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March 12, 2008

Dr. Diane Gould
U.S. Environmental Protection Agency, Region 1
1 Congress Street, Suite 1100
Boston, MA 02114-2023

STI-906058.02-3286

Re: Updated trace metals data analyses and meteorological typing and case study analyses from Casco Bay

Dear Diane,

Thank you for the opportunity to conduct additional data analyses using trace metals data collected at Casco Bay. The goal of these additional analyses was to update Sonoma Technology, Inc.'s (STI) report (Wu et al., 2005) with 2005 data, categorize deposition samples by meteorological regime, and perform case study analysis on large deposition events and selected meteorological events. This work consisted of two tasks, described in detail below: (1) update the previous analyses conducted by STI with 2005 data, and (2) perform meteorological and air quality data analyses. This deliverable incorporates comments received from EPA in January 2008. In particular, additional work examining ratios of deposition and Interagency Monitoring of Protected Visual Environments (IMPROVE) aerosol data has been conducted and graphics provide additional explanation.

<u>Task 1 – Update Previous STI Report with 2005 Data (see Attachment 1)</u>

In December 2005, STI delivered an annotated Microsoft PowerPoint presentation and executive summary of the analysis of 2003-2004 trace metals data. For this task, we incorporated 2005 data into that presentation and executive summary. The additional year of data enabled more robust statistical analyses of trends and relationships among species. This task included a Level 1 validation of the data and an update of plots and analyses. The original 2003-2004 data set appeared to be insufficient for source apportionment using the multivariate receptor model, positive matrix factorization (PMF); the data set is larger but still limited, so a PMF analysis may not yield satisfactory results.

<u>Task 2 – Meteorological and Case Study Analyses (see Attachment 2)</u>

The goal of this task was to identify different meteorological regimes that affect wet deposition, and perform case study analyses for selected dates on which high wet deposition or unique meteorological conditions occur, as well as utilize IMPROVE data to understand how these data relate to the wet deposition. First, synoptic charts were used to identify which deposition samples are impacted by a single weather system or by a combination of warm and cold fronts; only samples with more than trace precipitation were used. Each of the samples with data above detection was identified with a synoptic or frontal passage pattern. Then, the deposition concentrations were compared when these different weather types occurred. It is expected that some patterns will result in high deposition concentrations while others will not.

Next, five case study events were selected for further analysis. These case study events were convective/frontal events (rather than coastal events) for which we might expect a link between ambient aerosol concentrations and deposition. These events included a few outlier deposition events, and an example event from most meteorological regimes. For the case studies, back trajectories were run and the meteorology characterized. Additionally, the spatial and temporal patterns of the IMPROVE speciated $PM_{2.5}$ lead, manganese, and arsenic data on the days prior to and/or during the case study events were examined. These patterns will help us better understand the regional spatial and temporal ambient aerosol trends of the metals, which may have a bearing on the deposition of these metals at Casco Bay.

Summary of Work

Attachment 1 provides the updated PowerPoint presentation incorporating 2005 data, and the meteorological and case study analyses. Attachment 2 provides more detailed discussion and results of the meteorological and case study analyses.

Reference

Wu J., Brown S., and Hafner H. (2005) Casco Bay trace metal validation and preliminary analysis. Presentation prepared for the U.S. Environmental Protection Agency, Region 1, North Chelmsford, MA, by Sonoma Technology, Inc., Petaluma, CA, STI-904080.03-2883, December.

Best regards,

Steven G. Brown
Manager, Aerometric Data Analysis

Outline

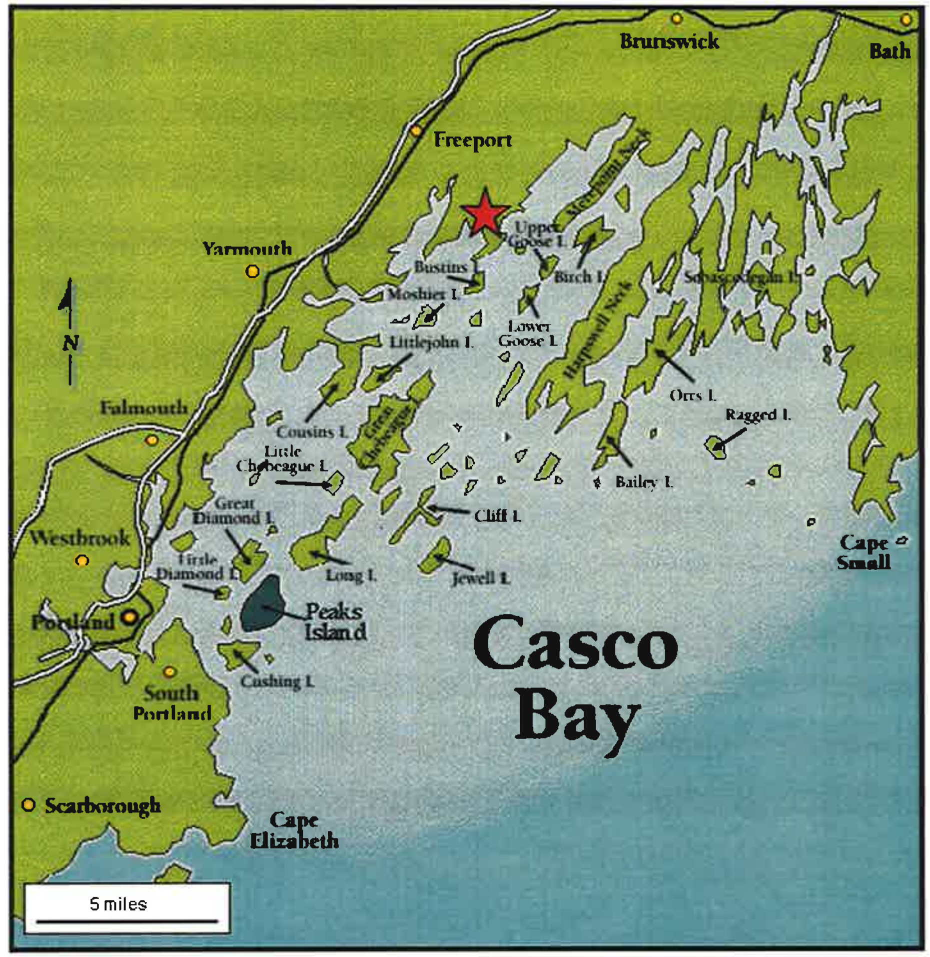
- Overview of Work Scope
- Summary of Past Analysis
- Data Validation
- Data Analyses
  - Seasonal Variations
  - Correlations
  - Scatter Plots
  - Time Series
  - Met Analysis
  - Case Studies and Ratio Analysis
- Summary
- Recommendations

Overview of Work Scope

- Update the previous analyses with 2005 data
  - Incorporate 2005 data into previous presentation and executive summary
  - Perform Level 1 validation of the data and update plots and analyses
  - Reassess the possibility of using the updated data set for source apportionment and make a recommendation in this regard
- Perform meteorological and air quality data analysis
  - Identify deposition samples impacted by a single weather system or by a combination of warm and cold fronts; classify samples with a synoptic or frontal passage pattern; compare the deposition/concentrations when these different weather types occur.
  - Identify up to five case-study events for further analysis (run back trajectories and characterize the meteorology that affected the site).
  - Examine the spatial and temporal patterns of the IMPROVE speciated $PM_{2.5}$ lead, manganese, and arsenic data on the days prior to and during the case-study events.

Data Overview

- Mercury Deposition Network (MDN) samples were collected at the Casco Bay, Maine, site (ME96) and analyzed by Frontier Geosciences for trace metals. The samples were collected from January 2002* through January 2006.
- Data were validated and then evaluated by season and year, by single events versus multiple events, and by event size and duration including trajectory analyses.



*Note that data collected prior to October 2002 were not available.

Previous Work

- Previous analyses focused on 2003-2004 data (*Wu et al., 2005*).
- Good correlations among many of the metals were found, indicating that source type or source region information may be discernible from the data set.
- Trajectory analyses were difficult to interpret because in most of the week-averaged samples, multiple precipitation events occurred.

Wu J., Brown S., and Hafner H. (2005) Casco Bay trace metal validation and preliminary analysis. Presentation prepared for the U.S. Environmental Protection Agency, Region 1, North Chelmsford, MA, by Sonoma Technology, Inc., Petaluma, CA, STI-904080.03-2883, December.

Available Data from the National Atmospheric Deposition Program (NADP)

- Weekly concentrations and depositions of Hg, AsICPMS, AsHGAFS, SeICPMS, SeAFS, Cd, Cr, Cu, Mn, Ni, Pb, Mg, and Zn from 2002 to 2005 (164 weeks).
- As and Se were measured by ICPMS and HGAFS.
- Quarterly summaries of concentrations and depositions for each species.
- Estimated detection limit (eMDL), 5*eMDL (similar to a lower quantifiable limit), and volume-weighted averages (VWA) for each species on a quarterly basis.
- Bottle capture volume, efficiency, and sample notes and observations.

