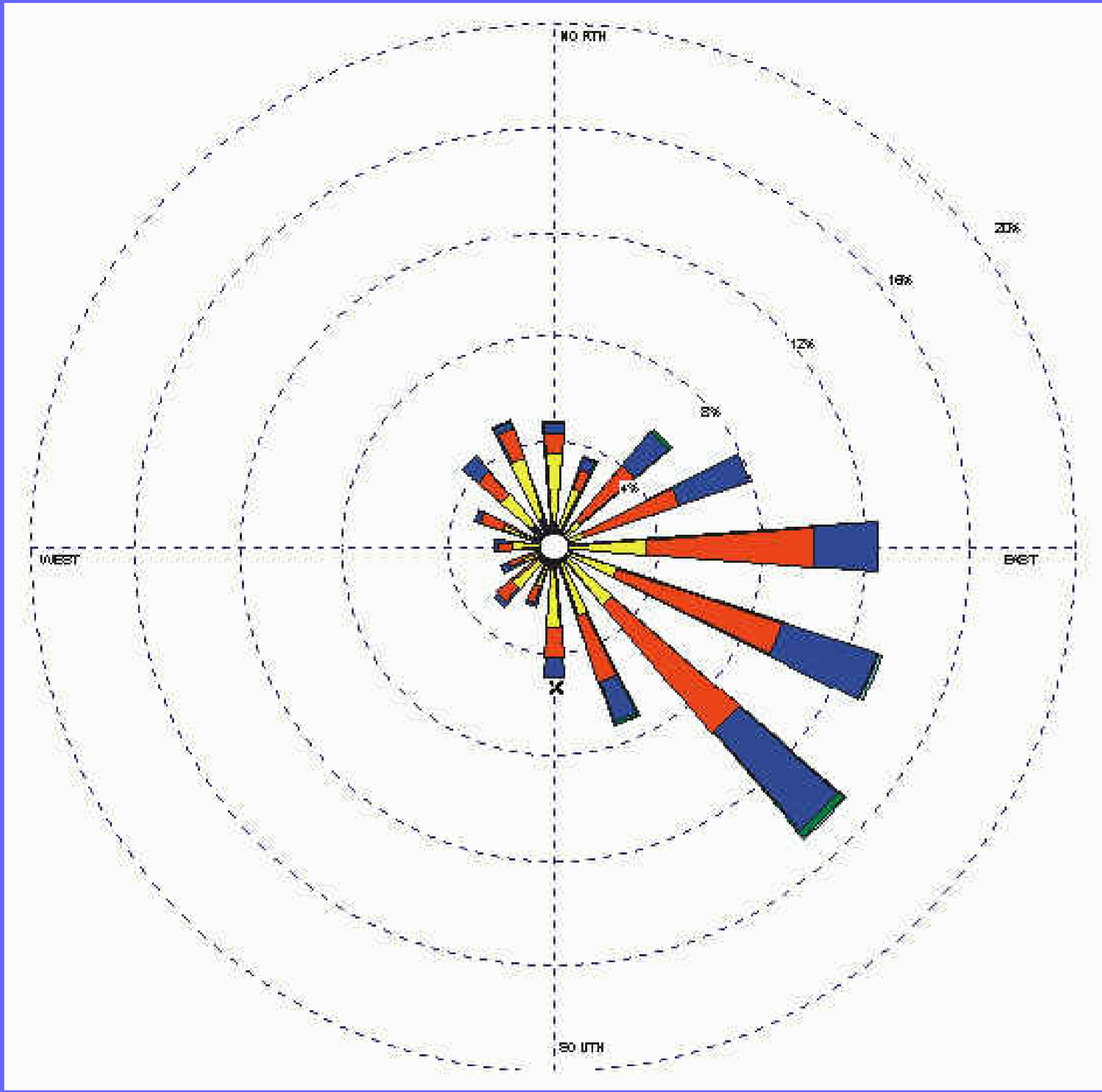
Where does the mercury come from?

The Big Picture

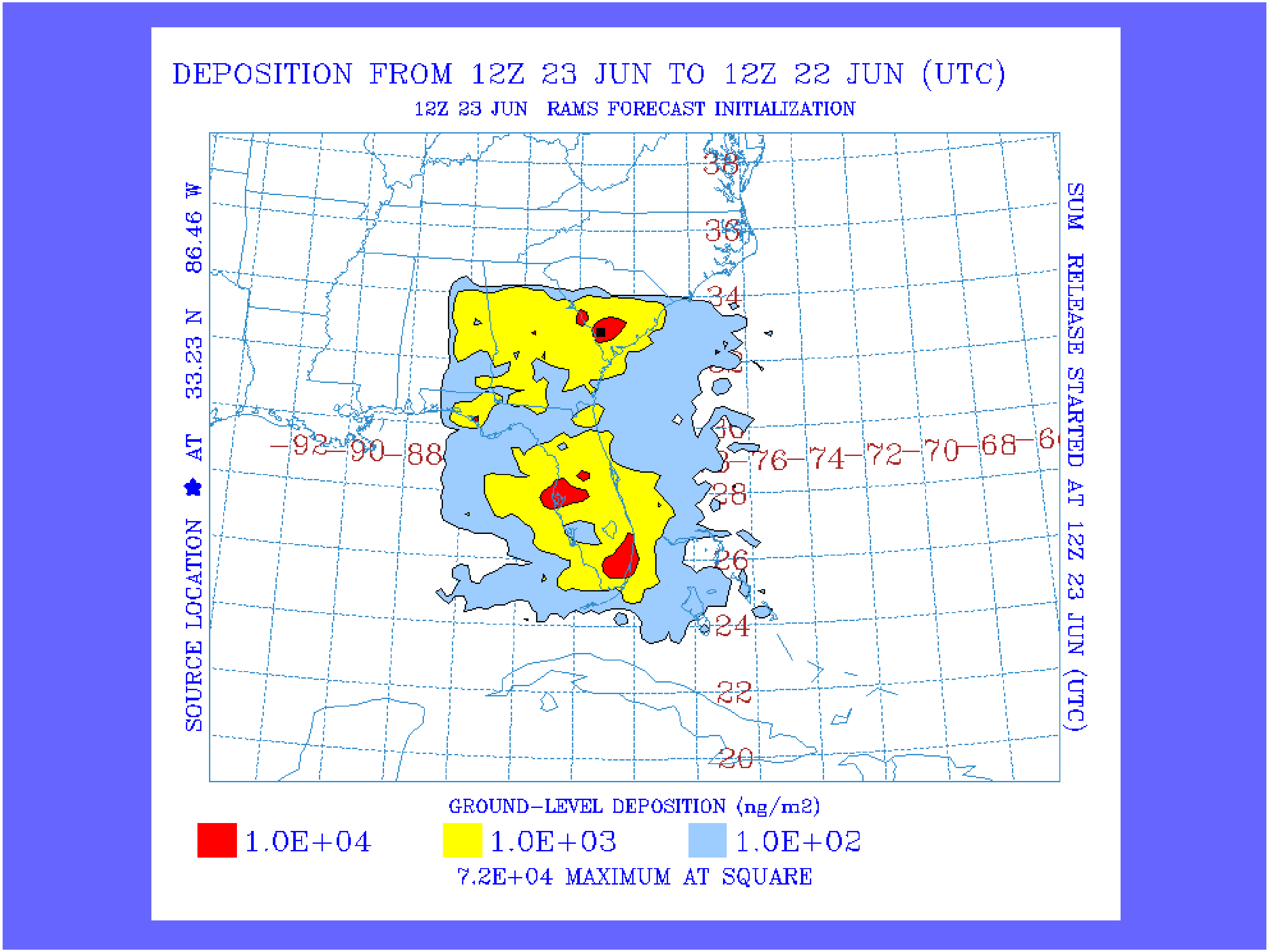
Mercury Emission and Transport




West Palm Beach
EAA
I
II
Big Cypress
Ft. Lauderdale
III
Miami
ENP



Wind Rose: Miami, Fla., Summer 6 mos., 1992


DEPOSITION FROM 12Z 23 JUN TO 12Z 22 JUN (UTC)
12Z 23 JUN RAMS FORECAST INITIALIZATION
SOURCE LOCATION ★ AT 33.23 N 86.46 W
SUM RELEASE STARTED AT 12Z 23 JUN (UTC)
GROUND-LEVEL DEPOSITION (ng/m2)
1.0E+04
1.0E+03
1.0E+02
7.2E+04 MAXIMUM AT SQUARE

> 50% Local Sources

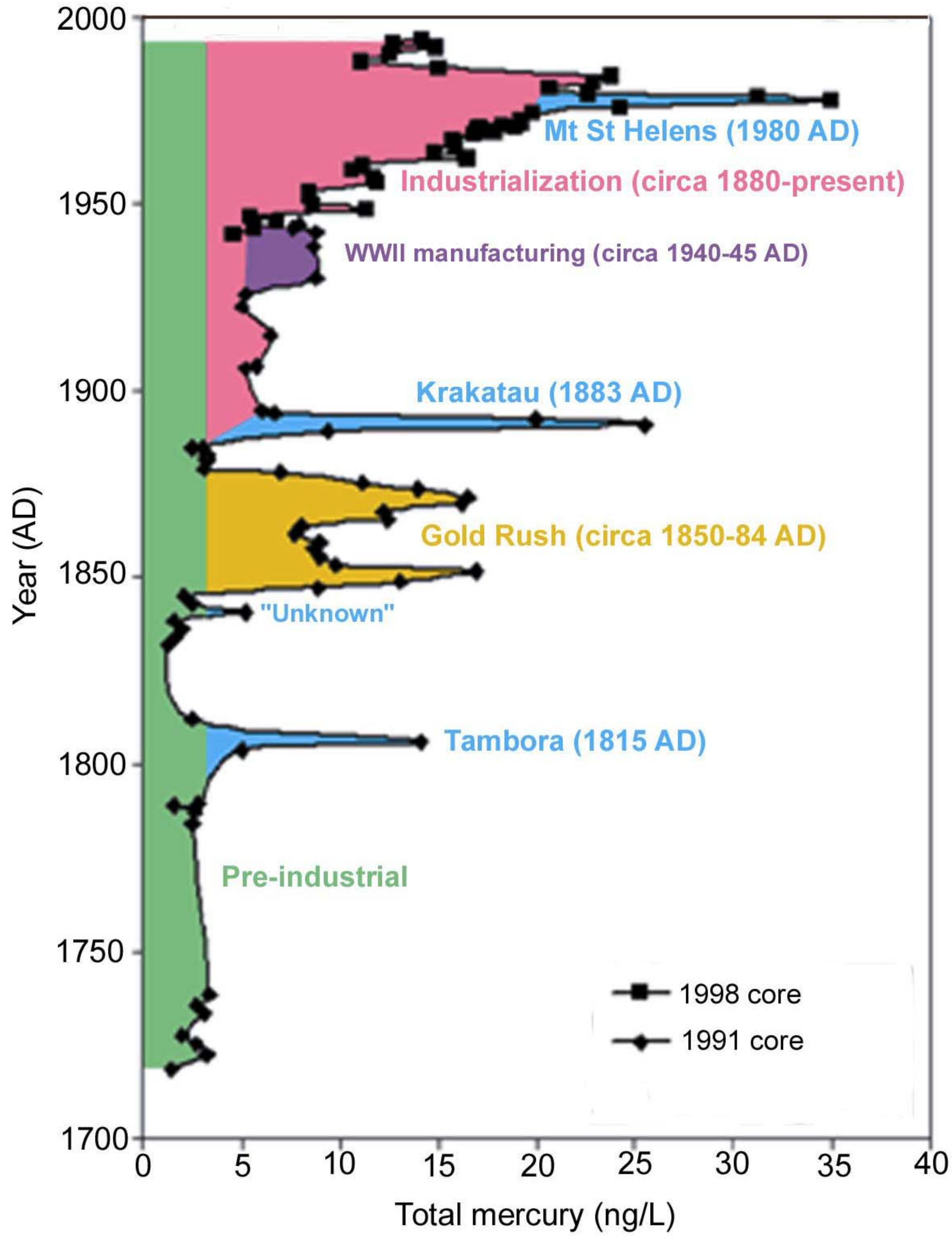
Florida Mercury TMDL Pilot Study

Mercury Trends

Recent Data From Florida

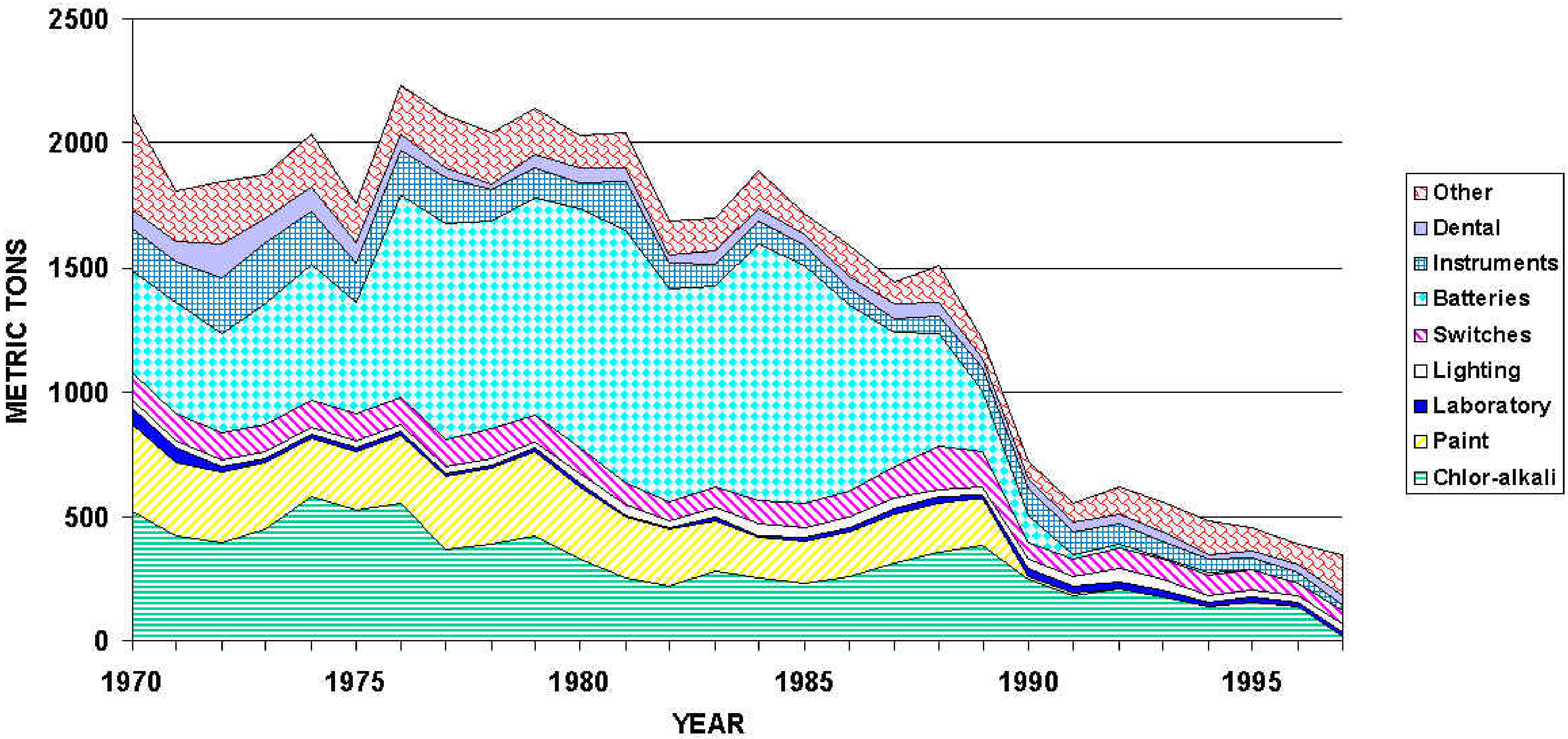
& Elsewhere

Figure 2



Mt St Helens (1980 AD)
Industrialization (circa 1880-present)
WWII manufacturing (circa 1940-45 AD)
Krakatau (1883 AD)
Gold Rush (circa 1850-84 AD)
"Unknown"
Tambora (1815 AD)
Pre-industrial
1998 core
1991 core
Year (AD)
2000
1950
1900
1850
1800
1750
1700
0
5
10
15
20
25
30
35
40
Total mercury (ng/L)

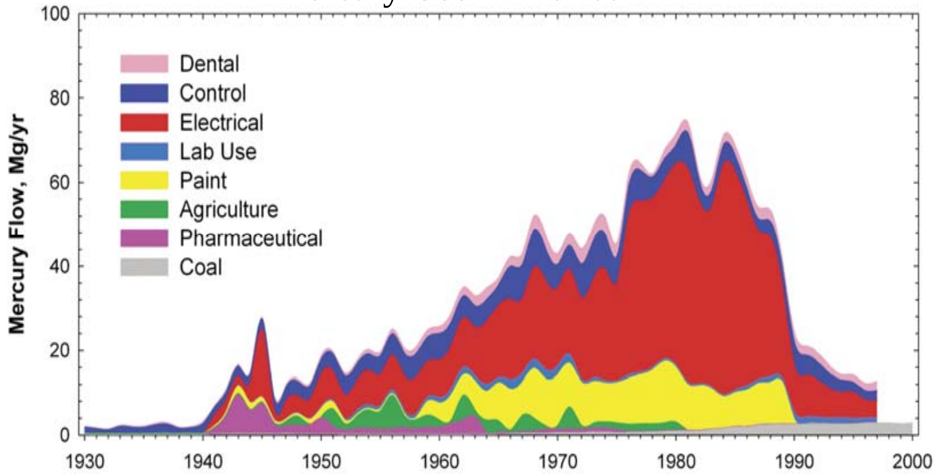

Materials Flow Cycle
Commodity supply
Production and manufacturing
Utilization
Waste or losses
Waste or losses
Post-consumer discards
Recycled flow
Recycling
Landfills, impoundments, deep wells, and ocean disposal
Renewable and nonrenewable resources
Environment
Releases to air, land, and water



2500
2000
1500
1000
500
0
METRIC TONS
1970
1975
1980
1985
1990
1995
YEAR
Other
Dental
Instruments
Batteries
Switches
Lighting
Laboratory
Paint
Chlor-alkali

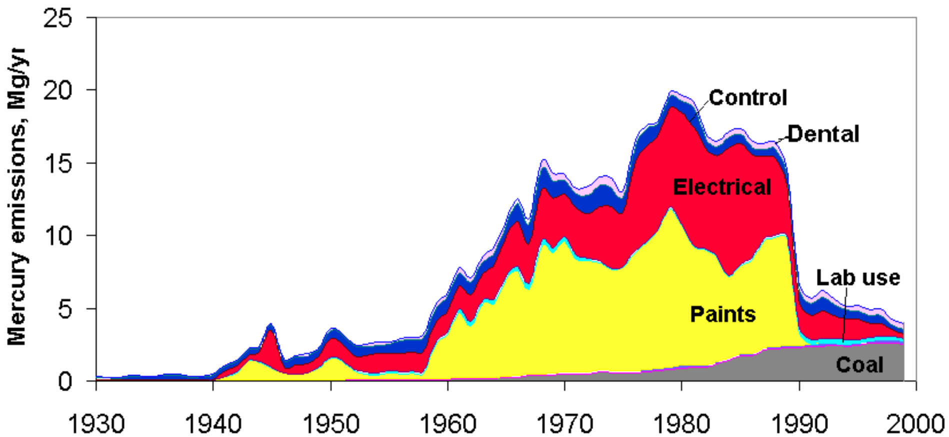
MERCURY Trends in Florida

Mercury Use in Florida



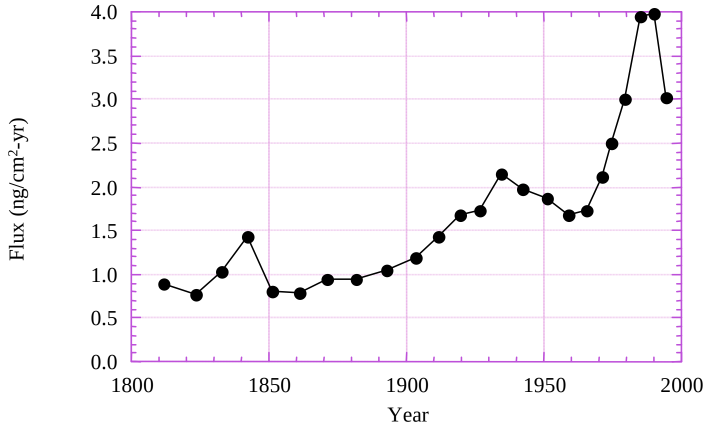
Husar & Husar, 2002

Trend of anthropogenic Hg emissions in Florida



RMB Consulting & Research, 2002

Net Accumulation Rate of Hg at Coring Site F3 in WCA-2A



Data and models: R. Abelak, C. Holmes, G. Keeler, R. Reddy, an d J. Robbins.