ICPMS = inductively coupled plasma mass spectrometry
HGAFS = hydride generation atomic fluorescence spectrometry

Data Validation: Not Reported and Below Detection Limit Data

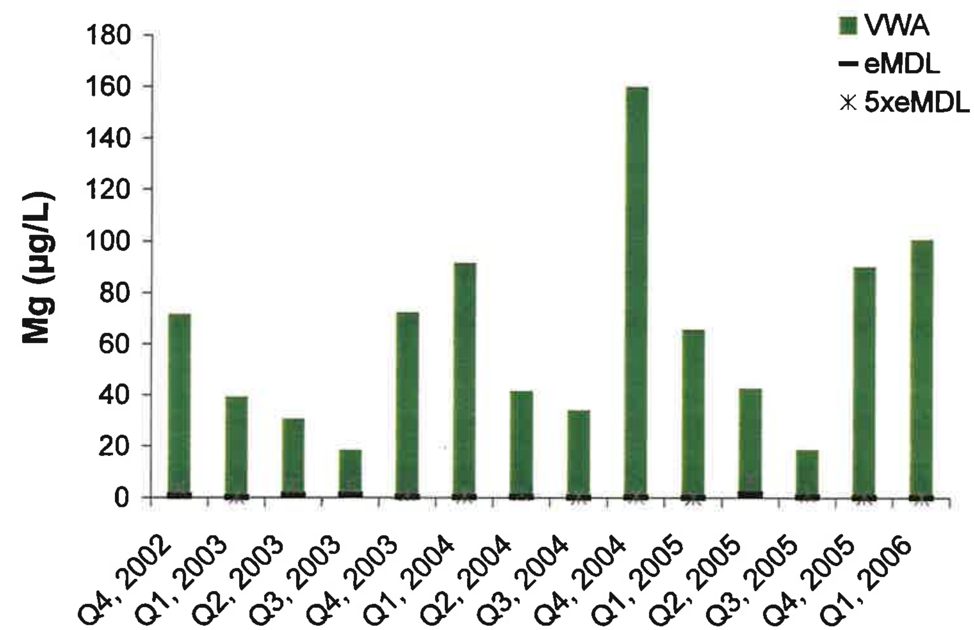
Species	Not Reported	Less than eMDL	Between eMDL and 5xeMDL	Greater than 5xeMDL	N Above eMDL
AsICPMS	1%	52%	45%	3%	62
AsHGAFS	15%	90%	10%	0%	13
SeICPMS	0%	74%	22%	5%	34
SeAFS	*51%*	*100%*	*0%*	*0%*	*0*
Cd	0%	40%	38%	22%	78
Cr	52%	81%	17%	2%	25
Cu	0%	35%	42%	24%	85
Mn	0%	24%	6%	70%	99
Ni	0%	37%	27%	36%	82
Pb	0%	18%	22%	61%	107
Mg	0%	13%	2%	85%	113
Zn	0%	25%	21%	54%	97
Be	0%	93%	7%	0%	9

Species in **bold** were not included in further analysis
Pink shading indicates the majority of samples were below the eMDL
Concentrations less than zero were treated as below the eMDL

- 130 samples were collected
- Similar to the last analysis, As, Cr, and Se were below detection most of the time
- 'Not Reported' includes dates when a sample was collected/analyzed, but a particular compound was not reported
- Cu was above detection in 65% of the samples, compared to 25% in the last analysis
- The following slides show example volume weighted averages, estimated detection limits, and 5 times the estimated detection limit by quarter; all species are shown in the appendix
- Hg VWA was not provided and was not available from MDN

Quarterly Summary

- This example shows a quarterly summary of volume weighted average Mg concentrations.
- This metal was nearly always above the eMDL and 5xeMDL.
- Q1 2004 VWA was high for most species; this quarter also had the highest number of low volume samples (5 out of 13), which could be impacting the VWA calculations.
- Quarterly summaries for all species are available at the end of this presentation.



Summary of Data Validation

- Samples with trace amounts of precipitation were flagged as "low volume" samples (*27 samples*)
- Field blanks were flagged and excluded from analysis (*7 blanks*)
- Negative sample values were treated as below the estimated detection limit (*7 samples*)
- The majority of samples of six species were below the estimated detection limit (As-ICPMS, As-AFS, Se-ICPMS, Se-AFS, Cr, and Be)
- The majority of samples of four species were greater than 5 times the eMDL (Mn, Mg, Pb, Zn)
- The majority of samples for two species were not reported (Cr and Se-AFS)
- Se-AFS had all reported data below the eMDL and will be excluded from analysis
- Other data errors observed in previous reports were not observed in the most recent data set

VWA Concentration by Quarter (1 of 2)

	High Quarter	
	Concentration	Deposition
Hg	NA	2nd
AsICPMS	1st	4th
AsHGAFS	1st	3rd
SeICPMS	1st	2nd
Cd	1st	2nd
Cr*	2nd	2nd
Cu	2nd	2nd
Mn	1st/2nd	2nd
Ni	1st	2nd
Pb	2nd	2nd
Mg	4th	4th
Zn	1st	2nd
Be*	2nd	2nd

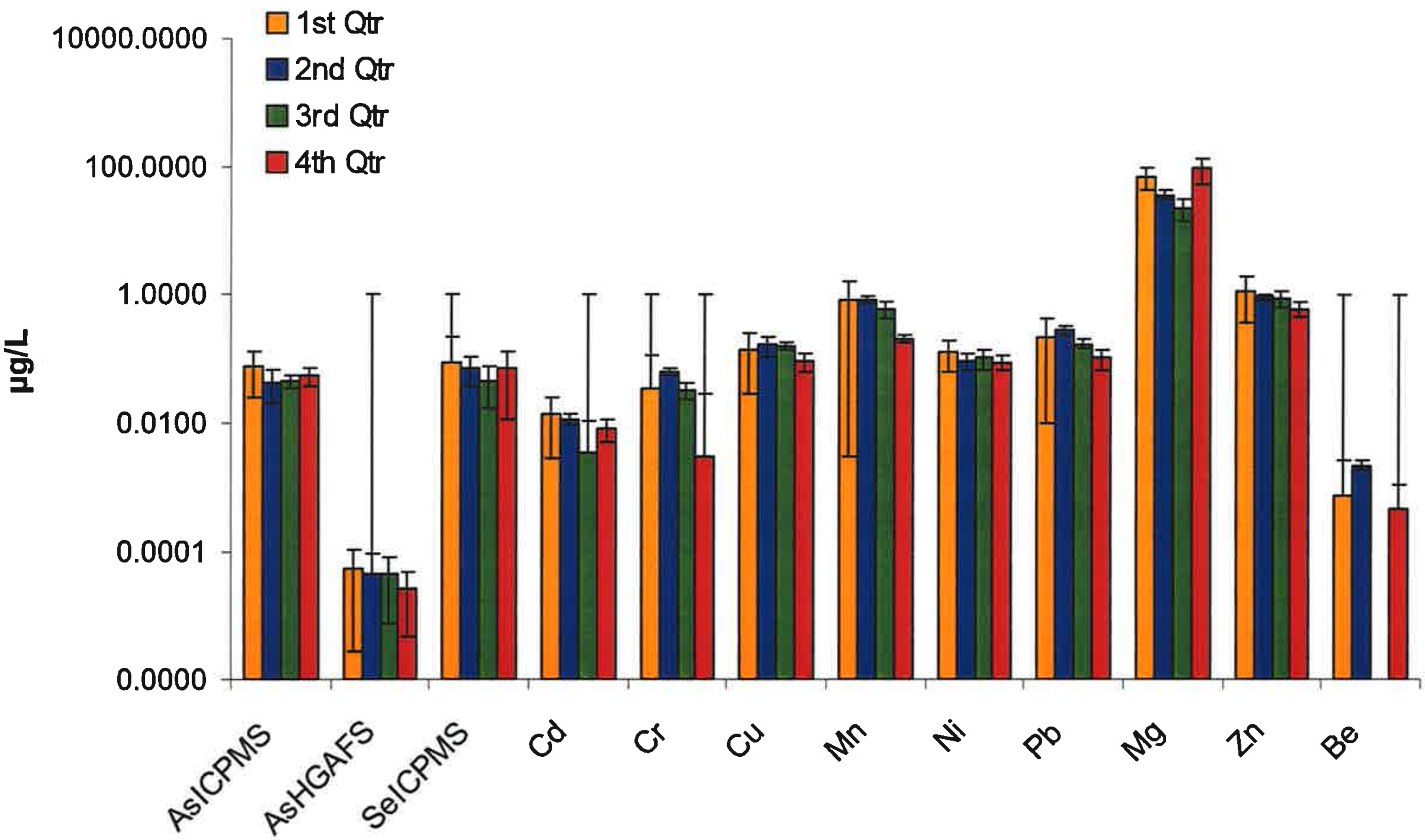
*4th quarter Cr deposition and 3rd quarter Be concentration and deposition removed due to negative values

- Similar trends were seen as with the previous analysis
- Deposition of most metals was highest in the second quarter
- Concentrations of most metals were highest in the second and/or first quarters

1st quarter = Jan – Mar, etc.

VWA Concentration by Quarter (2 of 2)

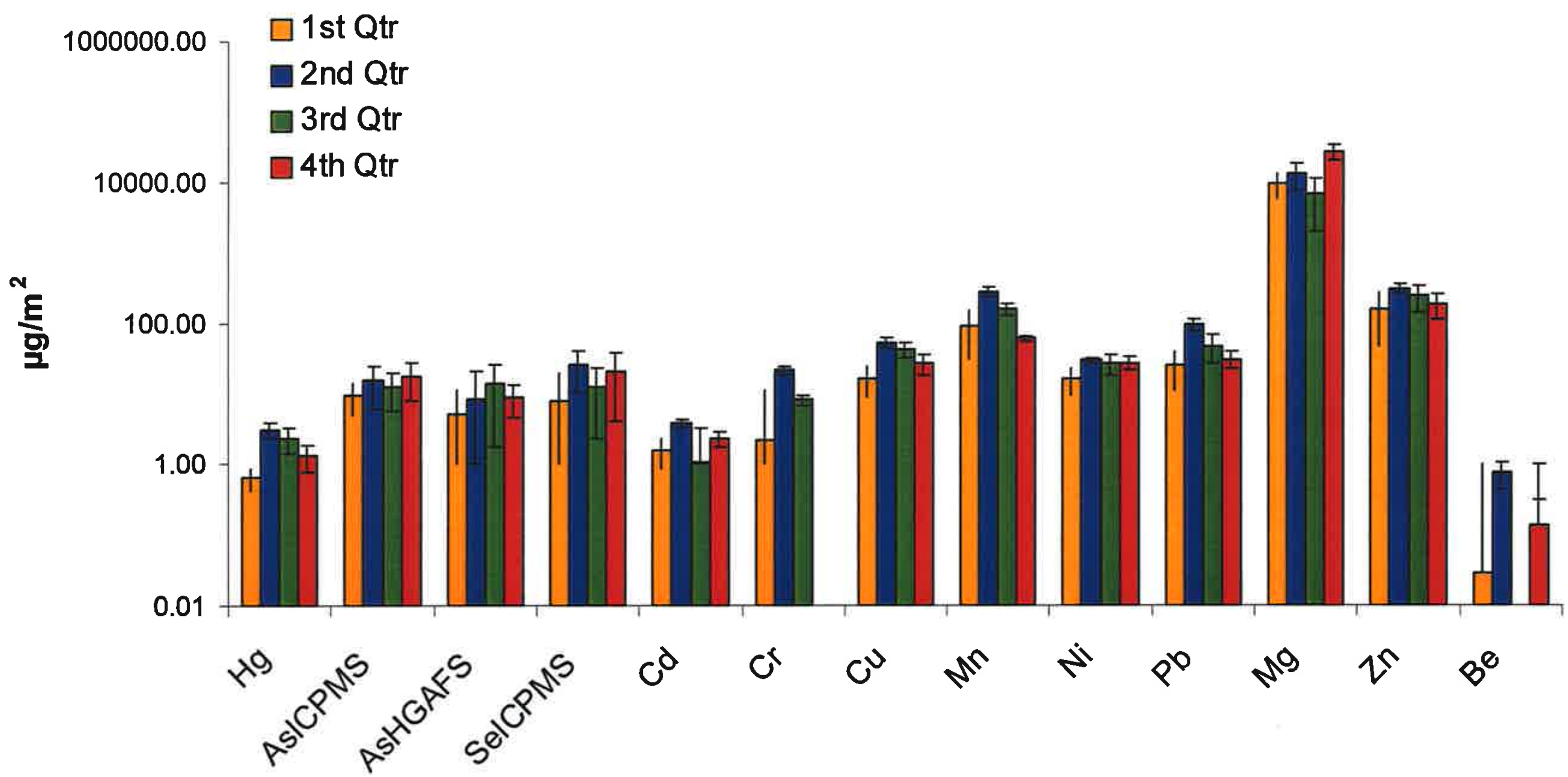
Error bars show +/- 1 standard deviation



*Quarterly averages calculated by Frontier Geosciences

Deposition by Quarter

Error bars show +/- 1 standard deviation



*Quarterly averages calculated by Frontier Geosciences

Summary of Concentration, Deposition Levels

- Concentrations of Mg are highest; next highest are Zn and Mn. Cu, Ni, and Pb have similar concentrations. Se and As (ICPMS) also have similar concentrations.
- Deposition shows similar relative patterns to concentration with Mg exhibiting the highest deposition values followed by Zn and Mn. Cu, Ni, and Pb have similar deposition values. Hg and Cd are also similar.

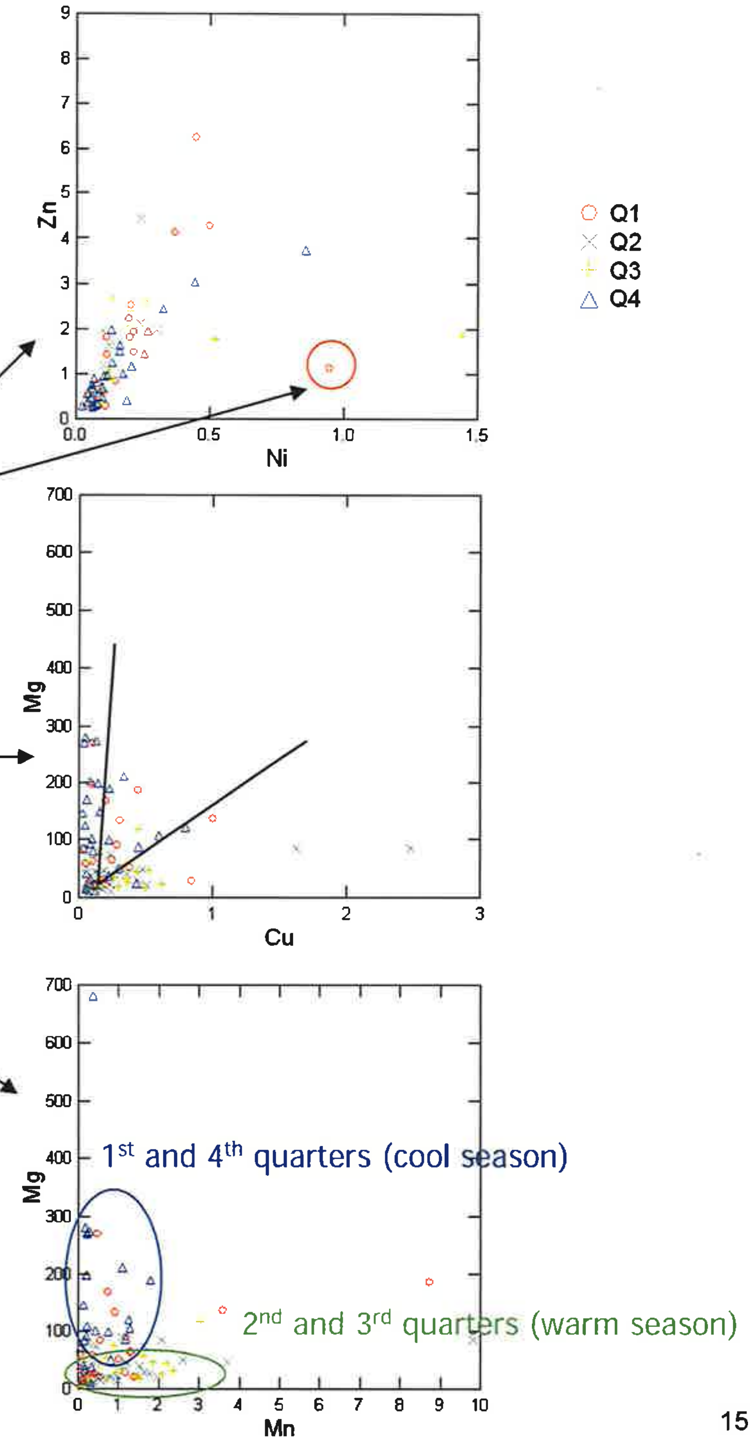
Correlations Between Species Concentrations

		CD	CU	HG	MG	MN	NI	PB	ZN
1st Quarter	CD	**1.0**							
	CU	**0.7**	**1.0**						
	HG	**0.8**	**0.8**	**1.0**					
	MG	0.3	0.1	0.3	**1.0**				
	MN	0.5	0.5	0.6	0.4	**1.0**			
	NI	0.5	0.3	0.3	0.1	0.2	**1.0**		
	PB	**0.9**	**0.7**	**0.9**	0.3	0.6	0.3	**1.0**	
	ZN	**1.0**	**0.7**	0.6	0.2	0.5	0.5	0.6	**1.0**
2nd Quarter	CD	**1.0**							
	CU	**0.9**	**1.0**						
	HG	0.3	0.3	**1.0**					
	MG	0.5	0.6	0.1	**1.0**				
	MN	**0.9**	**0.9**	0.4	0.4	**1.0**			
	NI	0.4	0.7	0.1	0.1	0.7	**1.0**		
	PB	**0.9**	**0.9**	0.5	0.5	**0.9**	0.6	**1.0**	
	ZN	**0.7**	**1.0**	0.1	0.5	**0.8**	**0.8**	**0.7**	**1.0**
3rd Quarter	CD	**1.0**							
	CU	0.3	**1.0**						
	HG	**-0.4**	0.1	**1.0**					
	MG	**0.6**	0.0	0.3	**1.0**				
	MN	**0.6**	**0.7**	0.5	0.4	**1.0**			
	NI	0.3	0.3	**0.9**	**0.8**	0.6	**1.0**		
	PB	**0.5**	**0.9**	0.1	-0.1	**0.8**	0.1	**1.0**	
	ZN	**0.9**	0.3	-0.1	0.0	0.3	0.2	0.4	**1.0**
4th Quarter	CD	1.0							
	CU	0.7	**1.0**						
	HG	0.6	0.7	**1.0**					
	MG	0.3	-0.1	0.0	**1.0**				
	MN	0.6	**0.8**	0.6	0.0	**1.0**			
	NI	0.6	**0.8**	**0.7**	-0.1	0.6	**1.0**		
	PB	**0.8**	**0.9**	**0.8**	0.1	**0.7**	**0.8**	**1.0**	
	ZN	0.7	**0.9**	**0.8**	0.0	**0.9**	**0.9**	**0.9**	**1.0**
All Quarters	CD	**1.0**							
	CU	**0.7**	**1.0**						
	HG	0.3	0.4	**1.0**					
	MG	0.2	0.0	-0.1	**1.0**				
	MN	0.7	**0.7**	0.4	0.0	**1.0**			
	NI	0.5	0.4	0.3	0.0	0.4	**1.0**		
	PB	**0.8**	**0.8**	0.5	0.1	**0.8**	0.4	**1.0**	
	ZN	**0.8**	0.6	0.2	0.0	0.5	0.5	0.6	**1.0**