MERCURY : The Bottom Line

- Reduction of atmospheric sources of mercury from within Florida has led to ~ 60% declines in mercury in Everglades fish and wildlife in less than 15 years since peak deposition.
- To the extent that mercury emissions are in the reactive form (RGM) one can expect to see benefits at local or regional scale within years to decades.
- The main driver of the Everglades mercury problem is mercury load - overwhelmingly from atmospheric deposition.
- There is synergy with co-deposition of Hg & Sulfate, which combine to exacerbate Hg methylation.

Challenges: Do We Have All The Answers ?

- Mercury Health Advisories are Prominent in the Atlantic and Gulf Coastal Plains
- Coastal Regions are disproportionately influenced by long-distance transport off the oceans
- Despite declines in local emissions of Hg, wet deposition in S. Florida is the highest in USA
- Trends outside of South Florida are shallow or nil

Atmospheric Hg Science Needs

- Sustain the the EPA / FL DEP Mercury speciation sites
  - How do Urban Plumes Interact with Hg Species?
  - What are the Mercury Removal Mechanisms?
  - Need Controlled Lab Studies of Hg Transformations
- Expand Background Hg Monitoring Sites Globally
  - New Background Sites in So. Hemisphere and Asia
  - Track Long-term trends of mercury in the atmosphere
  - Global-scale Mercury Modeling Capability
- Significant Everglades Mercury Problems Remain
  - High Biotransformation and Bioaccumulation in STA-2
  - ENP and STA2, especially cell 1, continue to show high levels MeHg and bioaccumulation

Truth crushed to earth
shall rise again;
the eternal years of God are hers.

But error, wounded,
writhes with pain,
and dies among his worshipers.

— *Bryant*

附錄三

Monitoring and Modeling Atmospheric Mercury Species in Support of Local, Regional, and Global Modeling

Monitoring and Modeling Atmospheric Mercury Species in Support of Local, Regional, and Global Modeling

Atmospheric Mercury Monitoring Workshop

February 24, 2005

Waikoloa, Hawaii

Matthew S. Landis

U.S. EPA Office of Research and Development, RTP, NC

EPA Mercury Research Strategy

Transport, Transformation & Fate Research Question

"How much methyl mercury in fish consumed by the U.S. population is contributed by U.S. emissions relative to other sources of mercury (such as natural sources, emissions from sources in other countries, and re-emissions from the global pool); how much and over what time period, will levels of methyl mercury in fish in the U.S. decrease due to reductions in environmental releases from U.S. sources?"

ORD Mercury Research Strategy:

- Develop/Evaluate Ambient Speciation Methods
  - Vapor and Particulate Phase Mercury
- Atmospheric Transport & Transformation
  - Atlantic
    - Coral Springs (Florida) & Aircraft Measurements
  - Pacific
    - Cheeka Peak (Washington) & Mauna Loa (Hawaii)
  - Polar
    - Barrow (Alaska), Ny-Alesund (Norway) & Terra Nova Bay (Antarctica)
  - Laboratory Halide Kinetics
- Quantify Impacts from Specific Source Types
  - Coal Combustion
  - Mercury Cell Chlor-Alkali
  - Hospital Waste Incineration
  - Mobile Sources

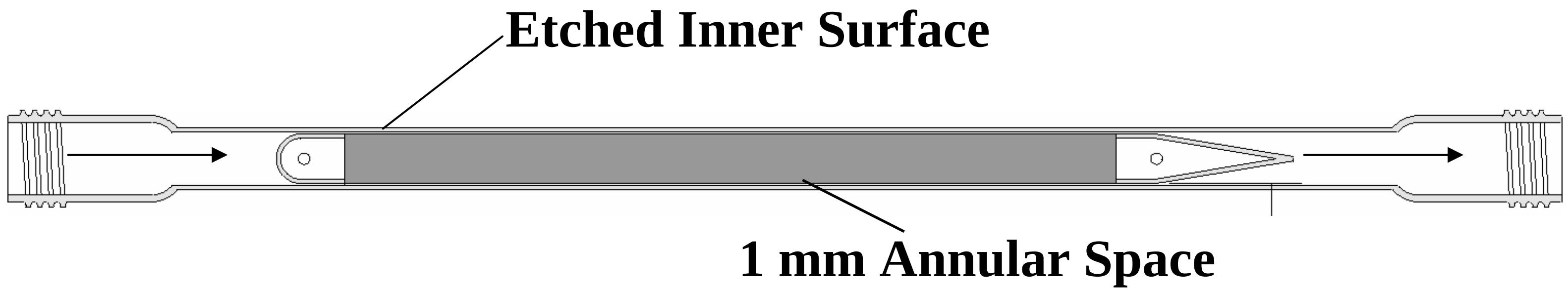
Why Speciate Mercury?

- **Species have Different Behaviors**
  - Elemental Mercury: Hg^0
  - Reactive Mercury: Hg^{2+}
  - Particulate Mercury: Hg(p)
- **Atmospheric Transport & Deposition Modeling**
- **Bioaccumulation, Exposure & Risk Assessment**

Ambient RGM Methodologies

- **Impregnated Filters**
- **Refluxing Mist Chamber**
- **Denuders**
  - Tubular
  - Annular

Quartz Annular Denuder



Manual Denuder Sampling Box

Quartz Thermal Filter Pack

Standard Filter Pack

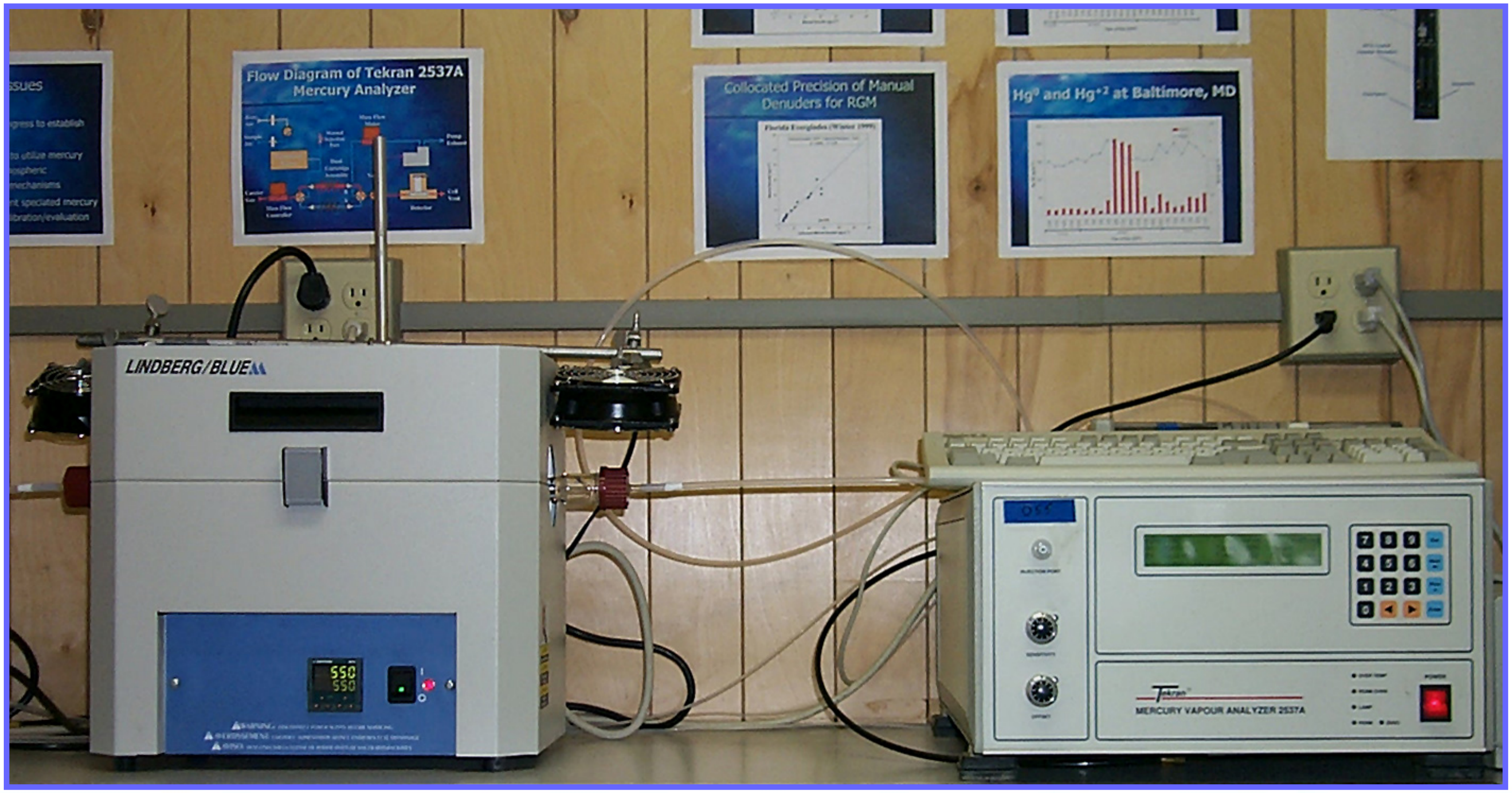
KCL - coated Annular Denuders

Elutriators

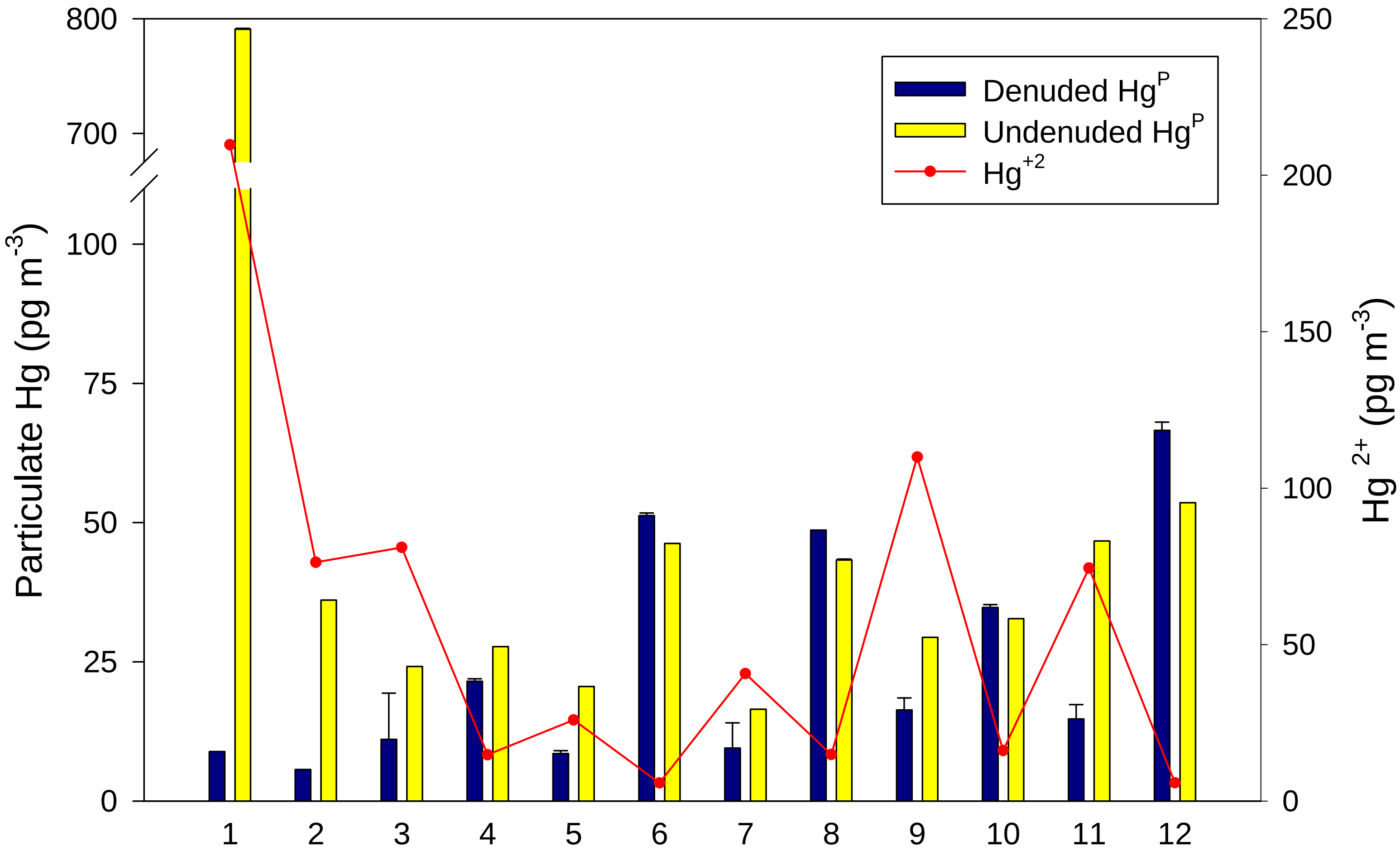
Sampling Box Heaters

Impactors

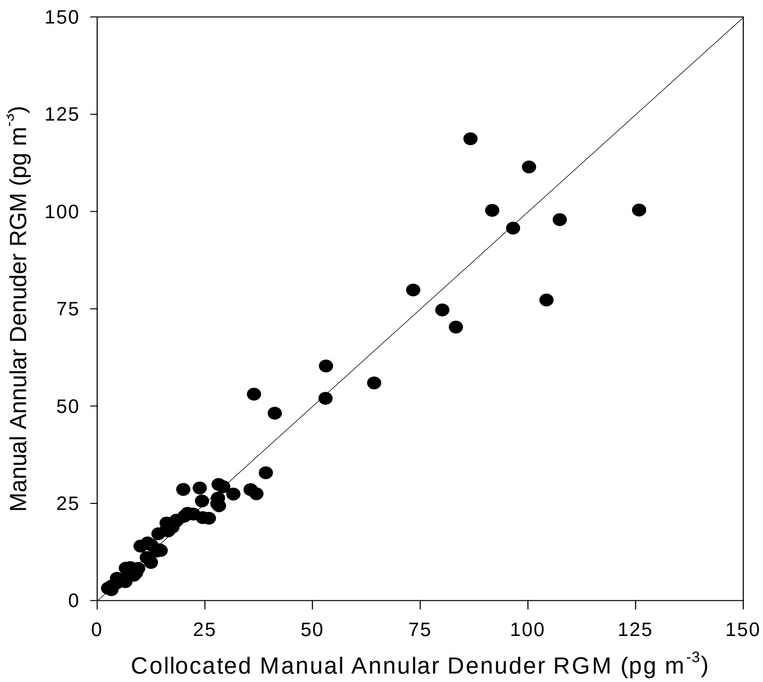
Analysis of Manual Denuder

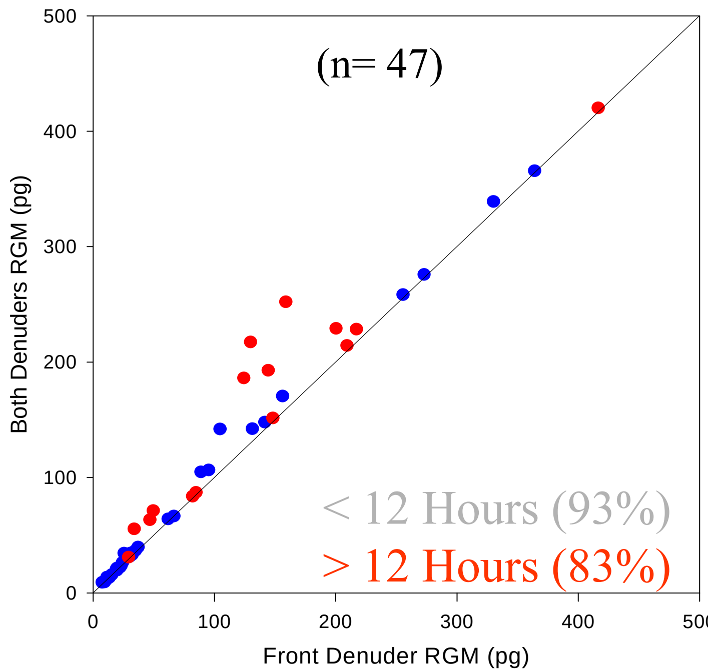


Collocated Denuded & Undenuded Hg(p)