- Correlations between species were examined to look for common sources, but this analysis is limited by the low number of samples.
- Species with <10 samples above detection were excluded, including As, Se, Cr, Cd, and Be.
- Pink shading indicates <5 pairs.
- Orange shading indicates 5-10 pairs.
- Bold indicates good correlation.
- A number of relationships between species are seen, and may suggest common sources or source areas.

Scatter Plot Analysis Concentration

- In addition to the R^2 values, scatter plots were examined by quarter to look for trends in the correlations and outlying events
- Several outliers were noted
- Some pollutants had two distinct edges, indicating more than one source
- Some species exhibited seasonal segregation, indicating source strength changes with season
- Full scatter plot analysis is available in the Appendix (attached)
- All units are µg/L

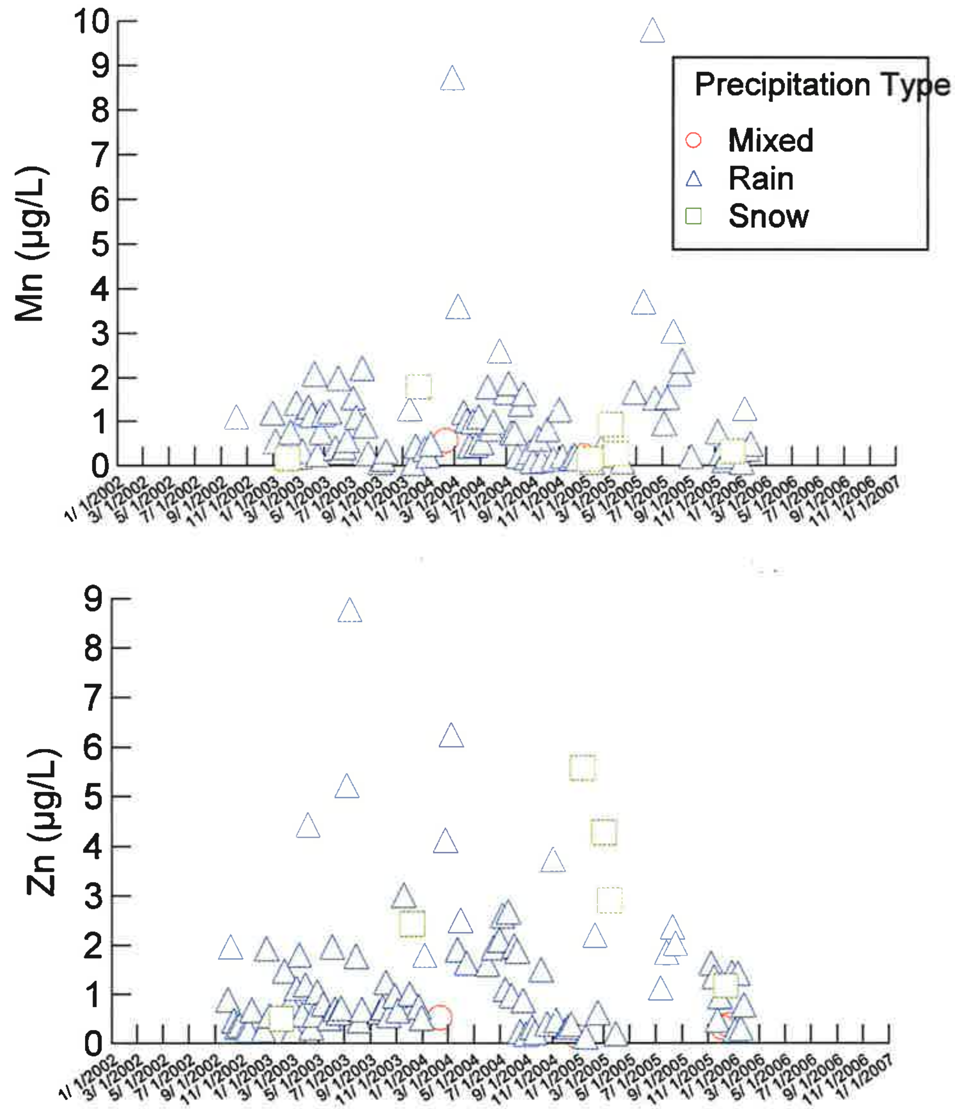


Summary of Scatter Plot Analysis

- Scatter plots showed the following relationships:
  - Hg did not correlate well with most metals overall, but did have moderate correlations with Cd, Cu, and Pb in the 1^{st} quarter and Ni, Pb, and Zn in the 4^{th} quarter.
  - As (ICPMS) correlated well with Cd, Pb, Cu, and Zn.
  - Cu correlated well with Pb and Zn.
  - Cd correlated well with most other metals. Its relationship with Mg indicates possible multiple sources. Cu showed a similar relationship with Mg.
  - Mn, Mg, and Se data did not strongly correlate with other metals.
  - Ni correlated well with Zn.
  - Many Pb samples correlated with Zn.
- It is difficult from these relationships to point to any single source types.
- Full scatter plot analysis is available at the end of this presentation.

Time Series Analysis

- Time series were examined by precipitation type (rain, snow, mixed) to determine if certain events were conducive to high concentrations.
- Highest concentrations of most species were during rain, which was the most common precipitation.
- Zinc concentrations were high for several samples during weeks when snow occurred.
- Full time-series analysis is available at the end of this presentation.



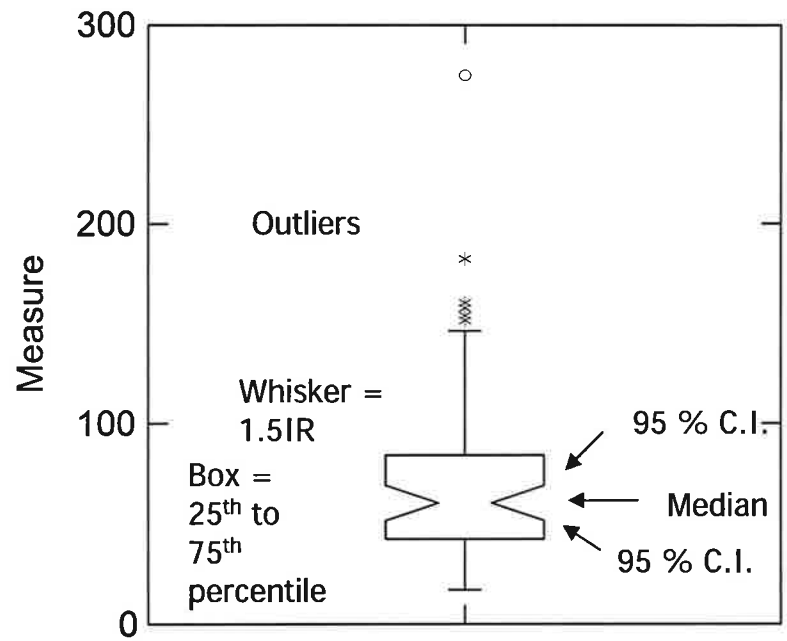
Ratio Analysis Overview

- Metals ratios in the deposition data were compared to source signatures to understand whether edges observed on scatter plots are indicative of individual source types.
- Goals were to attempt to answer the following:
  - Are ratios at Casco Bay in precipitation similar or dissimilar on a weekly basis?
  - Are ratios in precipitation the same as the aerosol?
  - Can we say anything about the source of aerosol and source of metals in precipitation?
- Source ratios from Sweet et al., 1998 were used for comparison to ambient ratios.

Clyde W. Sweet, Aaron Weiss, and Stephen J. Vermette. 1998. Atmospheric Deposition of Trace Metals at Three Sites Near the Great Lakes. *Water, Air, and Soil Pollution* **103**: 423-439.