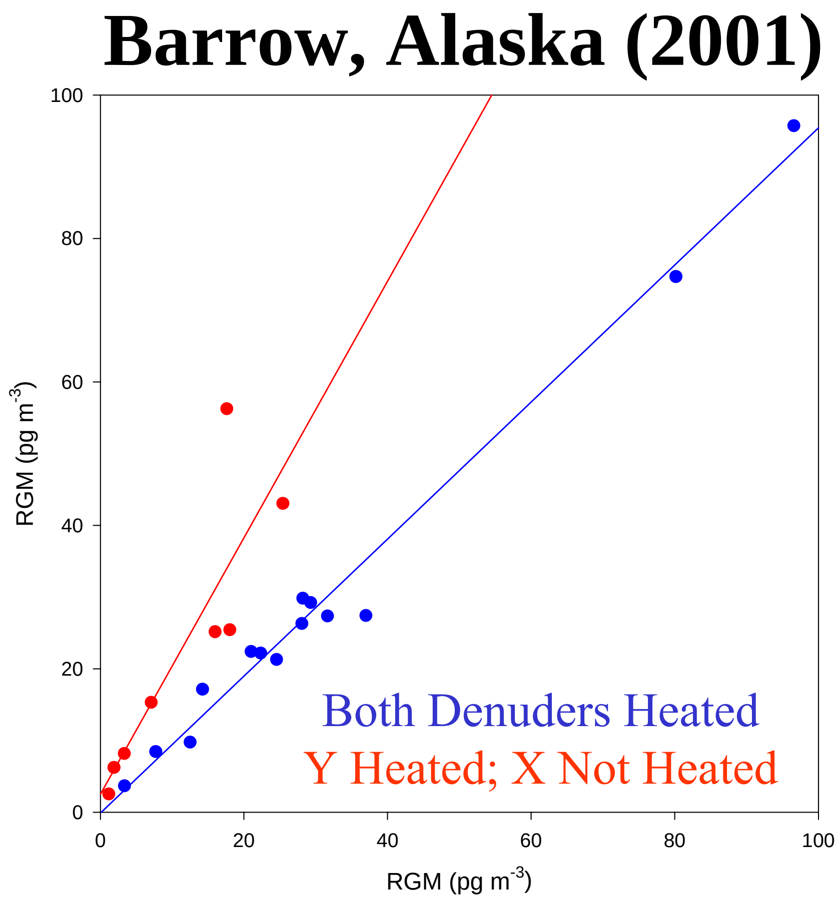


Annular Denuder Performance





Importance of Properly Heating Sampling System

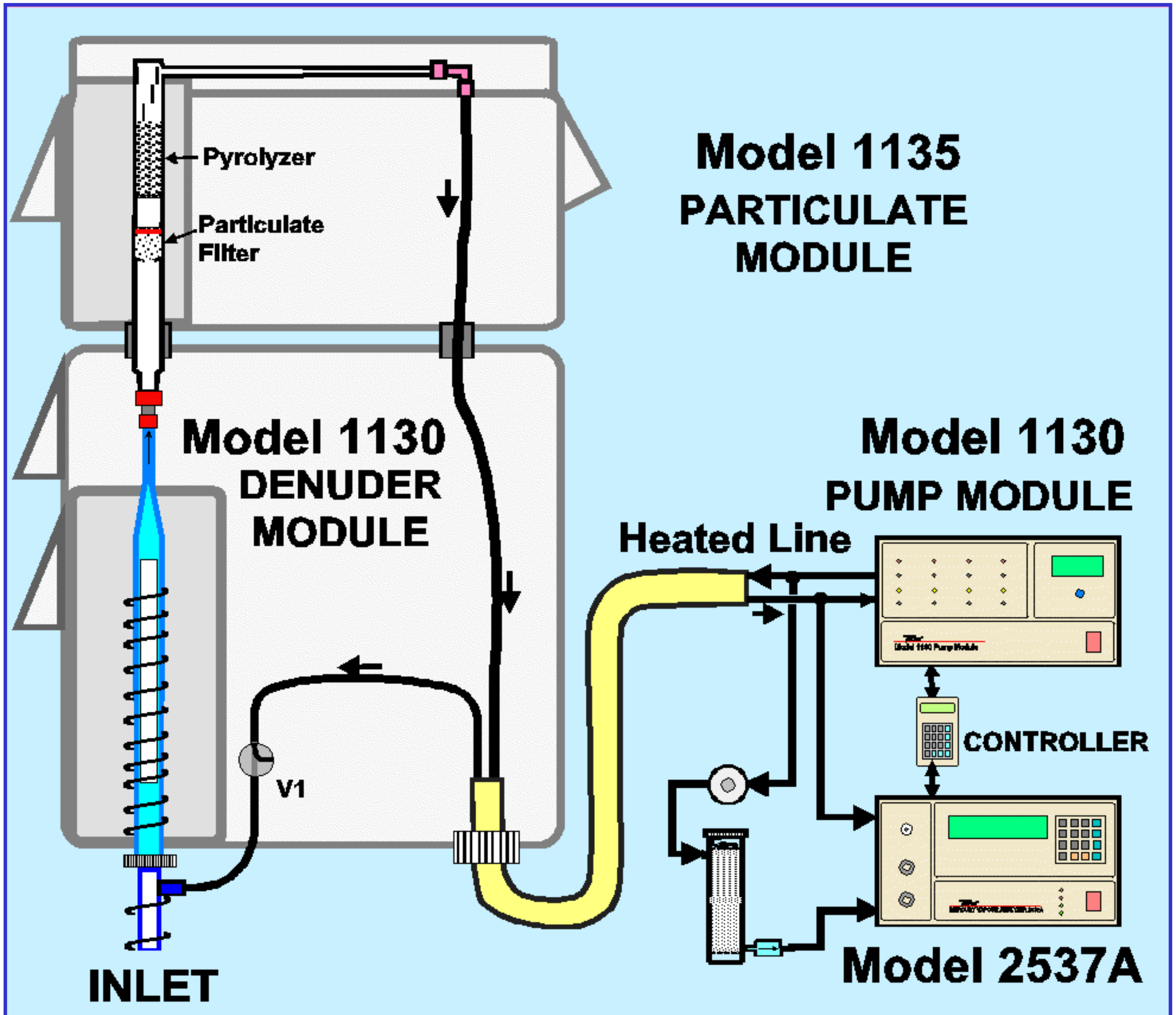


Tekran System Description

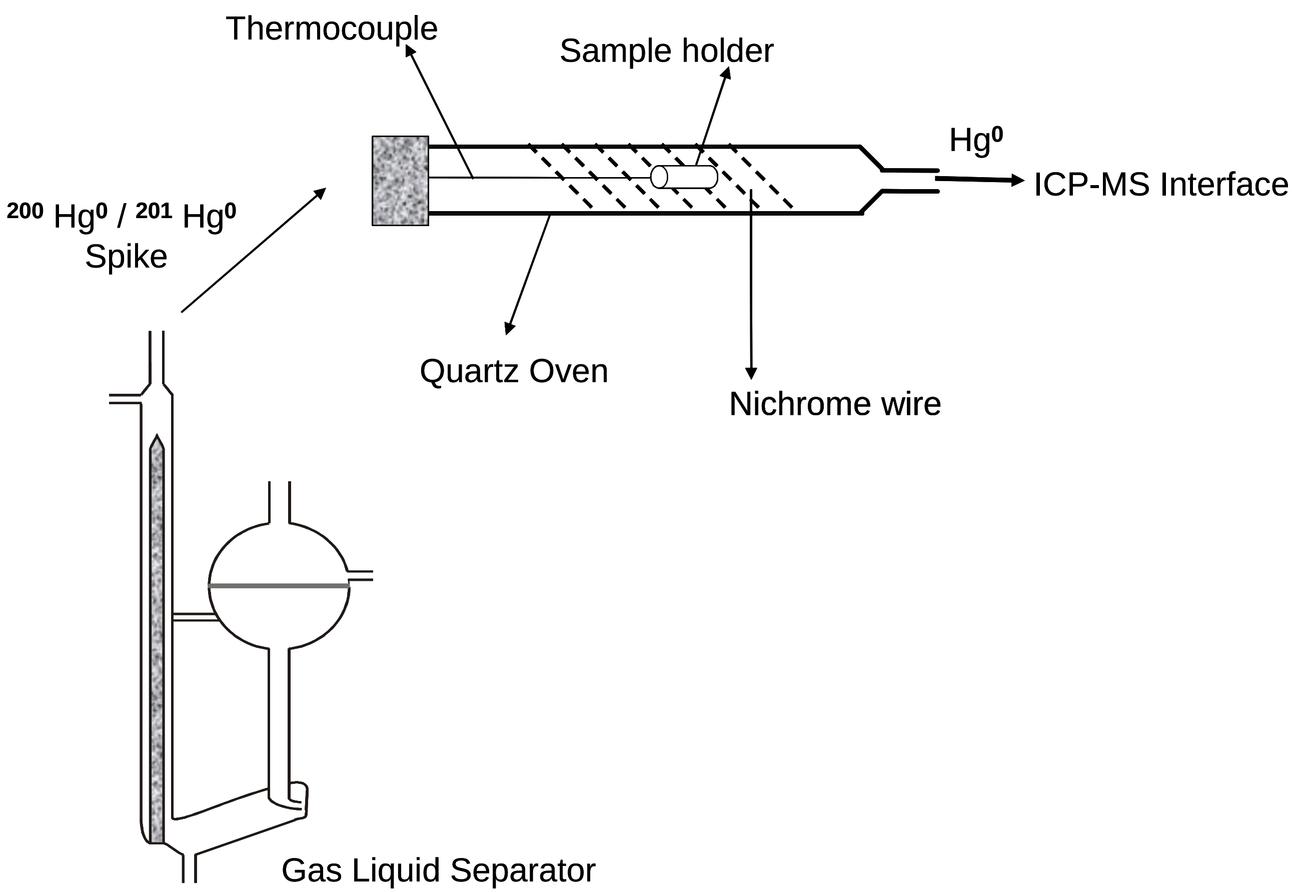
- **Model 2537A Vapor Phase Mercury Analyzer**
  - Semi-continuous Hg^0 Measurements
  - Gold Traps for Hg^0 Pre-concentration
  - Cold Vapor Atomic Fluorescence Spectrometer
- **Model 1130 Speciation Unit**
  - KCl Thermal Annular Denuder (Hg^{2+})
  - Zero Air Source & Pumping Module
- **Model 1135 Particulate Unit**
  - Thermal Quartz Filter & Pyrolyzer Column

* Landis et al. *Environ. Sci. Technol.*, **2002**, 36, 3000-3009

Automated Speciation Instrumentation

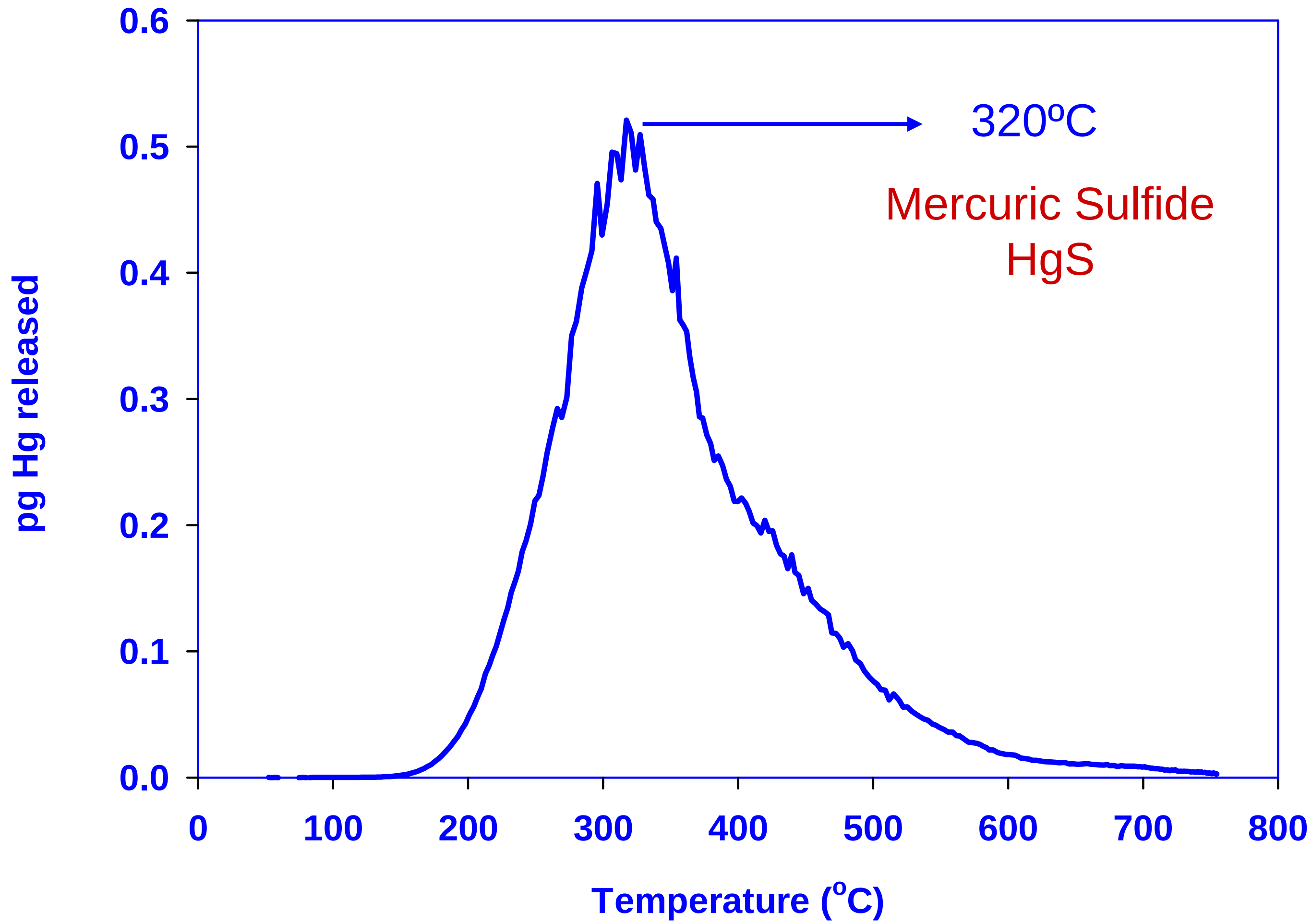


Cold Vapor Isotope Dilution Thermal Analysis HR-ICPMS



Mary Lynam, Ph. D. thesis, Univ. of Michigan, 2003

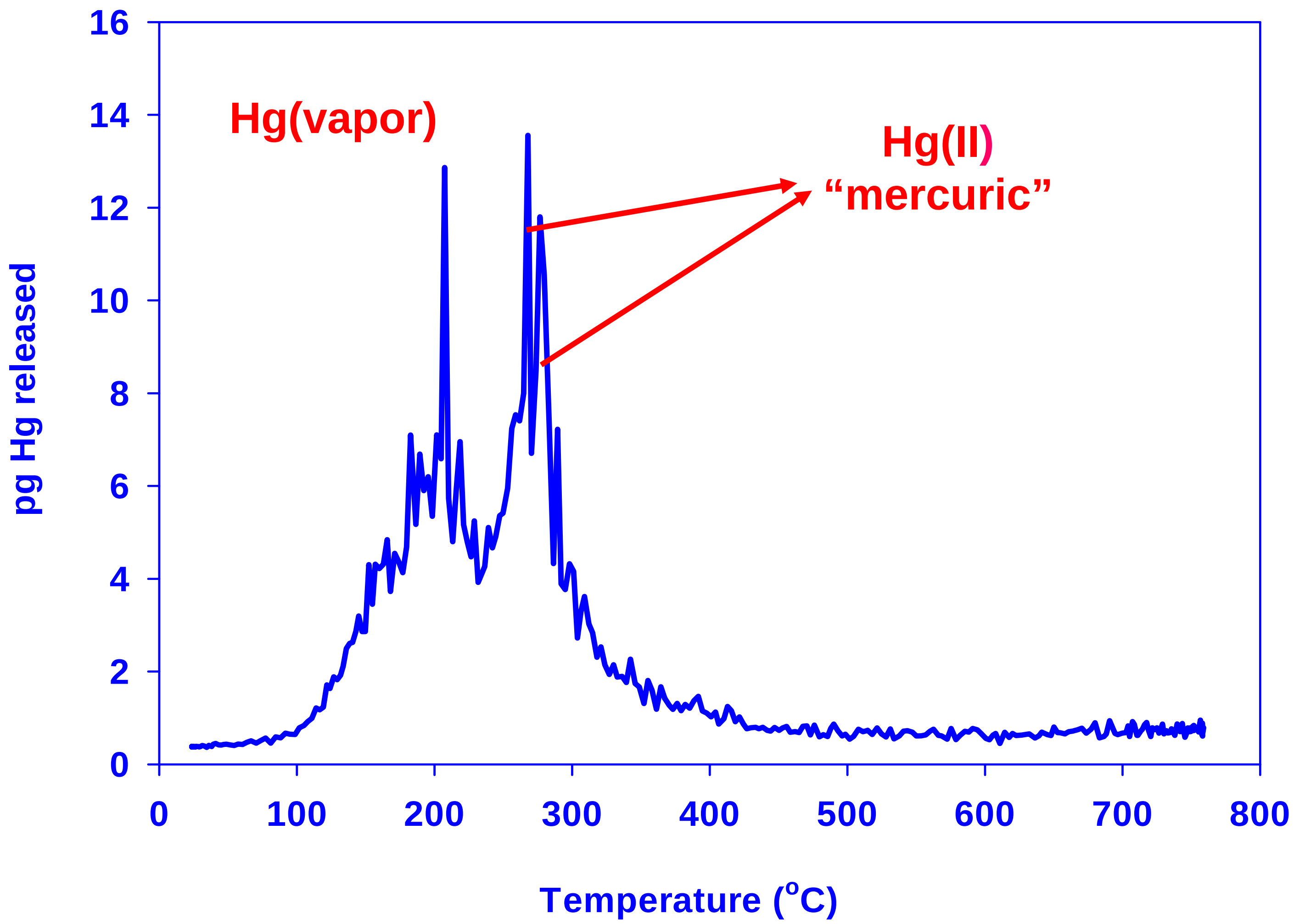
Analysis of NIST SRM 1633 (Fly Ash)



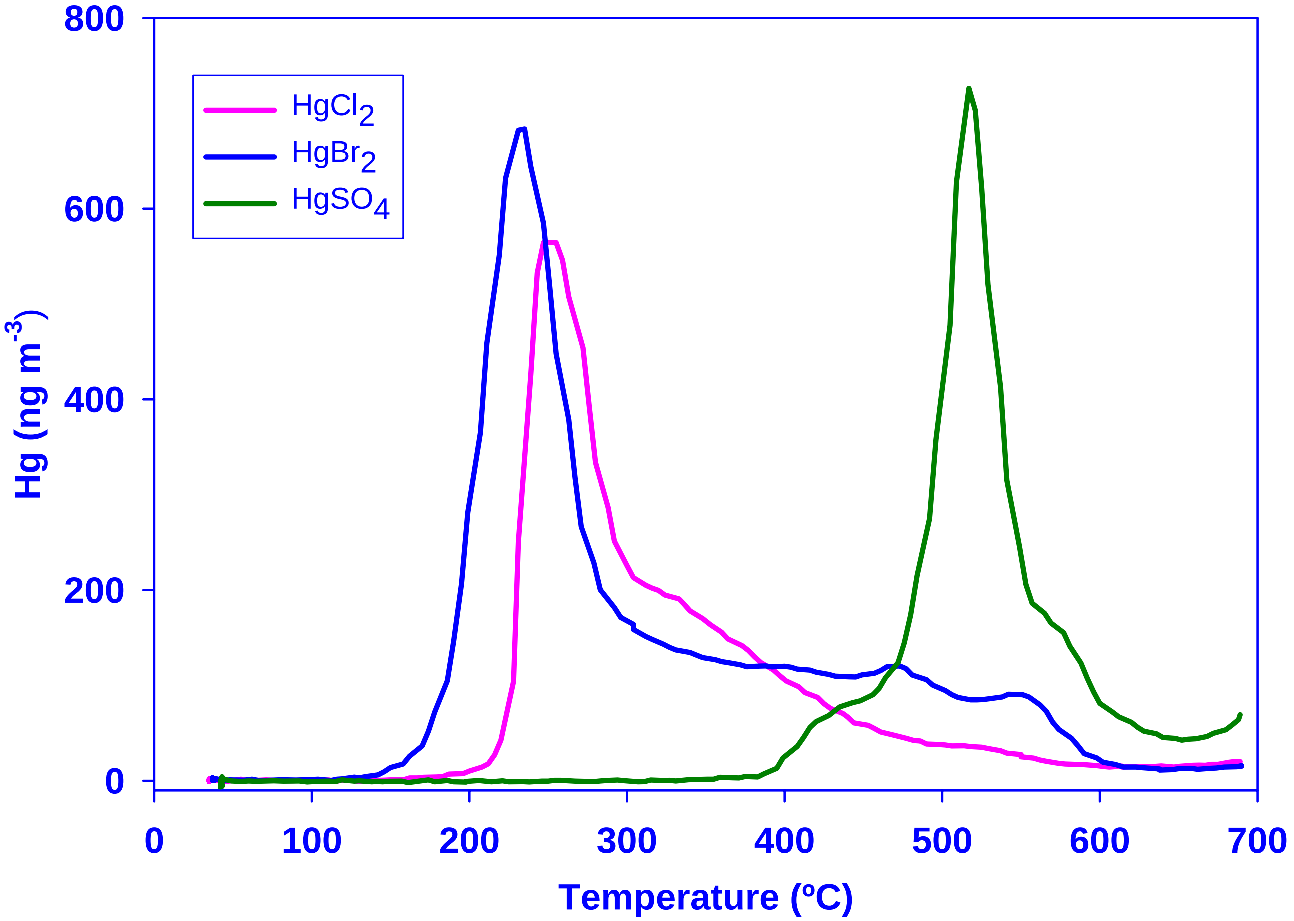
NIST **0.141 ± 0.019 mg kg^{-1} (CVAAS)**

This work **0.139 ± 0.009 mg kg-1 (CV-ID-TA-HR-ICPMS)**

Thermal Profile from $PM_{2.5-10}$ Sample (Detroit, MI)



Thermal Decomposition Profiles



Major Uncertainties Associated With Determinalistic Models

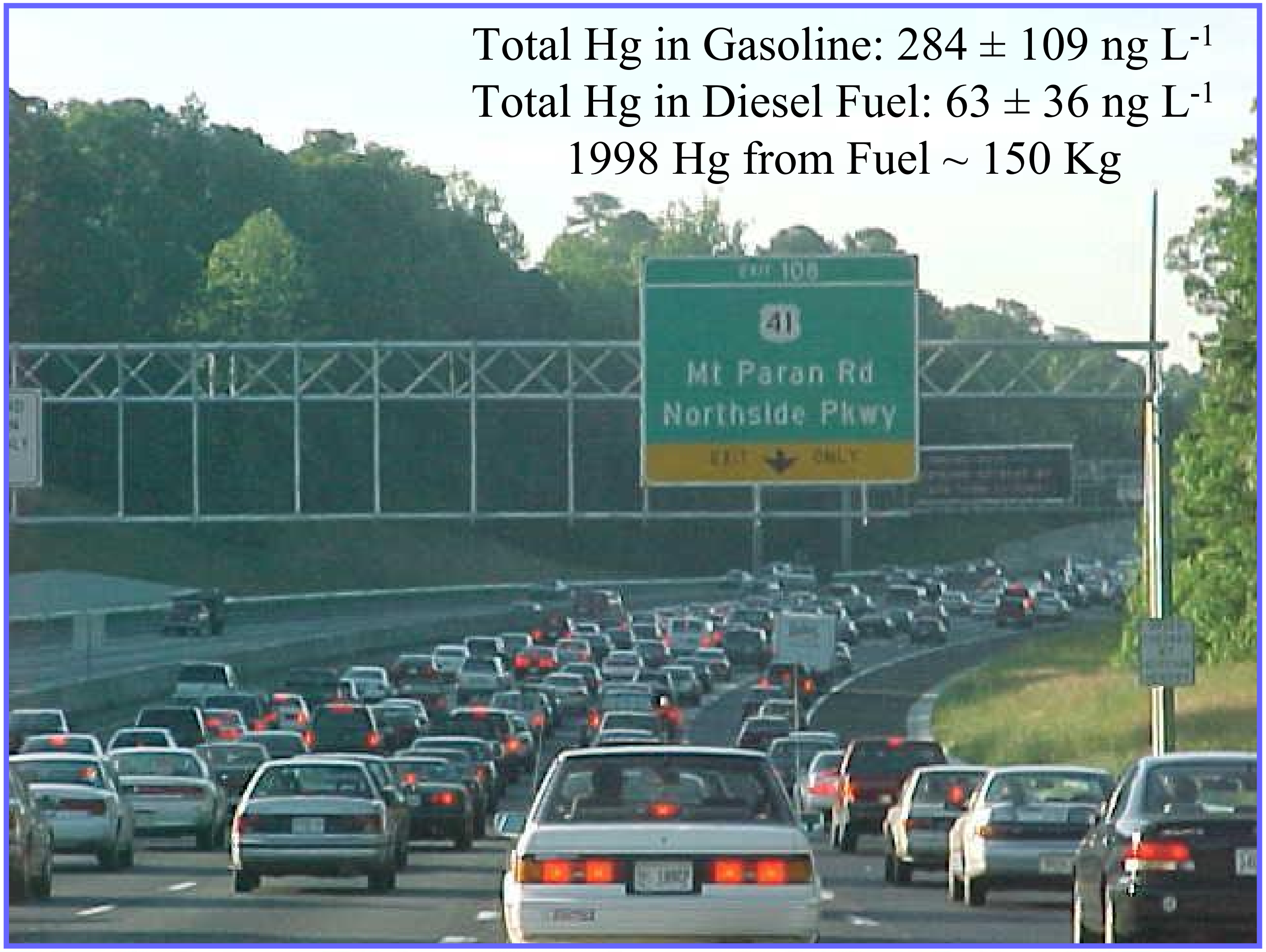
- Emission Inventory
  - Identify all Major Sources
  - Quantify Hg Emissions
  - Characterize Speciation of Emissions (in plume)
- Atmospheric Transport & Transformation
  - Oxidation/Reduction Reactions
    - Homogeneous & Heterogeneous Reactions
    - Boundary Layer & Free Troposphere
    - Polar Depletion Events
    - Halides
  - Gas/Particle Interactions
- Deposition
  - Dry Deposition
    - Gaseous & Particulate
  - Wet Deposition

Chlor-Alkali Emission Study

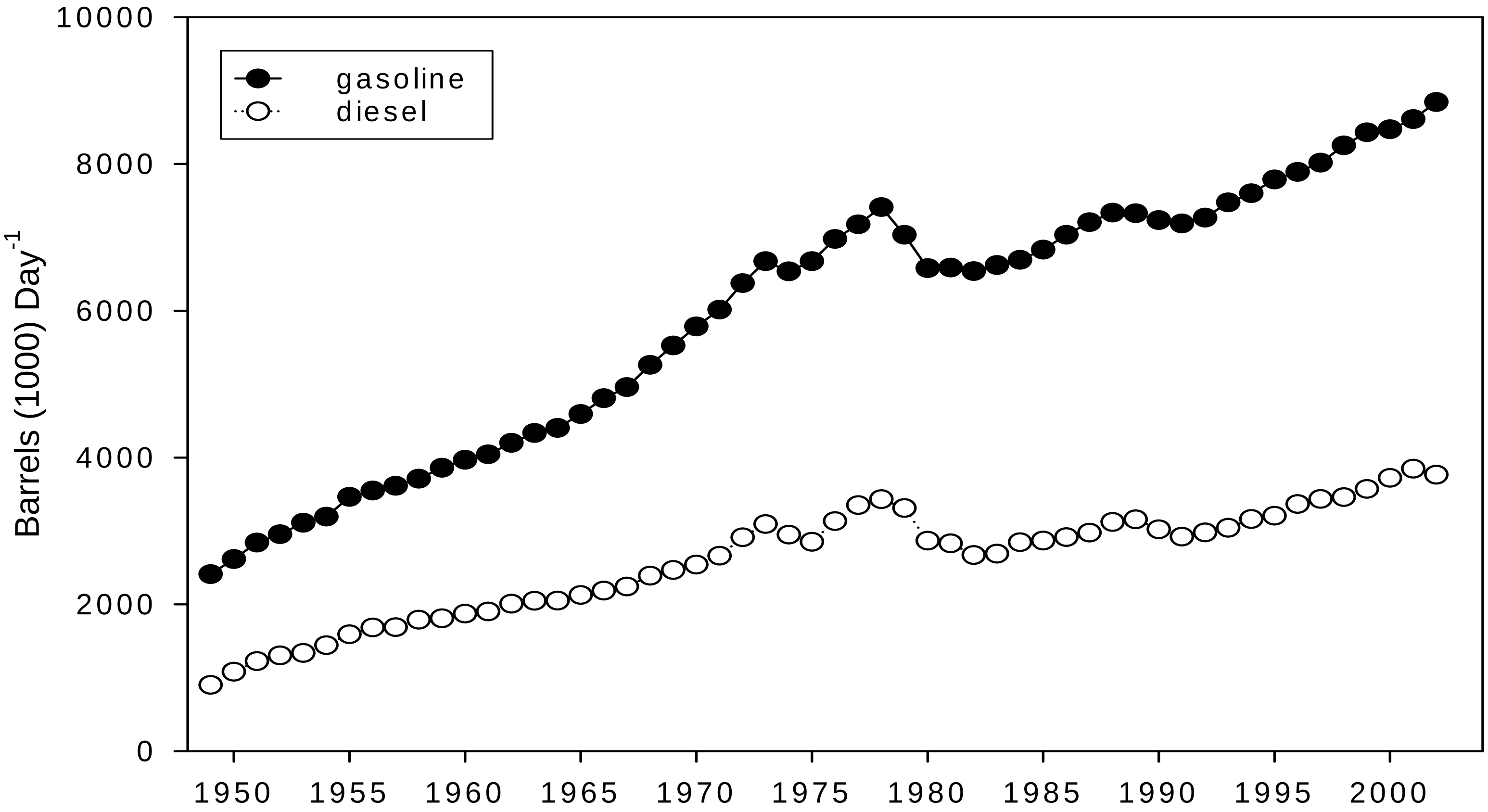
- Mercury Emissions Lower Than Previously Estimated
  - Hg^0 (518 g day^{-1})
  - $Hg(II)$ (10 g day^{-1})

Mercury Emissions From Mobile Vehicles (1998)

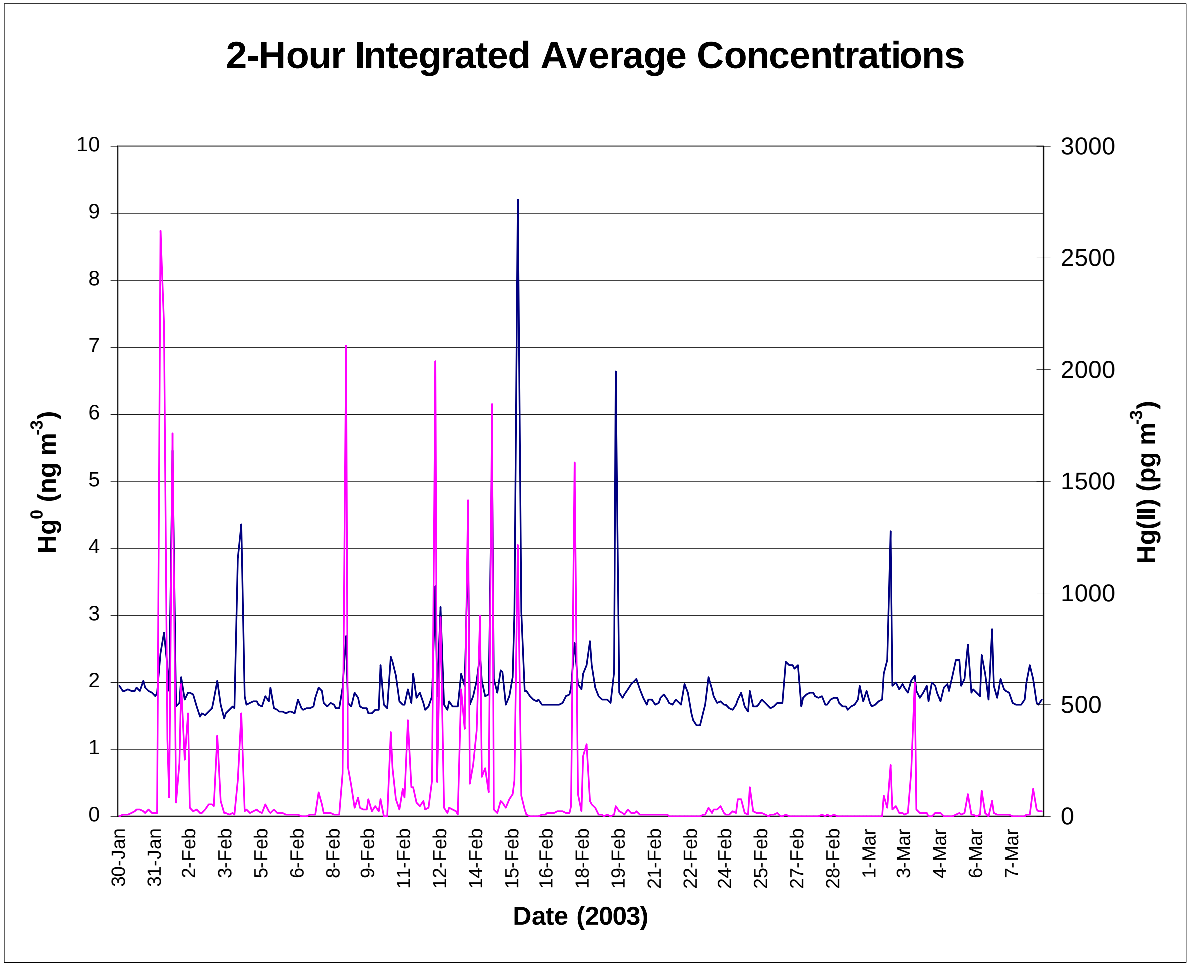
Total Hg in Gasoline: 284 ± 109 ng L^{-1}
Total Hg in Diesel Fuel: 63 ± 36 ng L^{-1}
1998 Hg from Fuel ~ 150 Kg



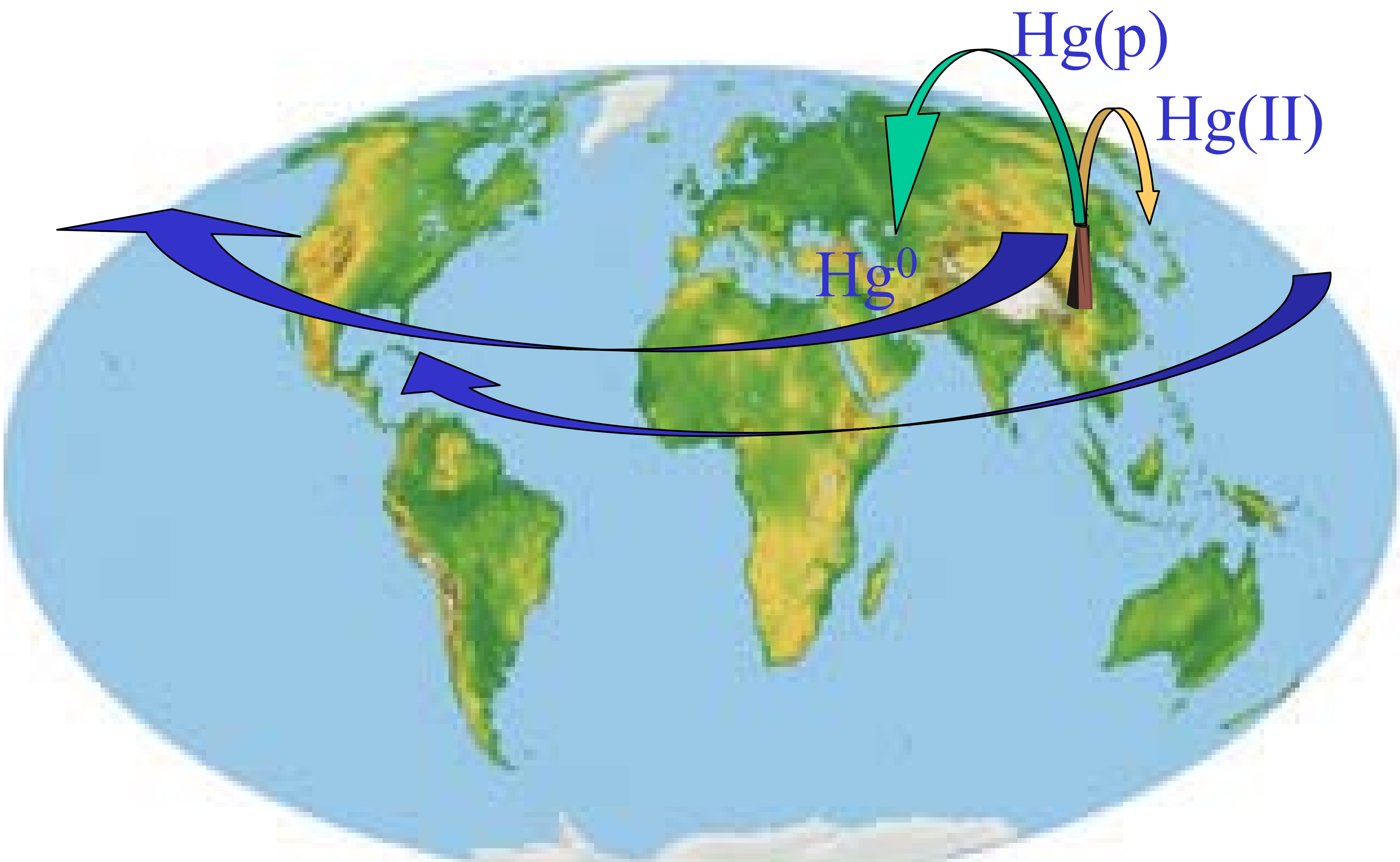
Gasoline & Diesel Consumption in U.S. (1949 - 2002)



Hospital Waste Incinerator Study

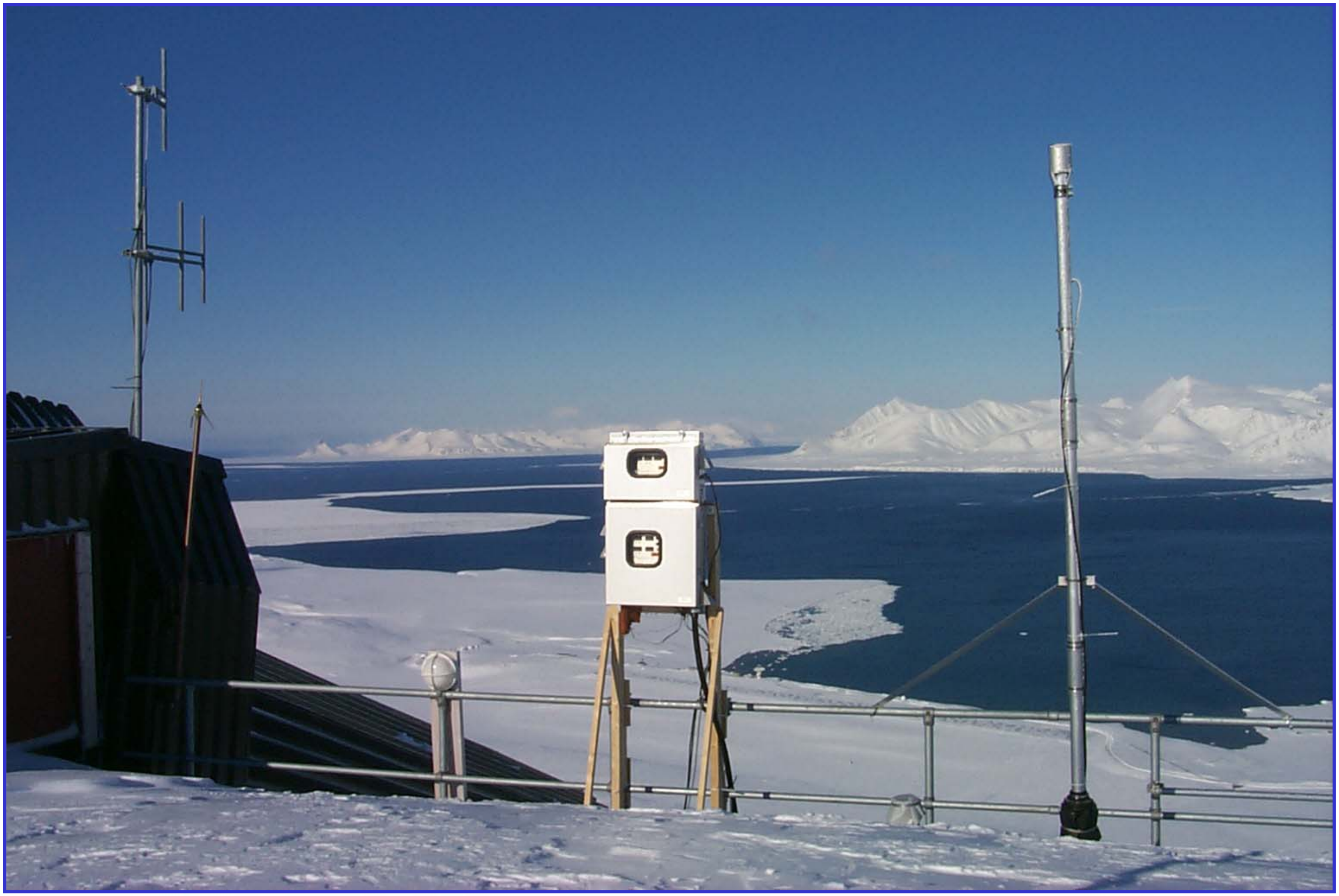


Contemporary Atmospheric Mercury Conceptual Model



Global - Regional - Local

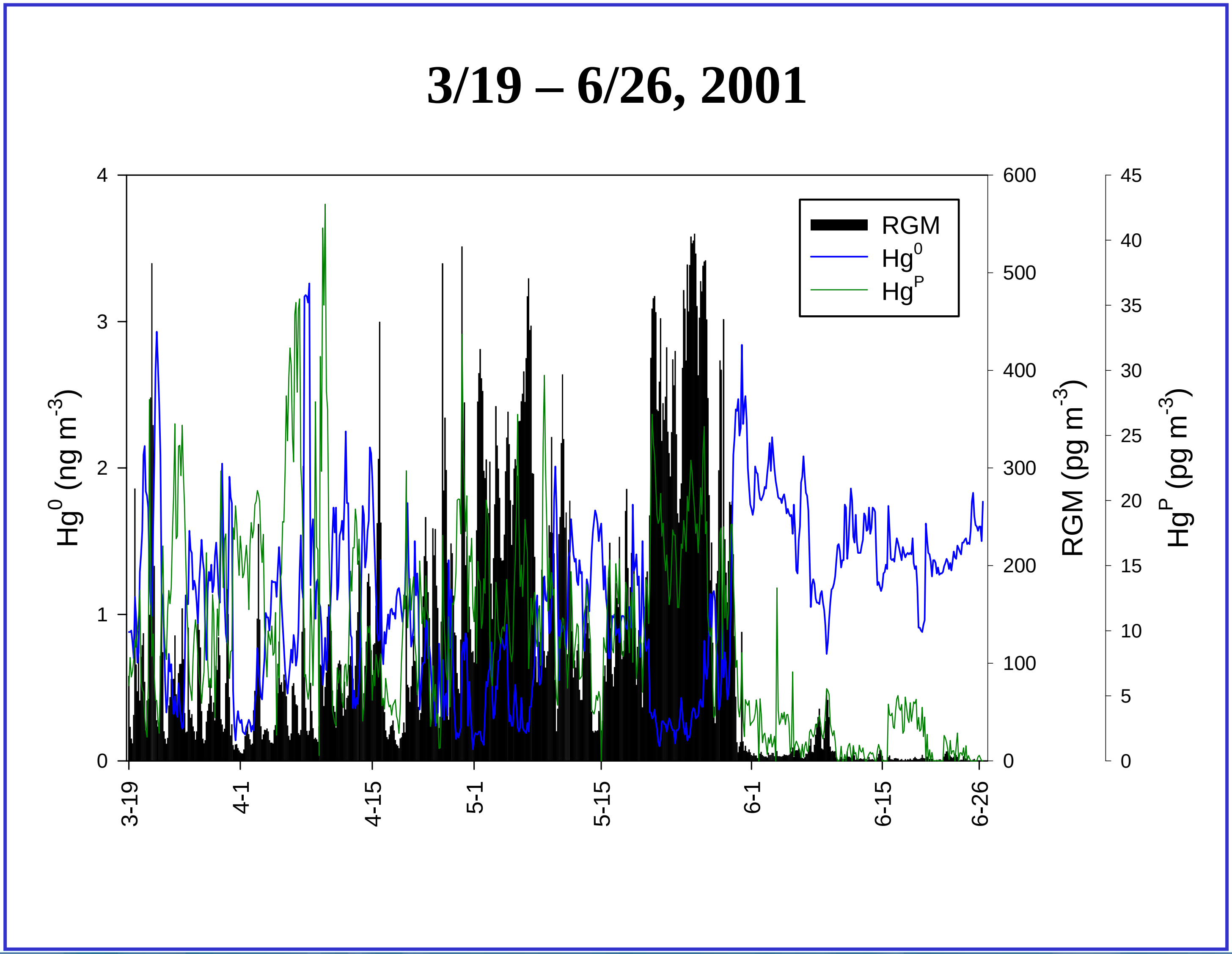
Ny-Alesund, Norway



Terra Nova Bay, Antarctica

Barrow, Alaska

Barrow Monitoring Summary



Aircraft Sampling Objectives

- Obtain Atmospheric Profiles (60 - 3500 meters) of Speciated Ambient Mercury off the South Florida Coast
- Investigate the Role of Long Range Transport of RGM to Florida in the Marine Troposphere
- Identify any Vertical Mercury Gradients that Might Indicate the Presence of Rapid Mercury Chemistry in Air or in Cloud Water