Interpreting Notched Box Plots

Notched Box Whisker
Plots in SYSTAT



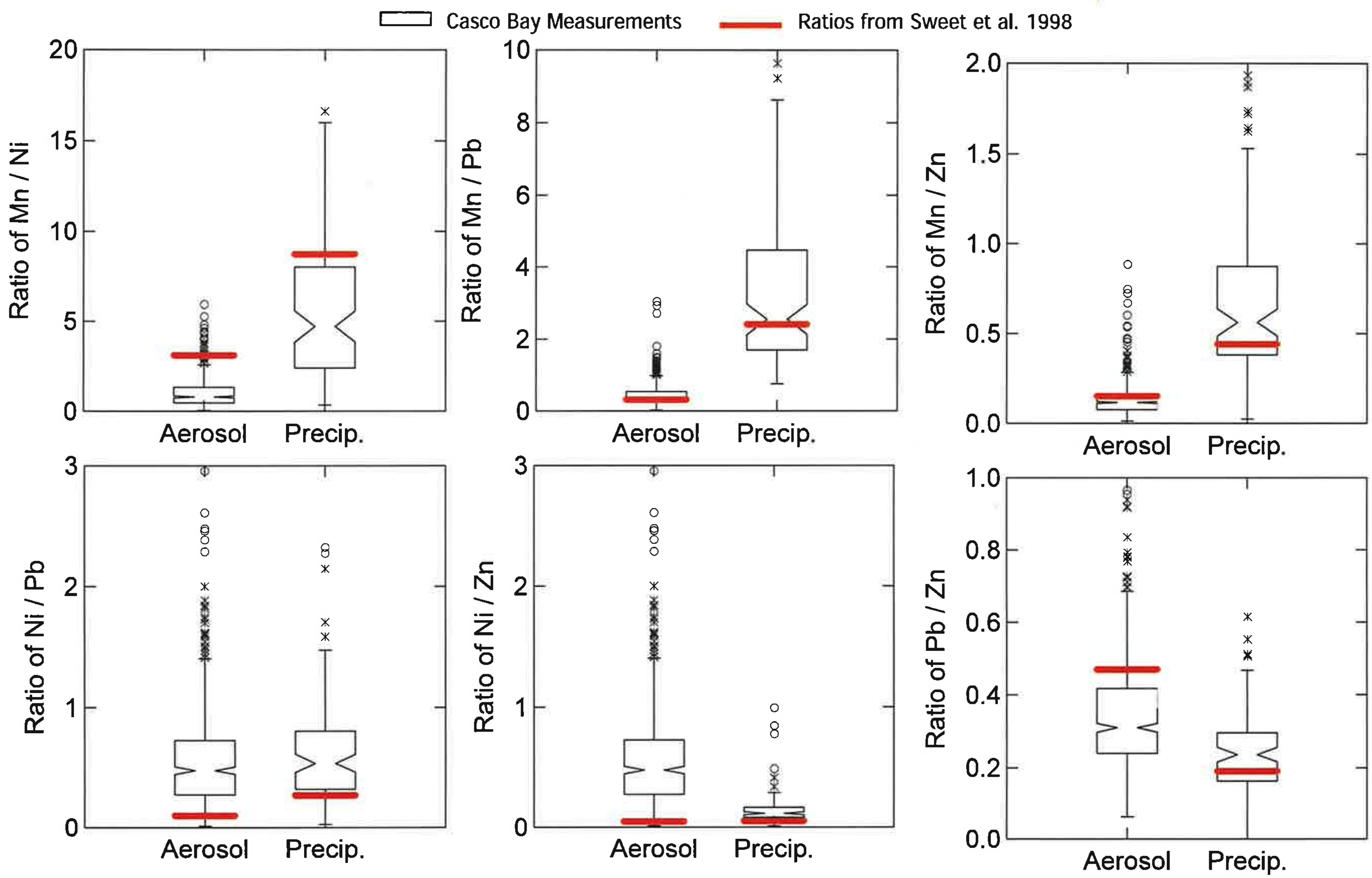
Ratios among Ni, Pb, Zn, and Mn in precipitation data were compared to ratios in collocated aerosol measurements using notched box plots.

where

IR = interquartile range

C.I. = confidence interval

Ratios in Precipitation vs. Aerosol



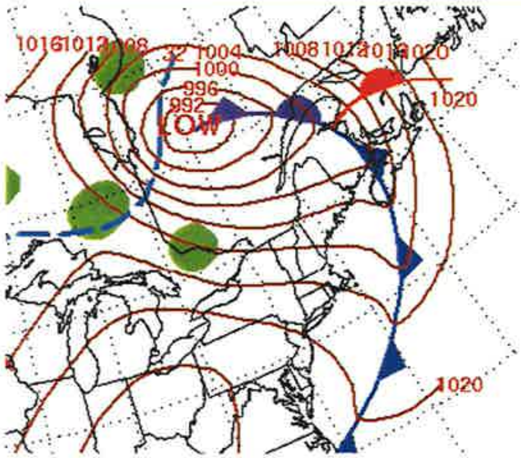
Ratios in Precipitation vs. Aerosol

- Comparing ratios in precipitation and aerosol showed the following results:
  - Mn ratios were significantly higher in Casco Bay precipitation data compared to the other metals. Ratios with Mn were also much more variable in the precipitation than in the aerosol. It is not clear why.
  - Ratios of Pb with Ni and Zn were similar in precipitation and aerosol measurements.
  - The ratio of Ni to Zn was lower and less variable in the precipitation data.
- The metals ratios were compared to deposition and aerosol data collected in Pennsylvania using similar methods (Sweet et al.,1998).
  - Precipitation ratios at Casco Bay were in relatively good agreement with the results in Sweet et al.
  - Aerosol ratios at Casco Bay were not always in agreement with results in Sweet et al. This is probably due to spatial and temporal differences of the aerosol measurements.
  - Concentrations of trace metals in precipitation may be influenced by longer and/or larger scale transport than aerosol concentrations.
  - Most of the ratios observed at Casco Bay are different than the what was seen in the earlier Pennsylvania data, suggesting there may be different sources impacting Casco Bay or source mixture has changed.

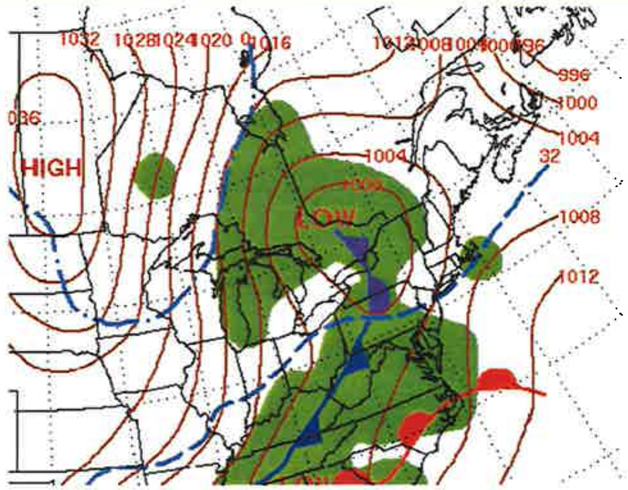
Meteorological Analyses

- Trace metal concentration and deposition data were analyzed by meteorological regime.
- Based on weather maps and local observations in Portland, Maine, six different weather patterns were identified for weekly samples with a single precipitation event occurring during that week; samples were also classified by rain, snow, or mixed precipitation. The next two slides show examples of the six patterns.
- Case study events for different weather patterns were also examined with IMPROVE and trajectory data to look for common patterns in the relative concentrations of the metals.

Meteorological Typing (1 of 2)



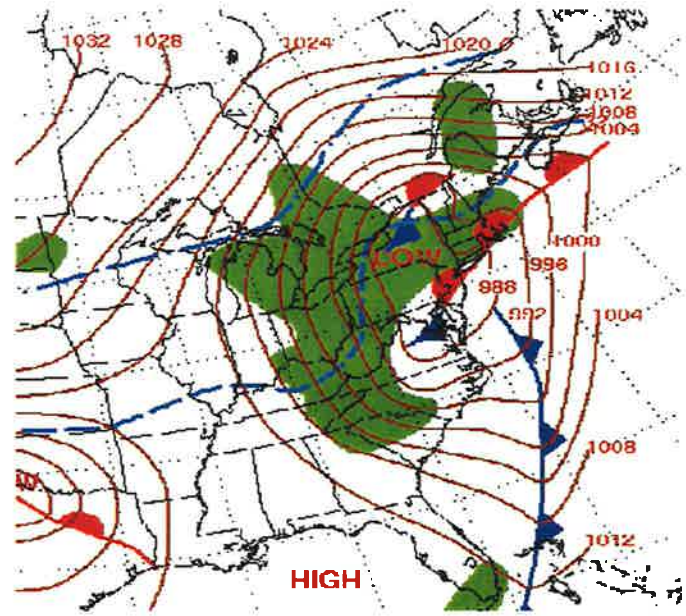
Pattern A: cold frontal passage. Example shown is November 7, 2005



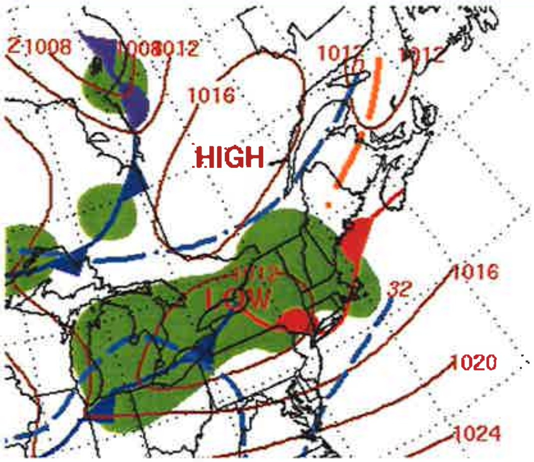
Pattern B:
low pressure system moving through from west to east. Example shown is January 17-19, 2004

The examples shown in this and the next slide provide representative days – not all weekly samples are shown. All sample designations are listed in the supplementary material.

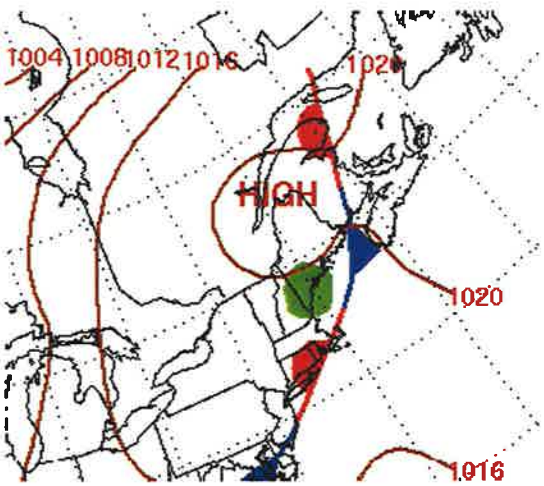
Pattern C : low pressure system moving up the coast. Example shown is February 22-24, 2003



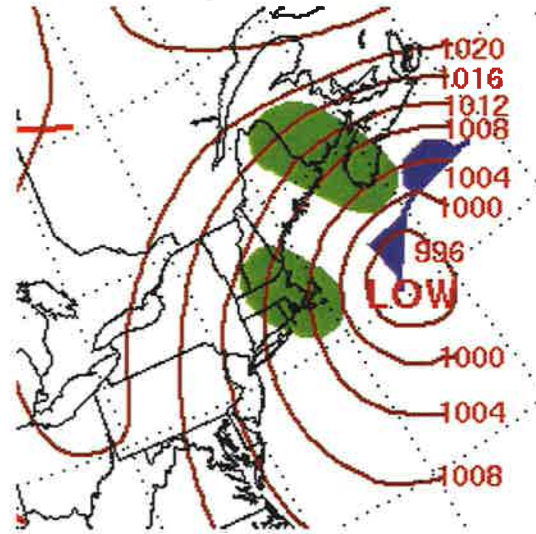
Meteorological Typing (2 of 2)



Pattern D: warm front approaching or moving through. Example shown is January 12, 2004



Pattern E: stationary front near the region. Example shown is September 26, 2003



Pattern F: low pressure system offshore. Example shown is May 8, 2005

Comparisons by Typing

- Trends were examined by season (summer and winter) to understand seasonal differences – i.e., were concentrations or depositions consistently higher or lower under certain types of weather patterns?
- Summer was defined as May through September; winter as November through February.
- In the following graphs, no consistent trend was observed among species or typings, possibly due to the low amount of data.
- Examples are shown in the next slides; more examples are provided in the technical memo (Attachment 2).

Box Plot Interpretation

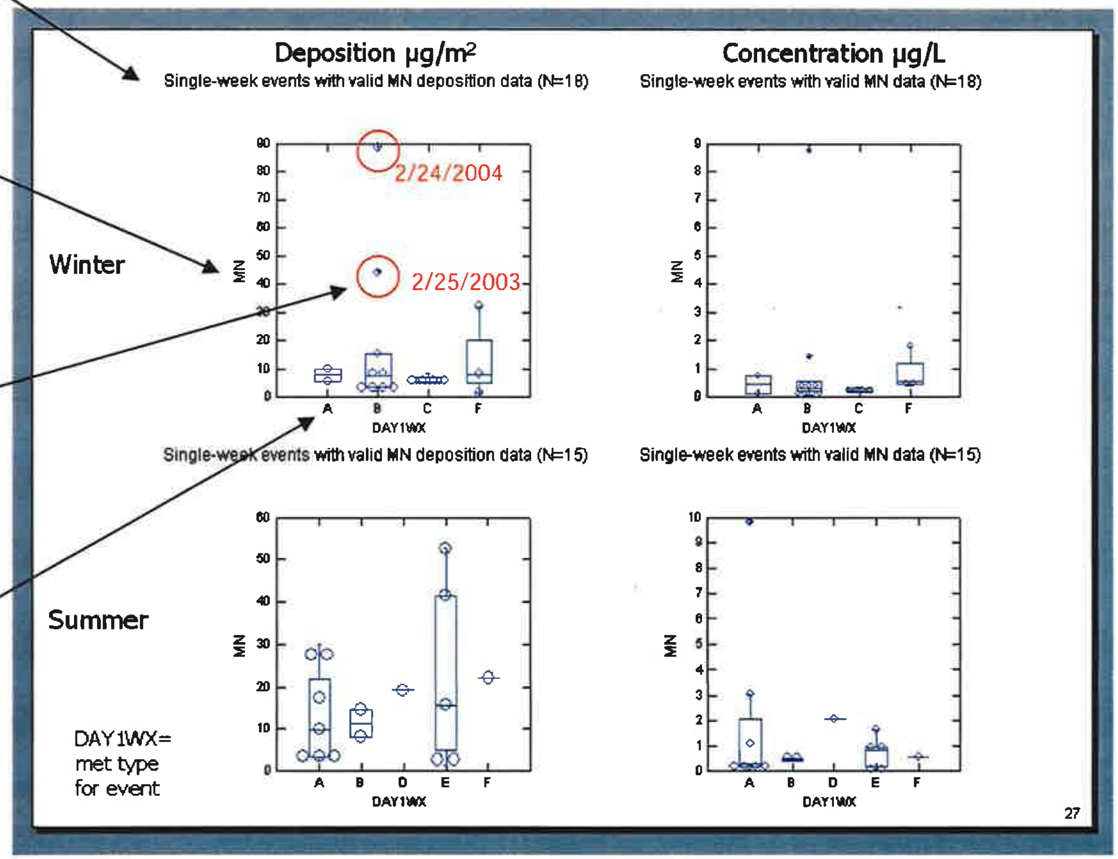
The description above each graph indicates what is plotted and how many data points were plotted. Overall, the number of data points was too low for robust interpretation of statistical differences.

The y-axis title indicates which metal is plotted as well as the observed deposition or concentration values.

Outlier concentrations are circled in red and marked with the date the outlier occurred.

The x-axis groups data by air mass type in order to investigate differences in observed concentrations due to the air mass type.

Figures for a single metal are organized in a matrix to show deposition and concentration for both winter and summer.

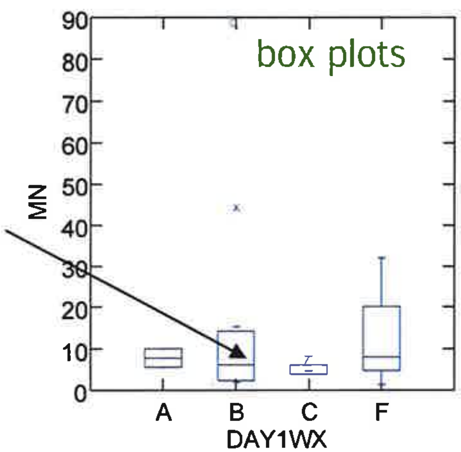


Box Plot Interpretation

Because of the low number of data points box plots and dot densities are combined in the figures.

Box plots are almost identical to notched box plots (see slide 19 for interpretation).

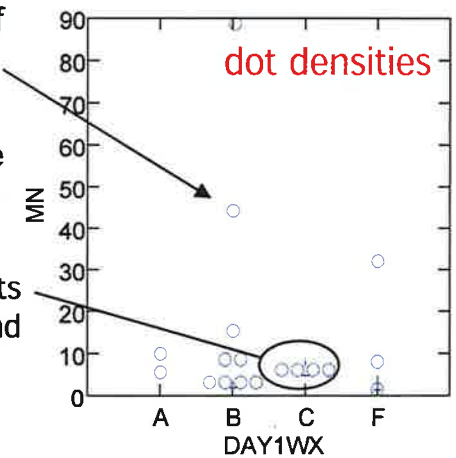
The only difference is that the median value is indicated by a vertical line in the middle of the box.



Dot densities show the value of each data point as indicated by the circles.

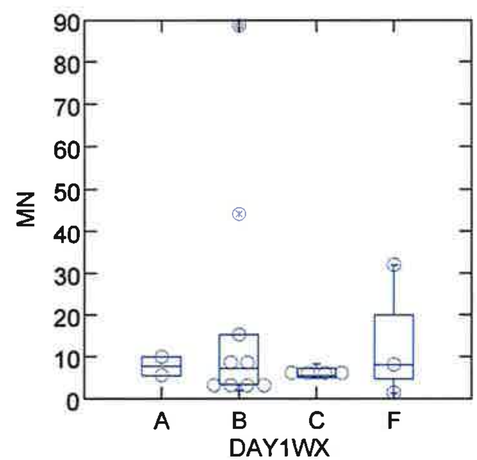
Data points that have the same value are placed next to each other in a horizontal line.

All four of the circled data points were from air mass type "C" and have the same value.



Combination of box plots and dot densities

The combination of the two figure types provides the advantage of summary statistics (box plots) and the distribution of individual data points (dot densities).