Aircraft Sampling Schedule

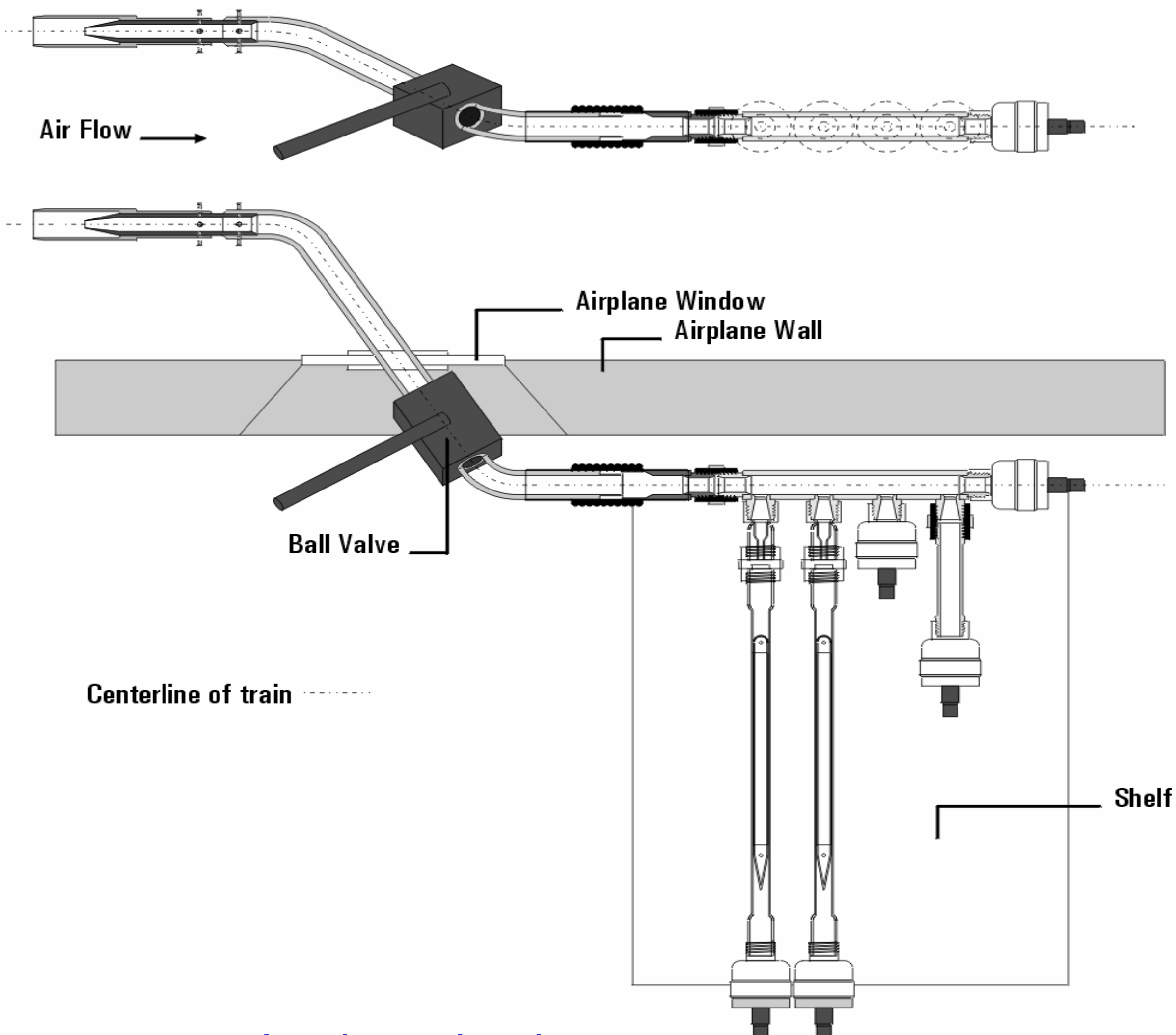
- Winter Flight Window (Jan/Feb 2000)
  - 3 Weeks
- Summer Flight Window (June 2000)
  - 4 Weeks

NOAA DeHavilland Twin Otter (DHC-6) Aircraft

Aircraft Sampling Metrics

- Aerosols
  - Mercury, Trace Elements, Major Ions, CCN
- Gases
  - Hg^0, Hg^{2+}, O_3, CO, SO_2, NO, NO_2, NO_x , NO_y

EPA NERL Aircraft Inlet Design



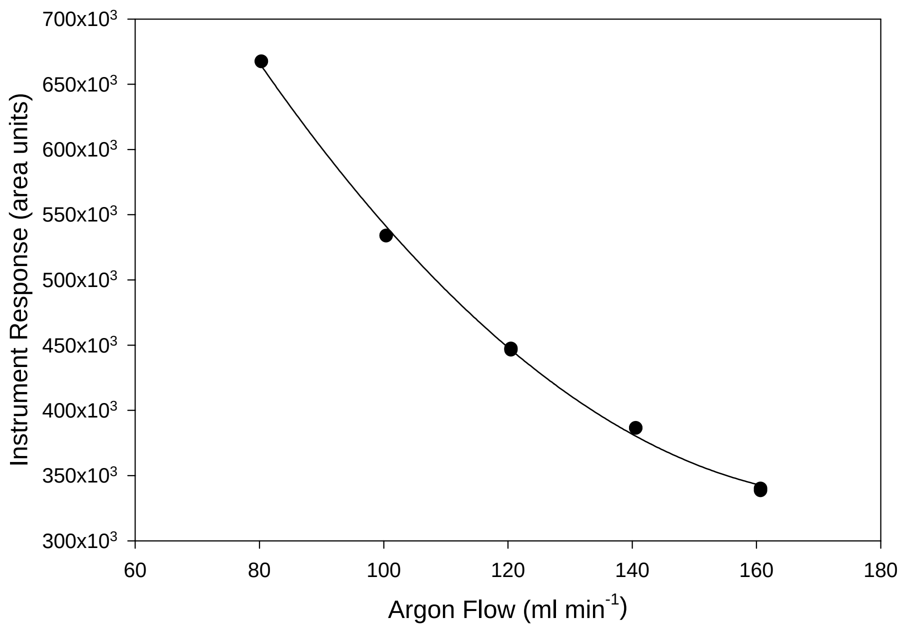
* Irshad et al., 2004, *Aerosol Sci. Technol.* 38, 311-321

EPA NERL Aircraft Sampling Inlet

Mercury Instrumentation Configuration

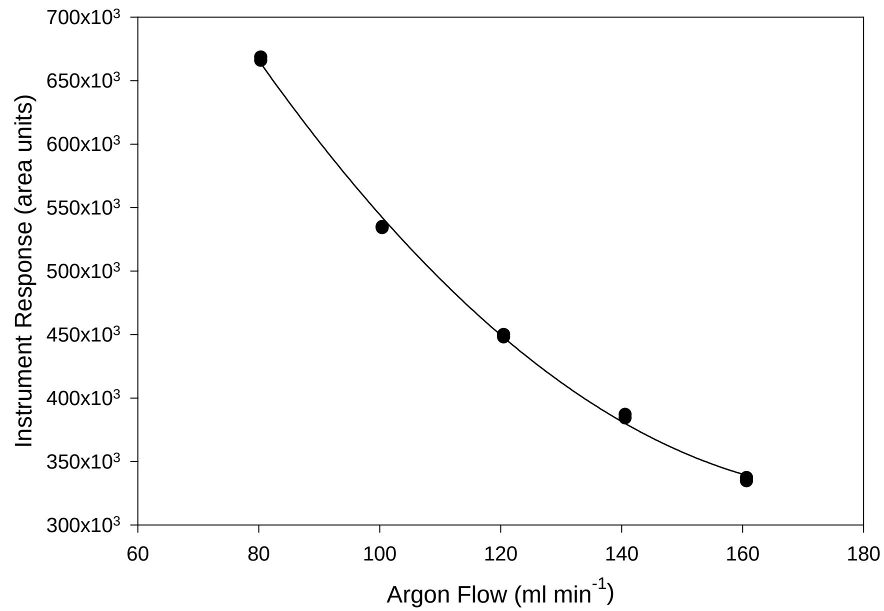
Tekran 2537A Altitude Correction

2537A #81



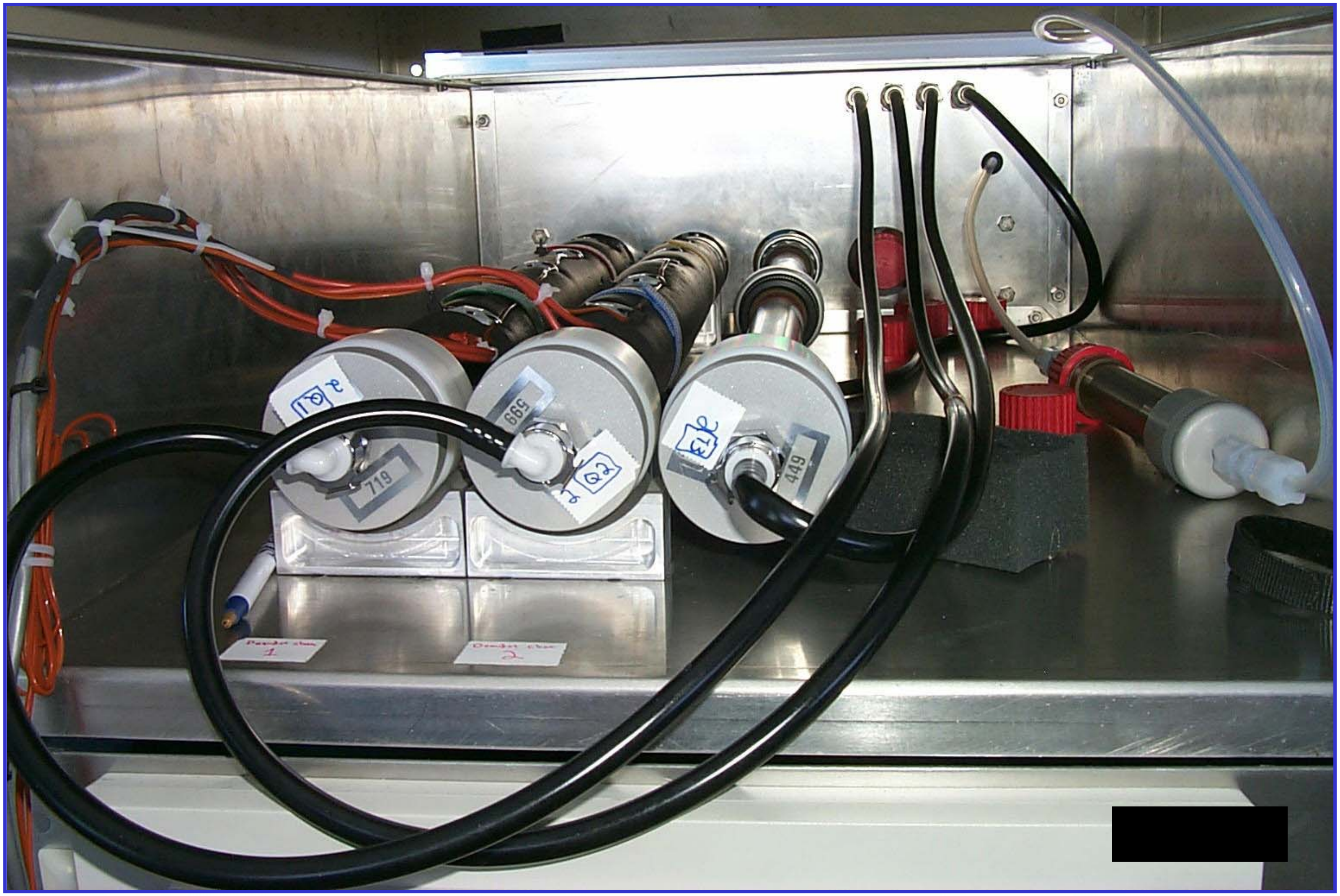
$$f = 1441352 – 12514 * x + 35 * x^2$$
$$r^2 = 0.9984$$

2537A #102



$$f = 1417858 – 12064 * x + 33 * x^2$$
$$r^2 = 0.9982$$

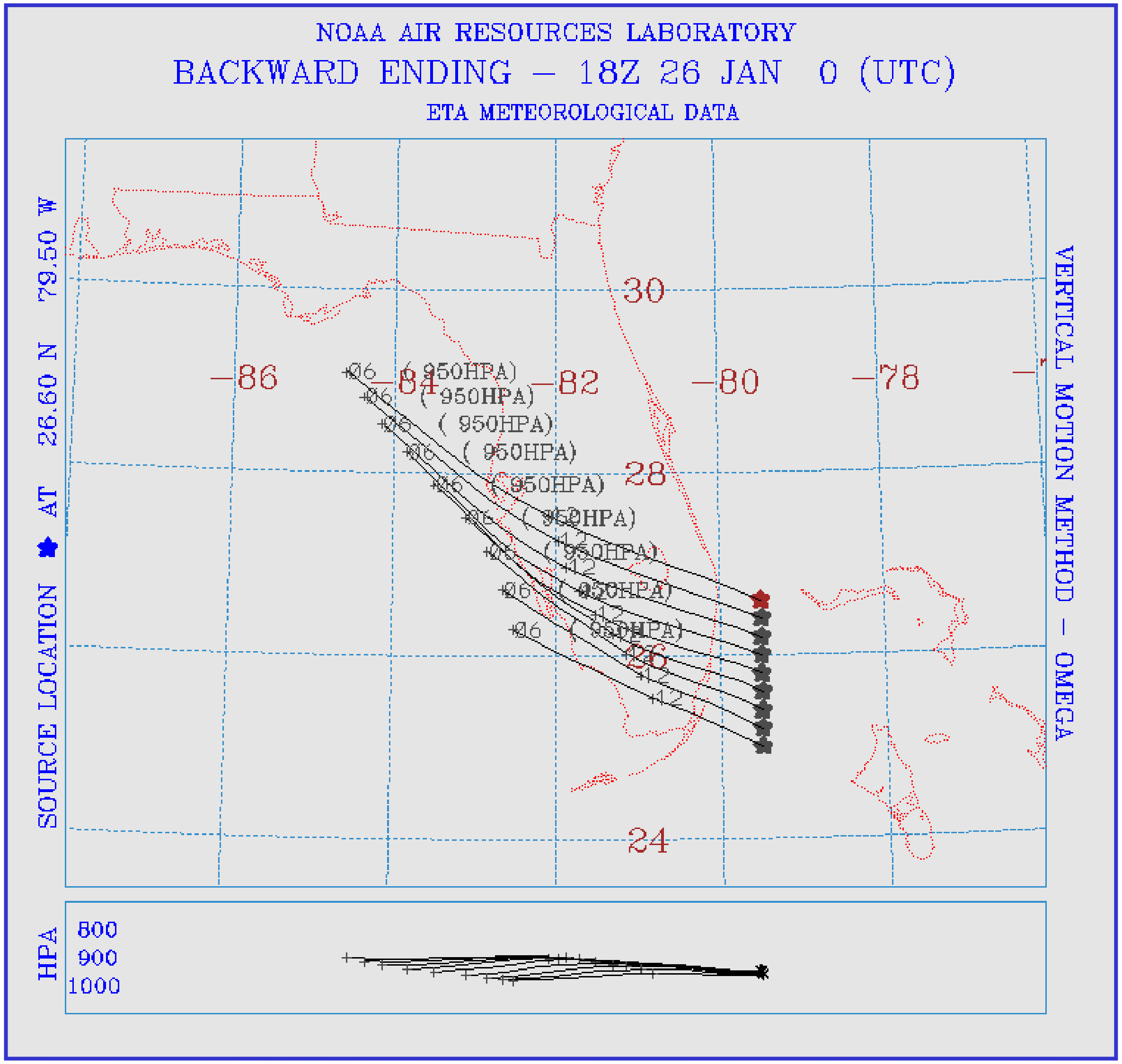
Aircraft Denuder Enclosure



Flight Operations

- Two 90-Minute Sampling Periods Per Flight
- Typically Evaluated Vertical Gradients
- Flight Tracks
  - Atlantic Ocean
  - Gulf of Mexico
  - Everglades

Air Mass Back Trajectories

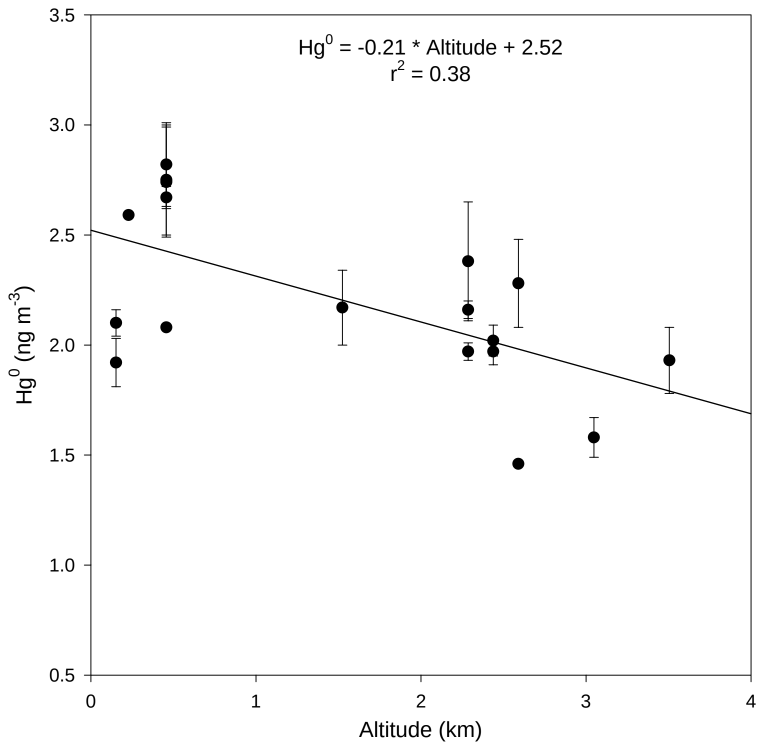


RESEARCH & DEVELOPMENT

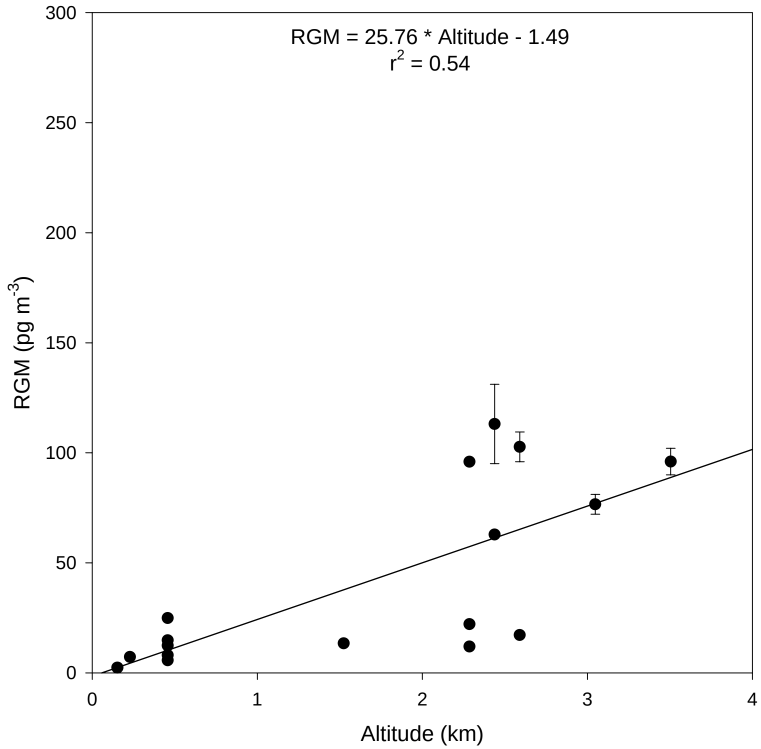
Building a scientific foundation for sound environmental decisions