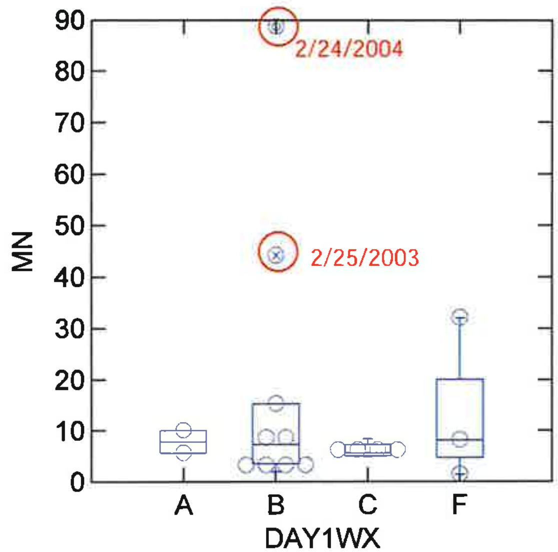


Deposition µg/m²

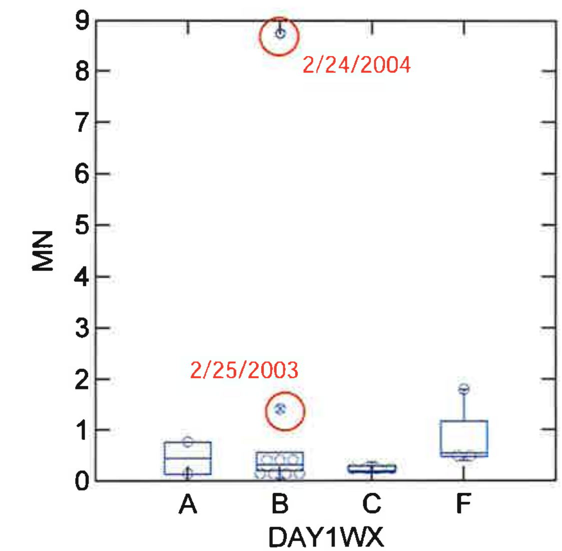
Concentration µg/L

Winter

Single-week events with valid MN deposition data (N=18)

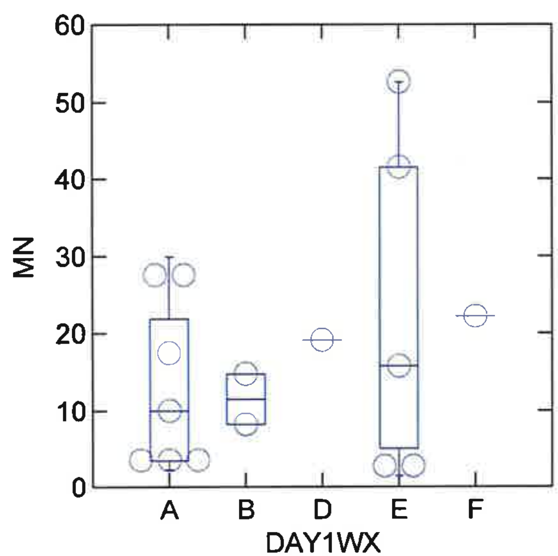


Single-week events with valid MN data (N=18)

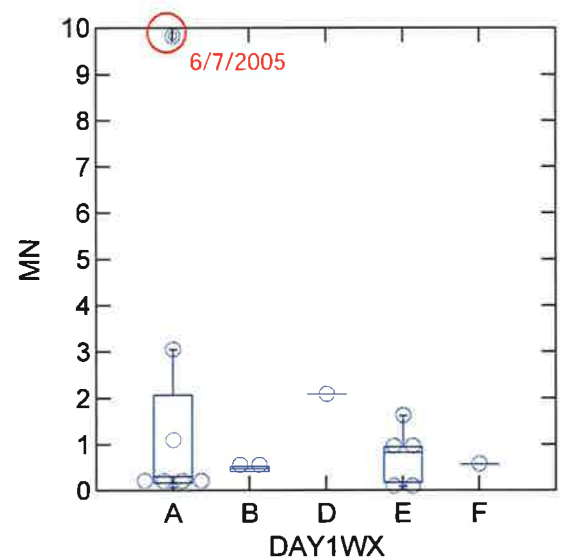


Summer

Single-week events with valid MN deposition data (N=15)



Single-week events with valid MN data (N=15)



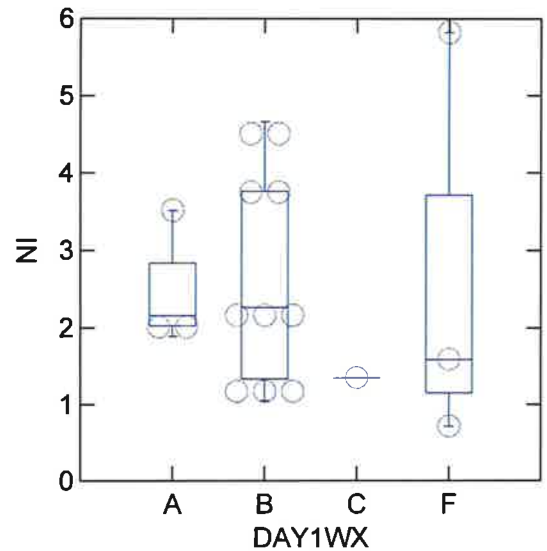
DAY1WX= met type for event

Deposition μg/m²

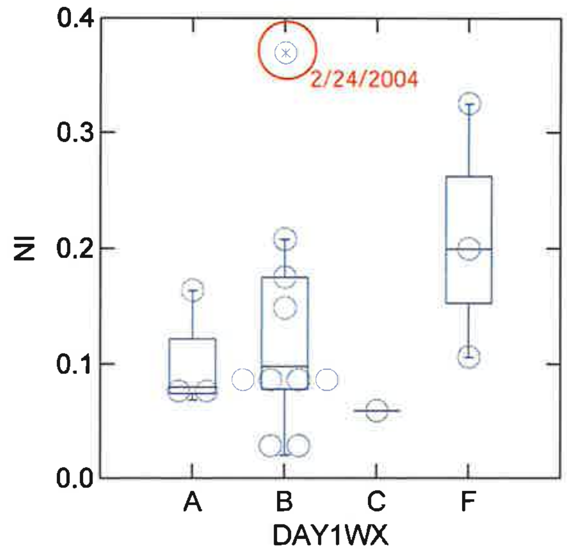
Concentration μg/L

Winter

Single-event weeks with valid NI deposition data (N=17)

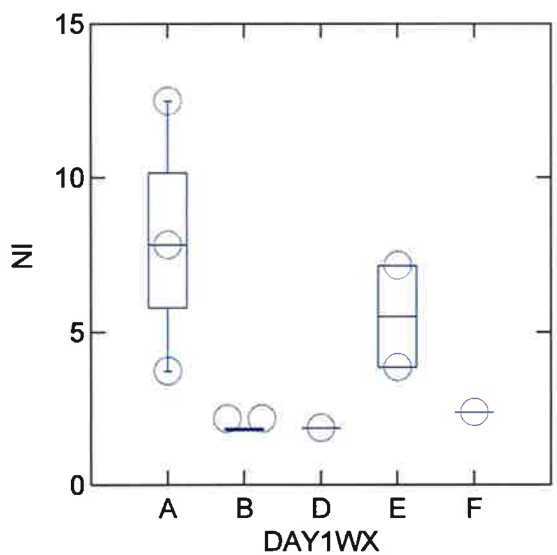


Single-event weeks with valid NI data (N=17)

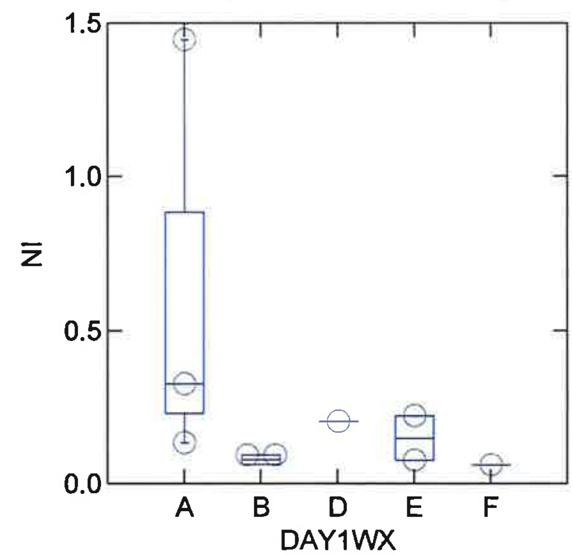


Summer

Single-week events with valid NI deposition data (N=9)



Single-week events with valid NI data (N=9)