January Gaseous Hg Summary

Elemental Gaseous Mercury

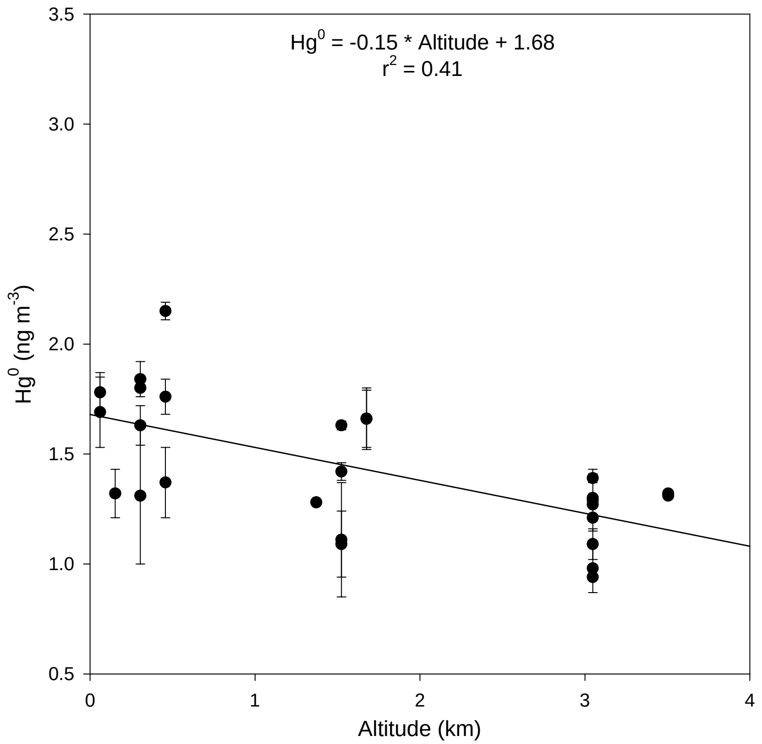


Reactive Gaseous Mercury

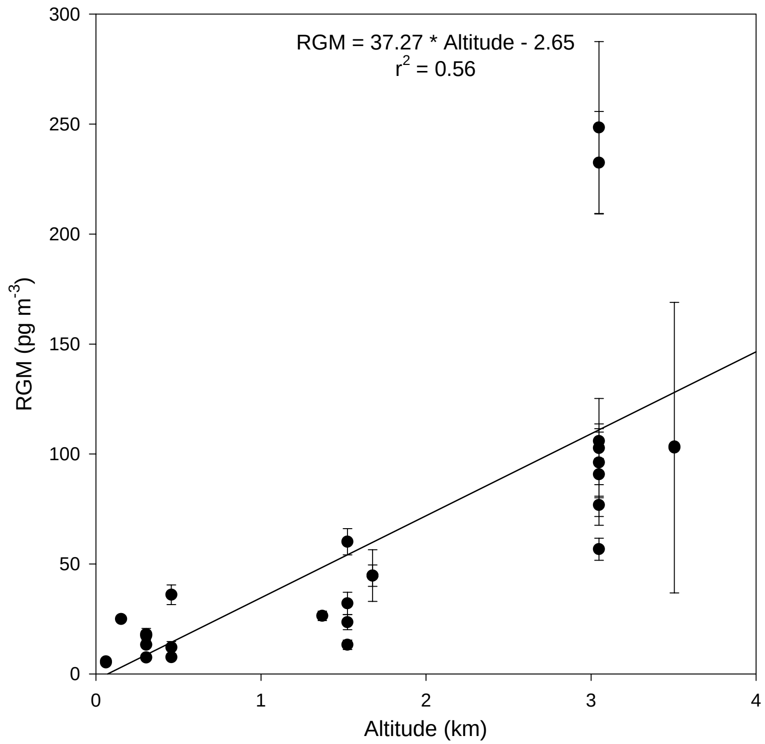


June Gaseous Hg Summary

Elemental Gaseous Mercury

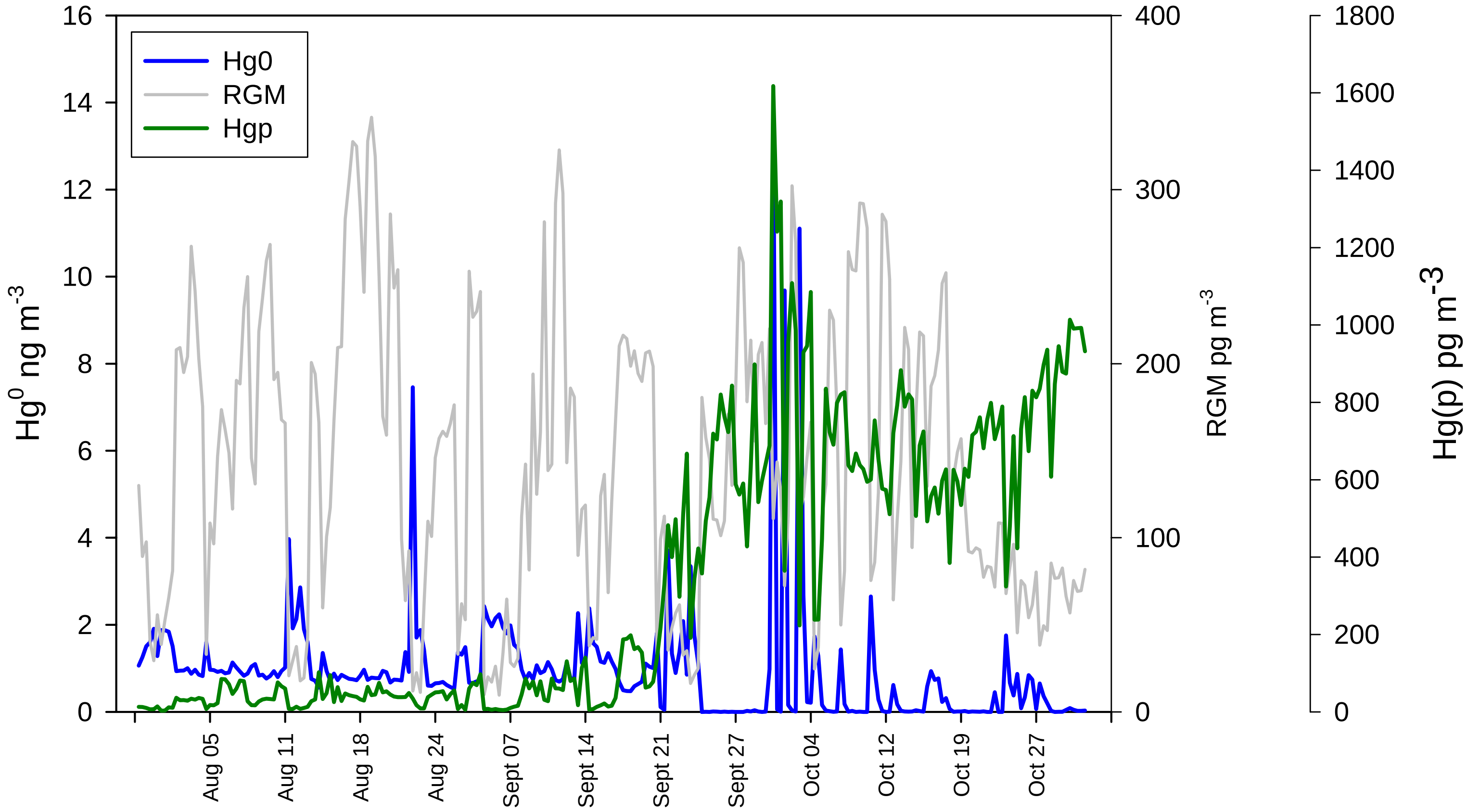


Reactive Gaseous Mercury

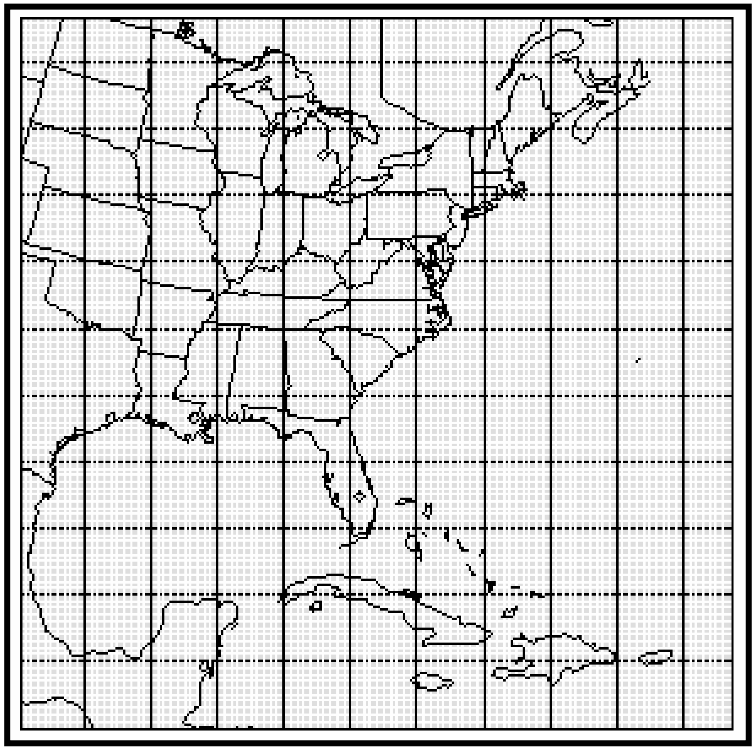


Mauna Loa, Hawaii Monitoring Site

Mauna Loa Hg Time Series
2001 "Downslope"



Florida Atmospheric Mercury Modeling (University of Michigan)

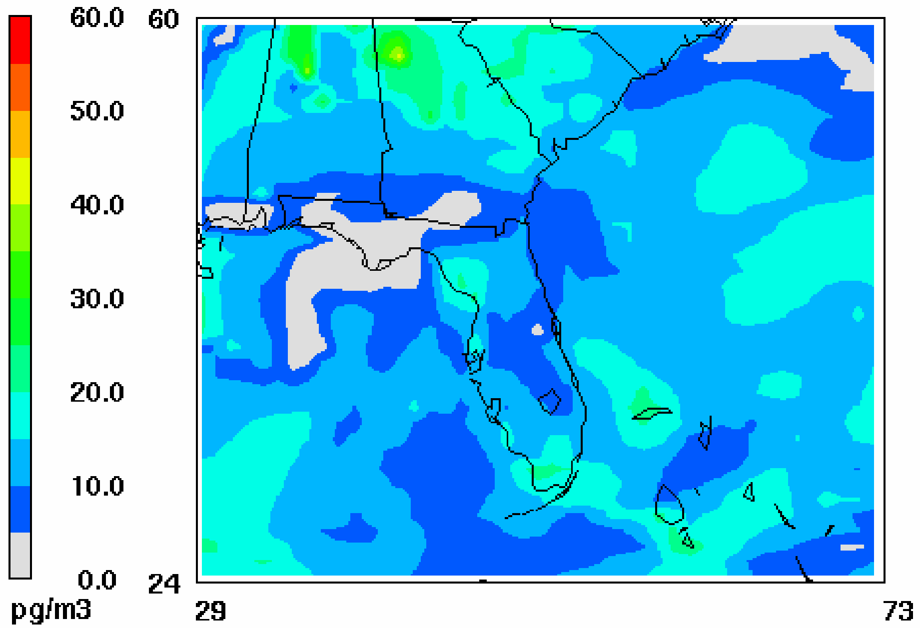


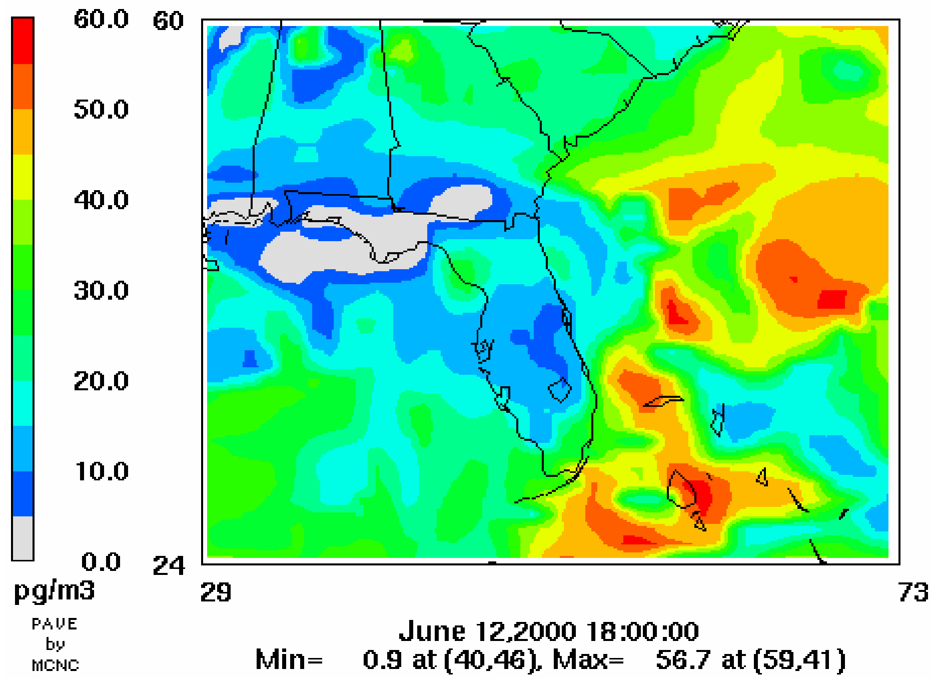
- **Meteorological Model:**
  NCAR/PSU MM5 Model
  - Initialized with NCEP Global
  - Analyses Data (1° x 1°)
- **Chemical Model:**
  USEPA CMAQ Model / Univ. of Michigan Hg Chemistry
  - Modified Hg chemistry mechanism
    - 300 gas phase reactions
    - 100 aqueous phase reactions
  - 21 vertical levels
  - BCs: 1.3 ng m^{-3} Hg^0 (constant with z), 1 pg m^{-3} RGM (increasing with z)

Modeled RGM
June 12, 2000 - Afternoon Flight

Layer #1- 100 meters

Layer #4 – 2500 meters

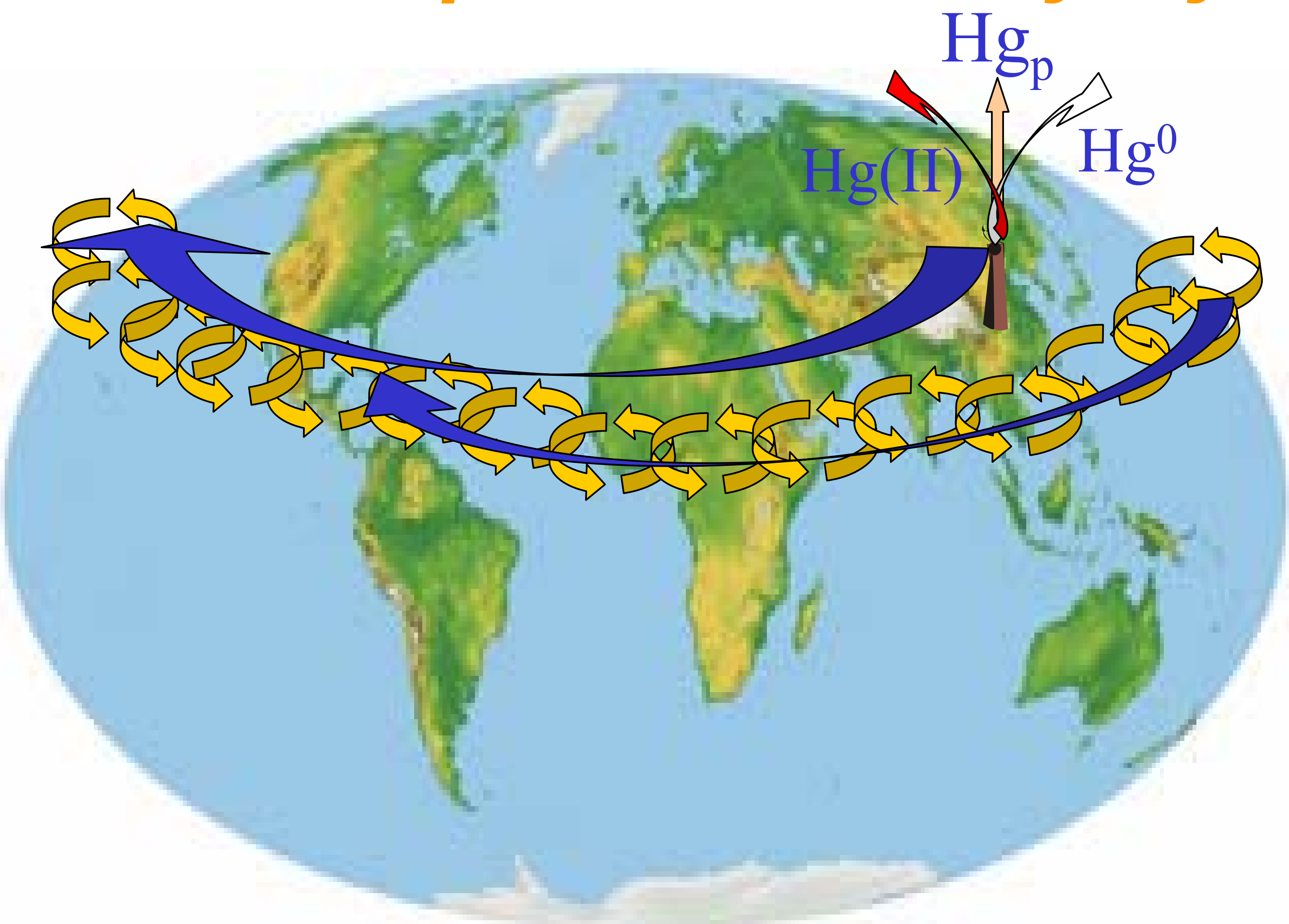




What Do We Know So Far …

- Elevated RGM and Hg(p) Observed in the Marine Free Troposphere Suggest Production and Long Range Transport
- Detailed Chemical and Meteorological Modeling can Reproduce the General Characteristics of the Observed Vertical Profile in Gaseous Hg Species
- Additional High Altitude Measurements are Necessary to Elucidate Exact Chemical Mechanisms

Global Atmospheric Mercury Cycle ?



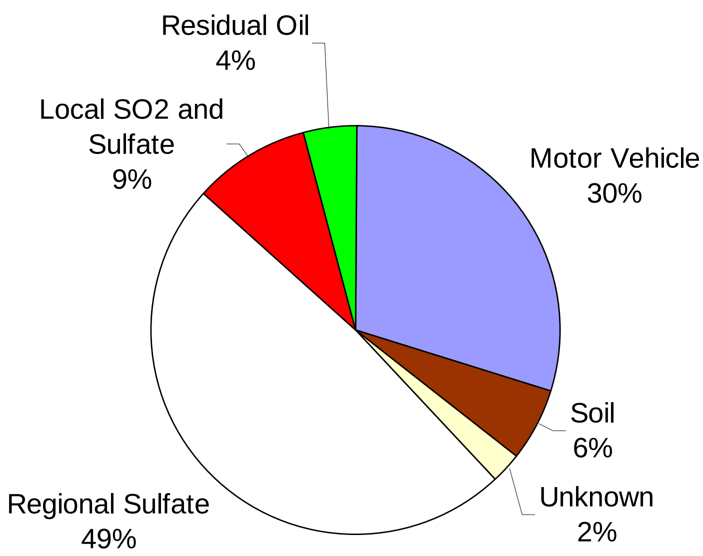
Rapid Oxidation, Deposition, Evasion ?

Statistical Source Apportionment Model Development

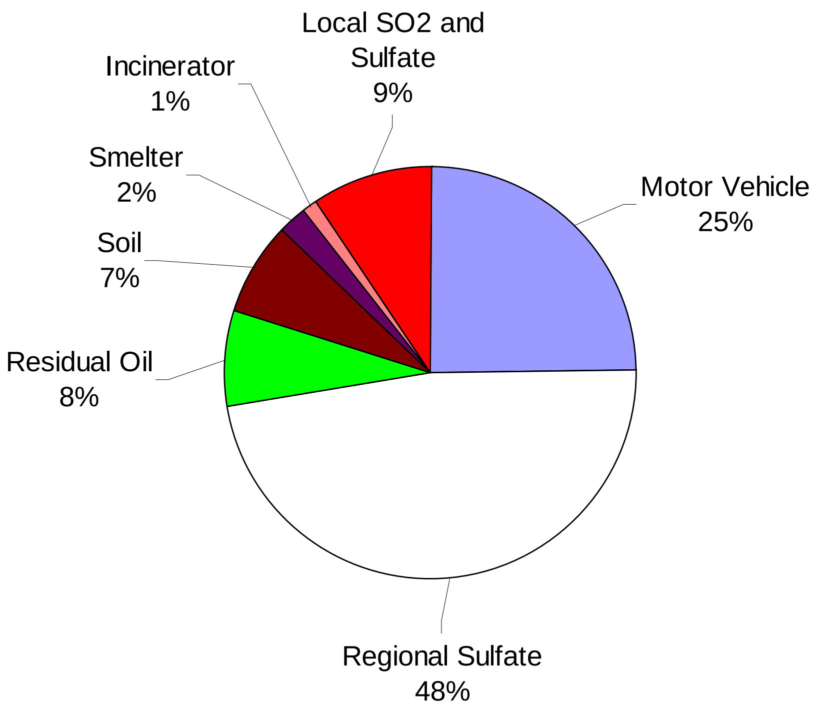
- **CMB 8.2**
  - Effective variance weighted least squares regression
  - Any number of samples
  - Requires selection of source profiles
- **UNMIX2**
  - Multi-linear model (Ron Henry – USC)
  - Usually requires at least 100 samples
  - Does not use data below MDL
  - Generates source profiles and uncertainties
- **Positive Matrix Factorization (PMF)**
  - Multi-linear model (Phil Hopke – Clarkson University)
  - Usually requires at least 100 samples
  - Uses data below MDL
  - Incorporates uncertainties and weights individual data points
  - Generates source profiles and uncertainties

$PM_{2.5}$ Source Apportionment Results Philadelphia, PA (1992-1995)

UNMIX2



PMF

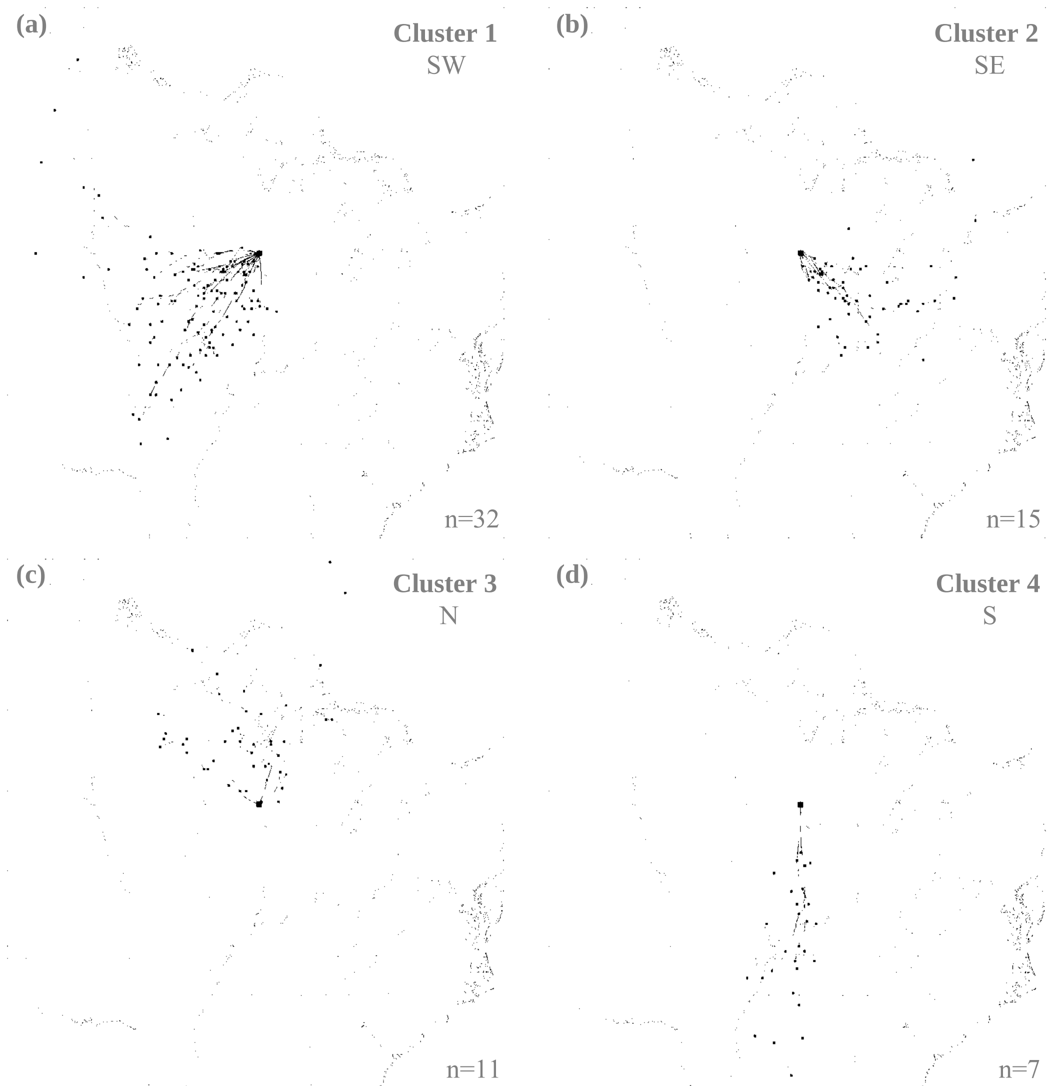


* Courtesy of Gary Norris

Hybrid Source Apportionment Model Development

- **Meteorological Transport Analysis**
  - Single-site analysis models
    - Wind sector analysis
    - Back trajectory analysis
    - Meteorological cluster analysis
- **Quantitative Transport Bias Analysis (QTBA)**
  - Multi-site back trajectory model (Gerald Keeler – U of M)

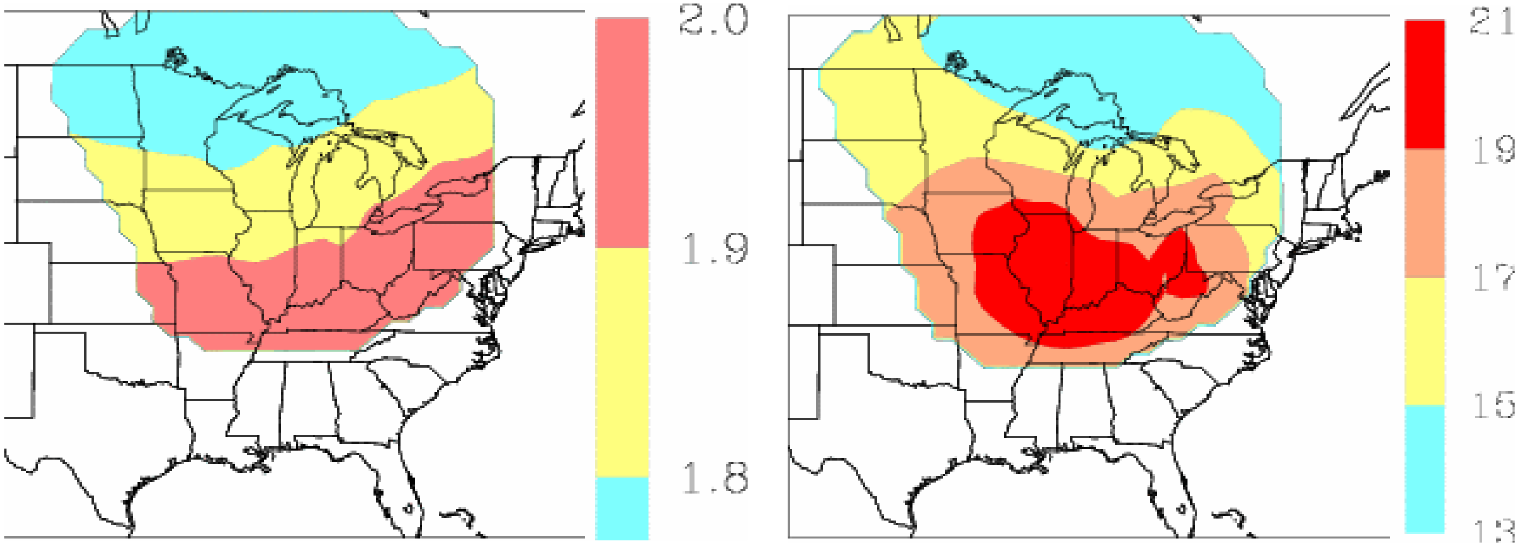
Example Meteorological Clusters



* Landis et al. *Environ. Sci. Technol.*, 2002, 36, 4508-4517

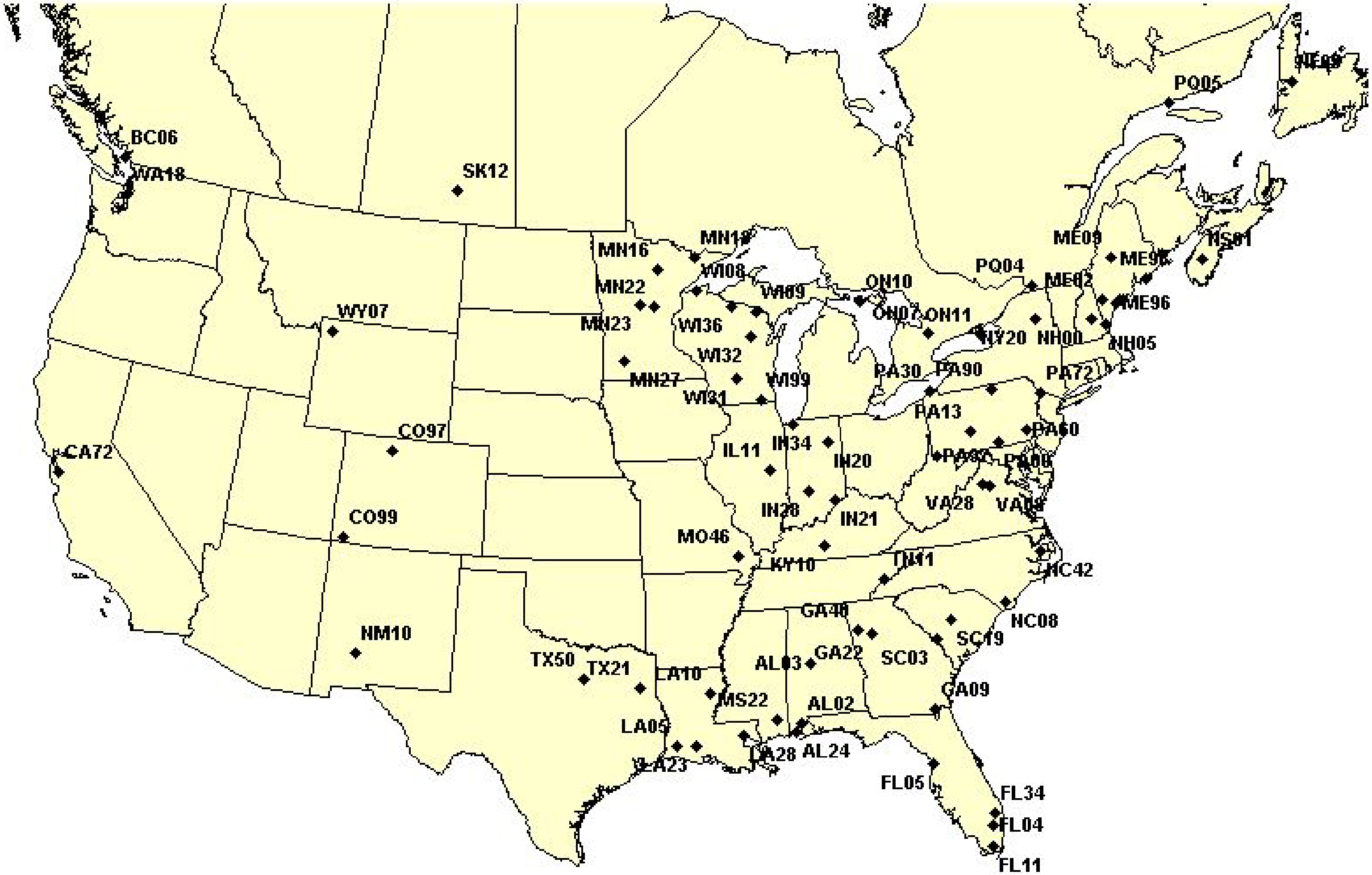
Example QTBA Results

Vapor Phase Hg (ng m^{-3}) **Particulate Phase Hg (pg m^{-3})**

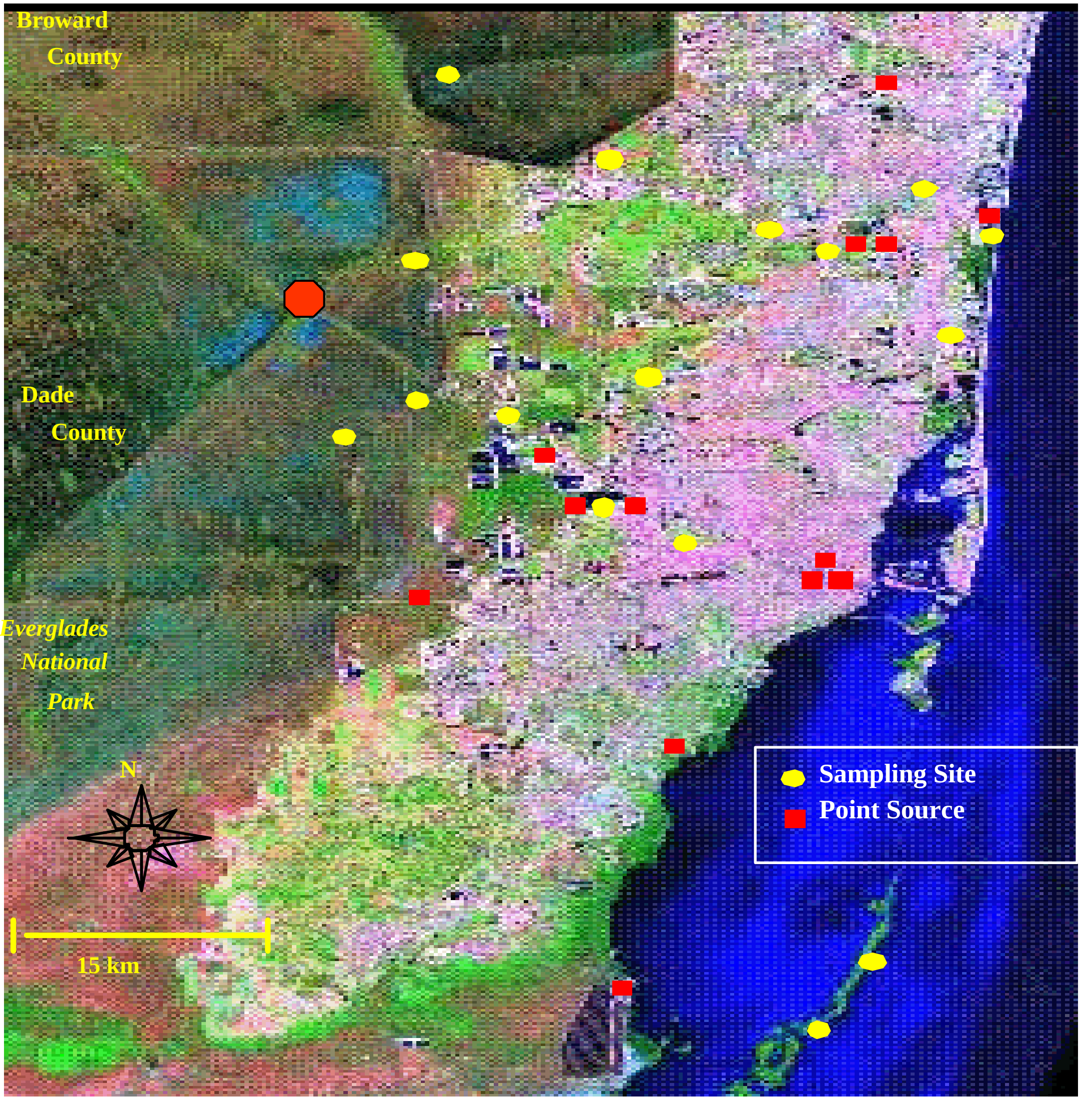


* Janet Burke, Doctoral Dissertation, University of Michigan 1998.

NADP Mercury Deposition Network Site Map



SoFAMMS Site Map



* Dvonch et al. *Environ. Sci. Technol.*, 1999, 33, 4522-4527

Hg in Event Precipitation During SOFAMMS (ng/L)

Site	N	Min	Max	VWM
ADK	12	12.4	40.1	19.1
AND	20	7.5	69.1	17.8
BCN	18	7.1	58.3	19.6
BCS	19	10.1	57.7	22.6
CGT	15	**4.5**	67.5	16.0
EVC	15	7.8	35.7	15.7
EVN	14	8.8	34.5	13.1
EVS	17	7.7	70.7	19.9
FLG	23	6.9	75.6	19.2
IND	20	7.5	80.2	24.8
JHL	16	7.6	41.4	**15.7**
MNS	21	13.4	80.1	26.6
NVR	19	7.5	72.5	**30.5**
PTI	19	10.5	80.1	24.3
SBI	22	6.2	**113.2**	25.5
SOT	18	8.7	42.2	23.0
THP	17	4.5	52.7	16.8

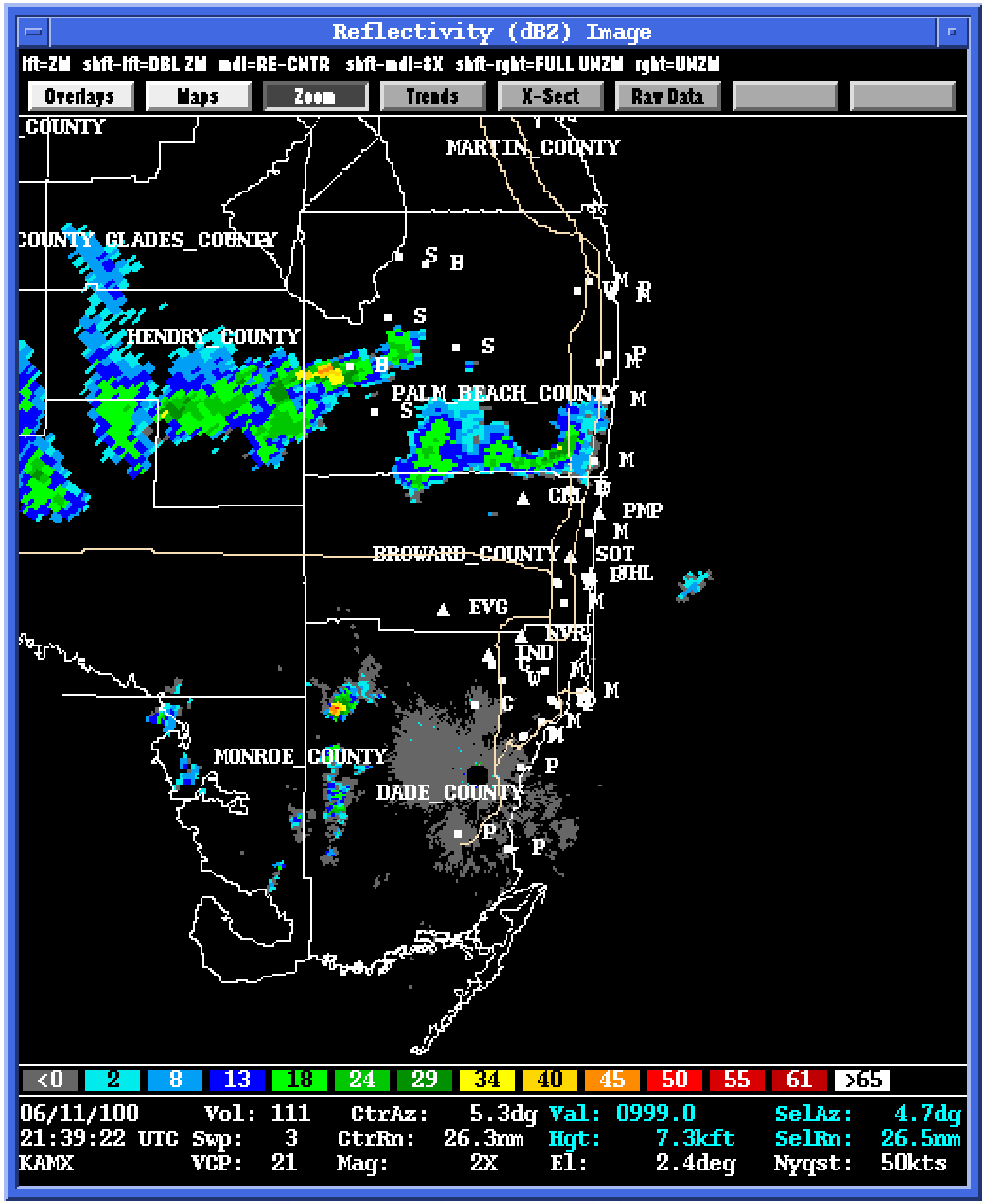
Sites can be used to determine a baseline.

Across street from MWI

Receptor-Modeled Source Contributions (SOFAMMS)

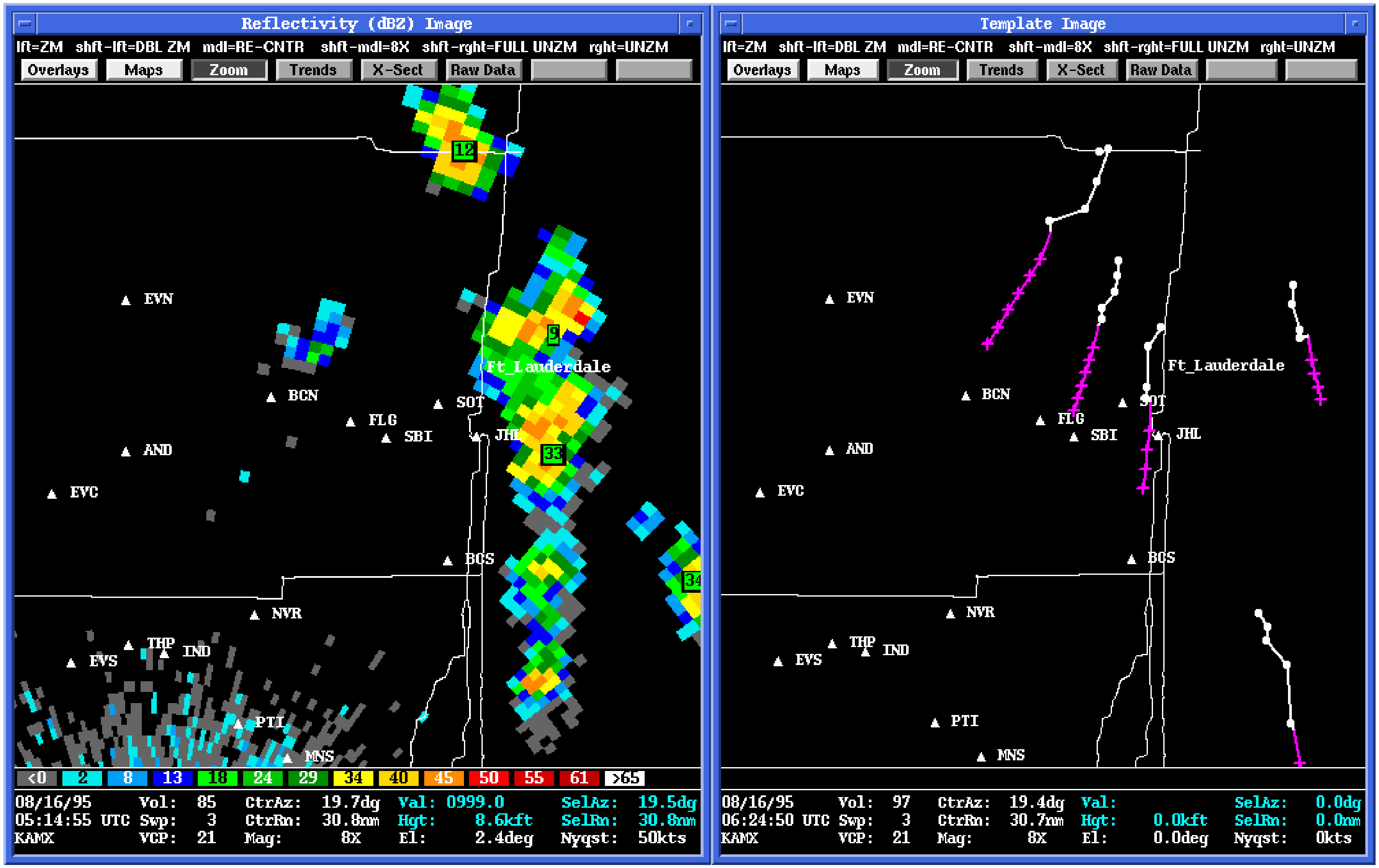
Source Type	Receptor Model Hg Source Apportionment (% of Total)
Municipal Waste Incineration	57 ± 7
Medical Waste Incineration	30 ± 16
Oil-Fired Boilers	14 ± 5

Stable Pb Isotope analysis of event precipitation and daily aerosol samples indicate Pb to be North American in origin.



Example NEXRAD Radar Data

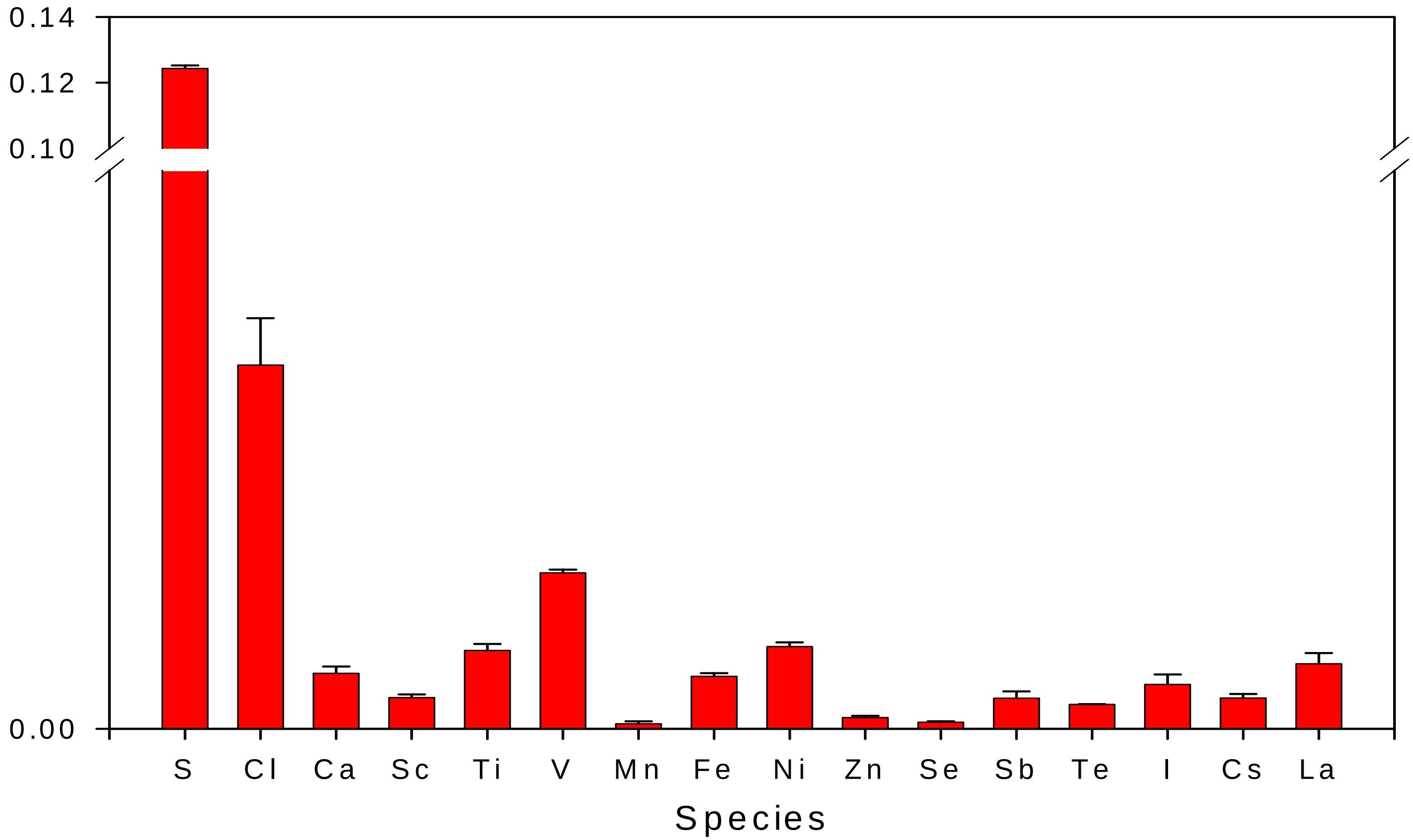
Example NEXRAD Radar Data



* Dvonch et al. *Sci. Total Environ.*, 1998, 213, 95-108

Oil Fired Utility Boiler Stack Test

Residual Oil Fired Utility Boiler XRF Emission Profile



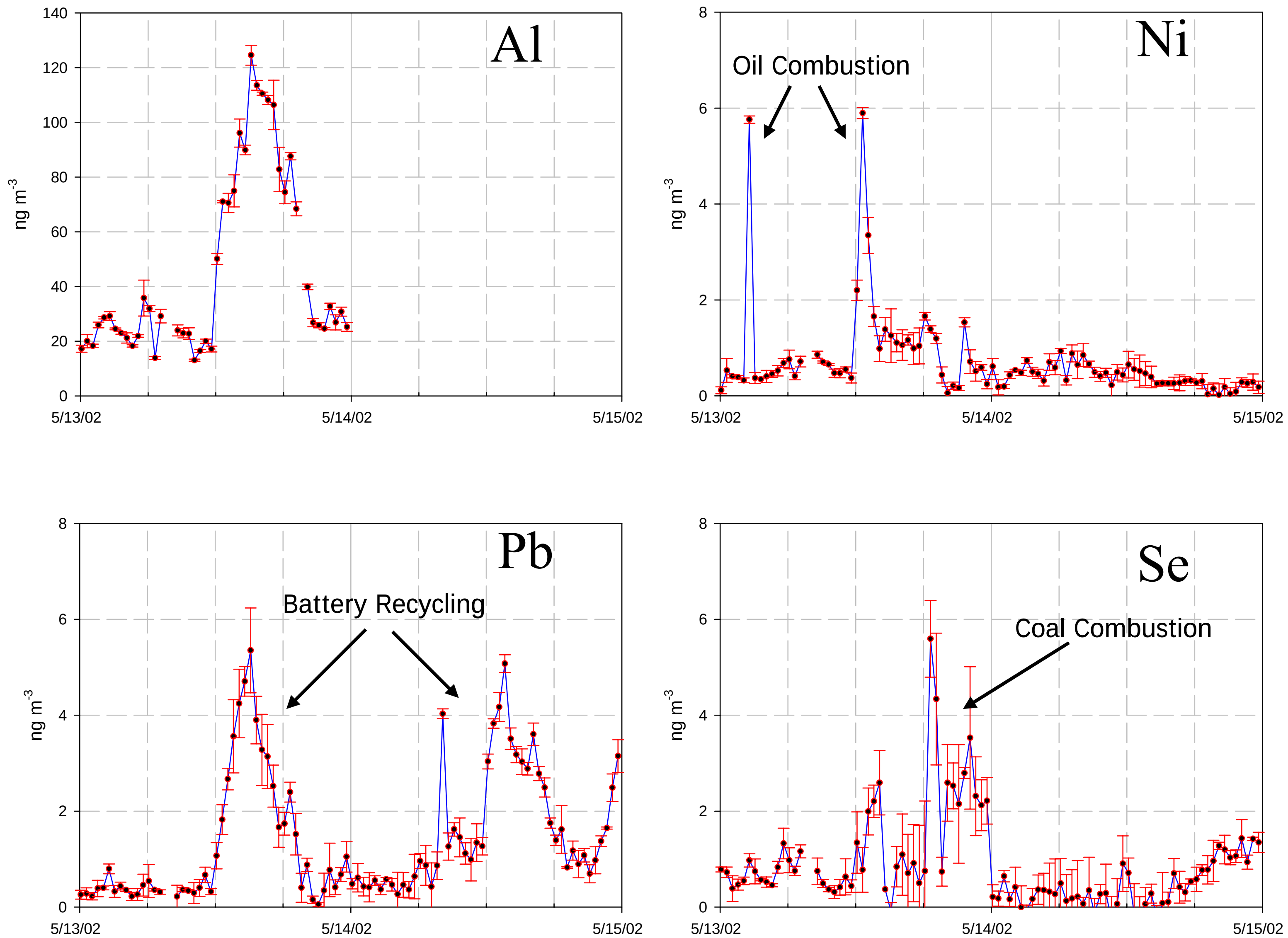
High Volume Slurry Sampler

* 30 minute $PM_{2.5}$ samples

High Resolution ICP-MS Capability
(Slurry Sample Aerosol Samples)

- Low Resolution
  - Li, Be, Rb, Sr, Mo, Ag, Cd, In, Sn, Sb
    Cs, Ba, La, Ce, Nd, Sm, W, Tl, Pb, U
- Medium Resolution
  - Na, Mg, Al, P, S, Ca, Sc, Ti, V, Cr
    Mn, Fe, Co, Ni, Cu, Zn
- High Resolution
  - K, As, Se
- Stable Isotope Ratios
  - Pb

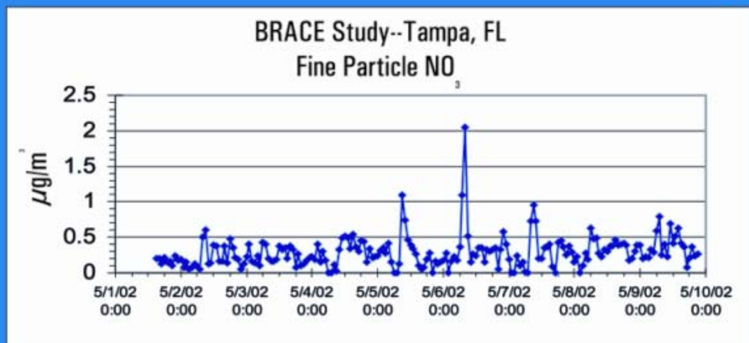
Example Slurry Sampler Data

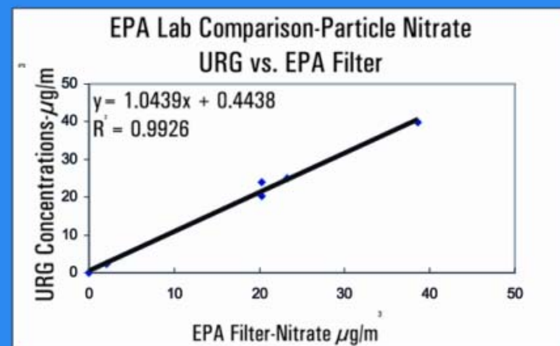


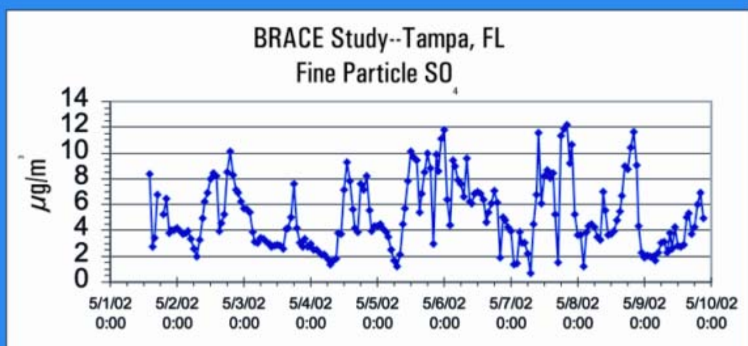
Continuous Gas & Particulate Phase Ambient Ion Monitor

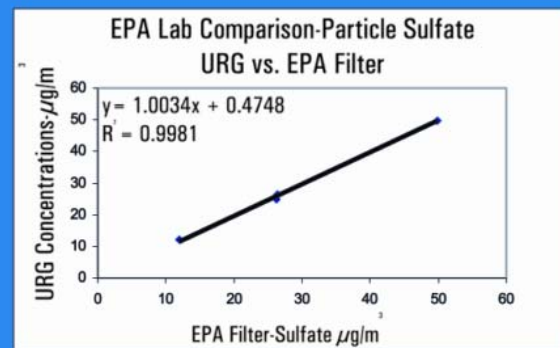
Example Ion Monitor Data

Testing Data









Hourly Measurements of Fine Particle Nitrate and Sulfate Measured in Tampa, FL as part of the BRACE Study in May, 2002

Instrument Response Versus Laboratory Generated Nitrate and Sulfate Aerosol

Semi-Continuous PM Monitors

TSI Nephelometer

R&P TEOM

Magee Scientific Semi-Continuous IOTA EC Monitor

Sunset Laboratories Semi-Continuous NDIR OC/EC Monitor

Example EPA Monitoring Site

Steubenville Metrics

- **Aerosols** (Daily) – R&P Sequential Dichotomous Samplers
  - Trace Elements, Carbon, Pb Isotopes
- **Aerosols** (Continuous)
  - Mercury, Nephelometer, TEOM ($PM_{2.5}$), Aethalometer
- **Precipitation** (Event)
  - Total Mercury, Trace Elements, Major Ions, Pb Isotopes
- **Gases** (Continuous)
  - Hg^0, Hg^{2+}, SO_2, CO, O_3, NO, NO_2, NO_x
- **Meteorology** (Continuous)
  - T, RH, BP, WS, WD, SI, PD

Steubenville Monitoring Platform

Steubenville Monitoring Shelter

Additional Intensive Metrics (New Mobile Lab)

- **Aerosols**
  - High Volume Slurry Sampler (30 min.)
  - Continuous Sunset Analyzer for OC/EC (1 hour)
  - URG 9000 Ambient Ion Monitor (1 hour)
  - VAPS (12 hour; denuders; aerosols; SEM; IC; HR-ICPMS)
  - MOUDI Impactor for Size Segregated Aerosols (24 hour)
  - API Particle Counter
  - TISCH Sampler for Speciated Organics (12 hour; 24 hour)
- **Gases**
  - Hg^0, Hg^{2+}, SO_2, CO, O_3, NO, NO_2, NO_x
- **Meteorology**
  - T, RH, BP, WS, WD, SI, PD

EPA Mobile Mercury Laboratory

EPA Mobile Laboratory Features:

- Continuous Mercury Speciation
- Aerosol Characterization
- Criteria Gas Instruments
- Full Meteorological Capability
- High Flow Sampling Manifold
- Integrated Sampling Platform
- Class 100 Laminar Flow Bench
- Refrigerator/Freezer Storage

Thoughts …

- Current Deterministic Models are Inadequate
  - Need Comprehensive Global Emission Inventories
  - Need Improved Understanding of Hg Kinetics
  - Need Improved Dry Deposition Parameterizations
- Current Monitoring Activities Generally Inadequate for Comprehensive Source Apportionment Modeling
  - Need Event Precipitation
  - Need Comprehensive Tracer Species
  - Need Coordinated Monitoring Strategy
  - Need Global Background/Trend Sites

Disclaimer

Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy


Questions ???
2/1/2000