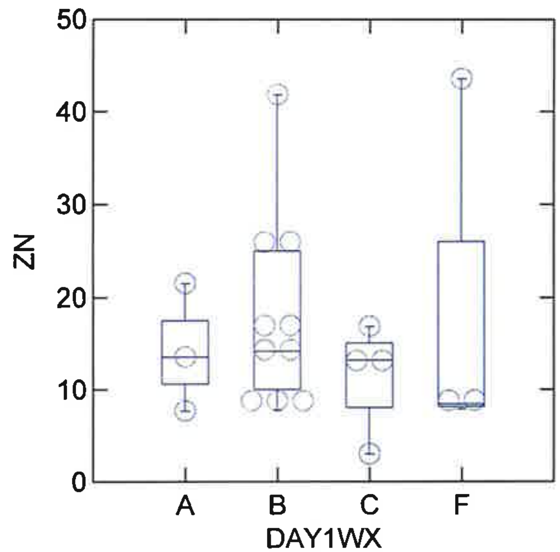


Deposition µg/m²

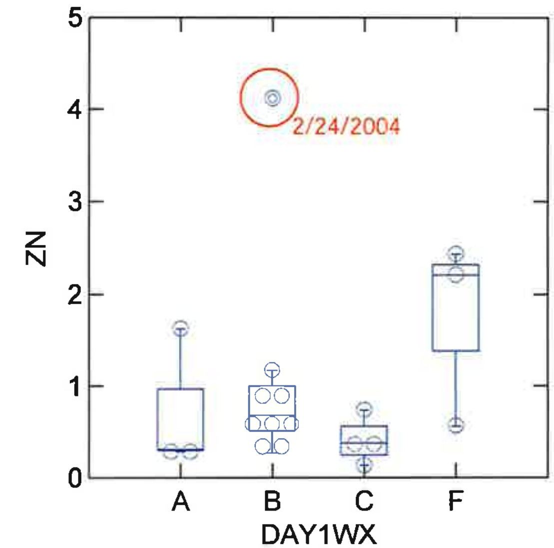
Concentration µg/L

Winter

Single-event weeks with valid ZN deposition data (N=19)

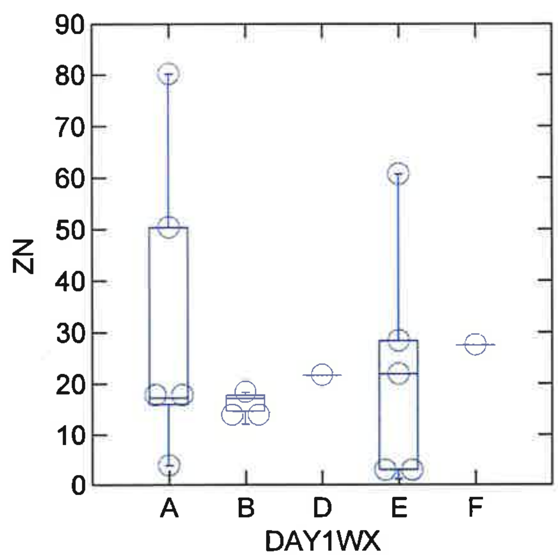


Single-event weeks with valid ZN data (N=19)

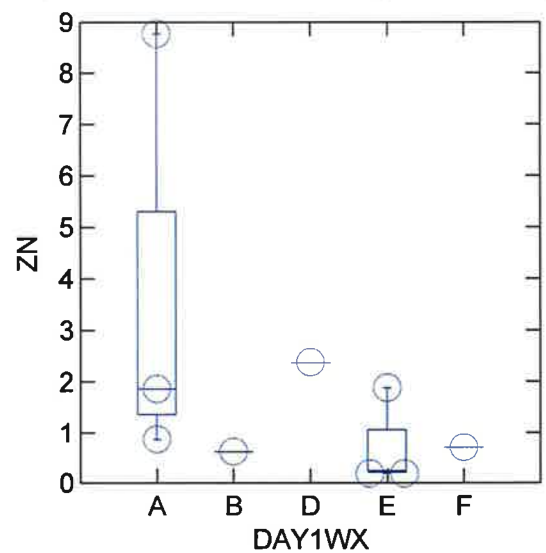


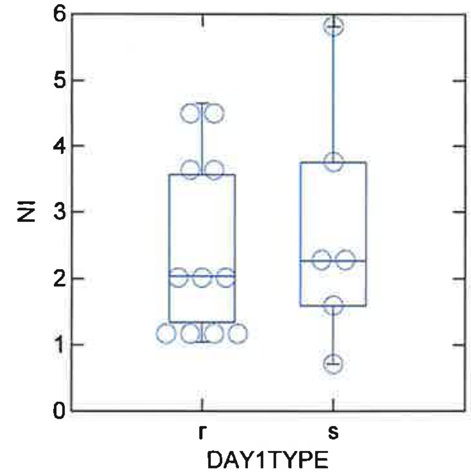
Summer

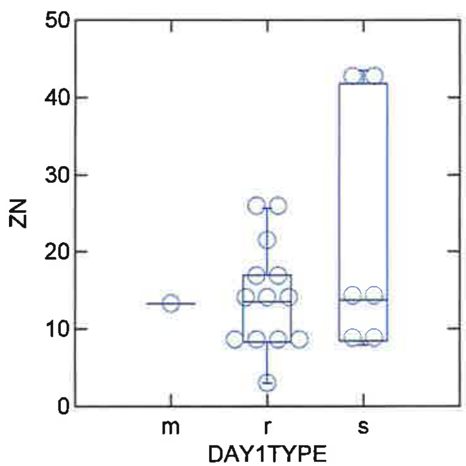
Single-week events with valid ZN deposition data (N=8)

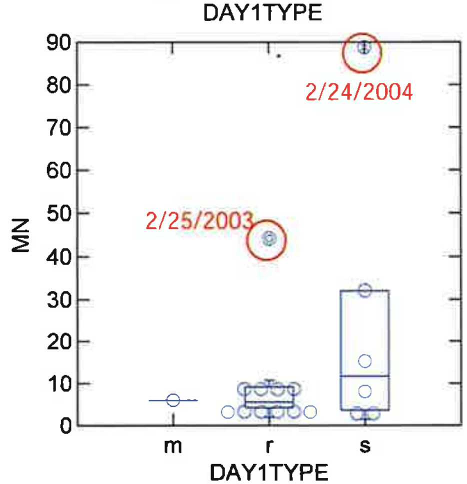


Single-week events with valid ZN data (N=8)



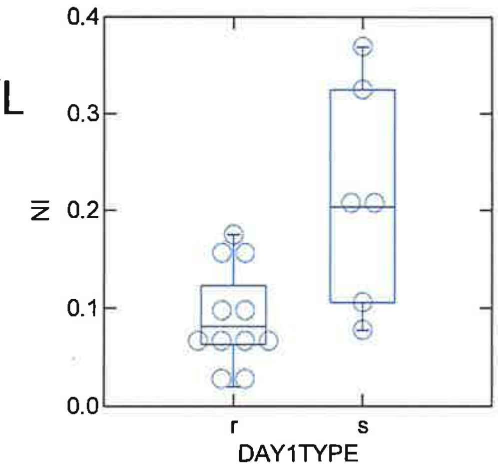


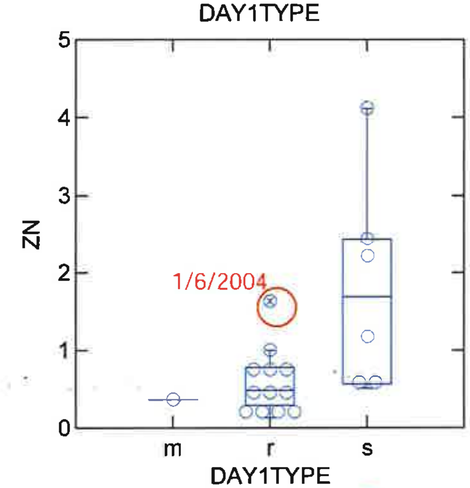


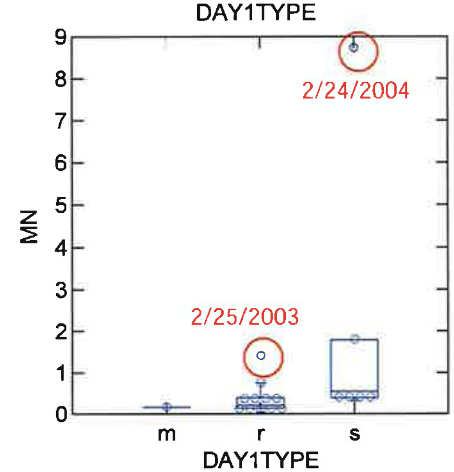


Deposition μg/m² Concentration μg/L

- Only a handful of snow events occurred, so while snow events had higher deposition and concentration for Zn and Mn (and concentration for Ni), there is an insufficient number to be conclusive
- Lead showed no difference between rain and snow







Case Studies

- For six weekly samples with a single precipitation event (events can be more than one day in duration), trajectories were run from the date of the precipitation event. The case studies were chosen to cover a range of meteorological types and seasons.
- These trajectories were overlaid with nearby IMPROVE $PM_{2.5}$ aerosol data to understand if there is a relationship between $PM_{2.5}$ composition/concentration and deposition or if different regional patterns are evident when there are differences in deposition between events.
- The following slides orient the reader to the full case-study summary pages.

Sources in the Literature

- PMF results of $PM_{2.5}$ data in Vermont were presented by Polissar et al. in 2001. Back trajectories of the resulting factors were also investigated, making this work an excellent comparison to Casco Bay case-study data.
- The following source results were described by Polissar et al.:
  - Zn had two major sources:
    - Cu smelting → from Midwest and East Coast
    - Zn/Pb factor from a mixture of sources → from Midwest
  - Pb had two major sources:
    - Canadian smelting and mobile sources → from Canada
    - Zn/Pb factor from a mixture of sources → from Midwest
  - Ni had one major source:
    - Oil fueled power plants → from East Coast
  - Mn had one major source:
    - Canadian smelting and mobile sources → from Canada

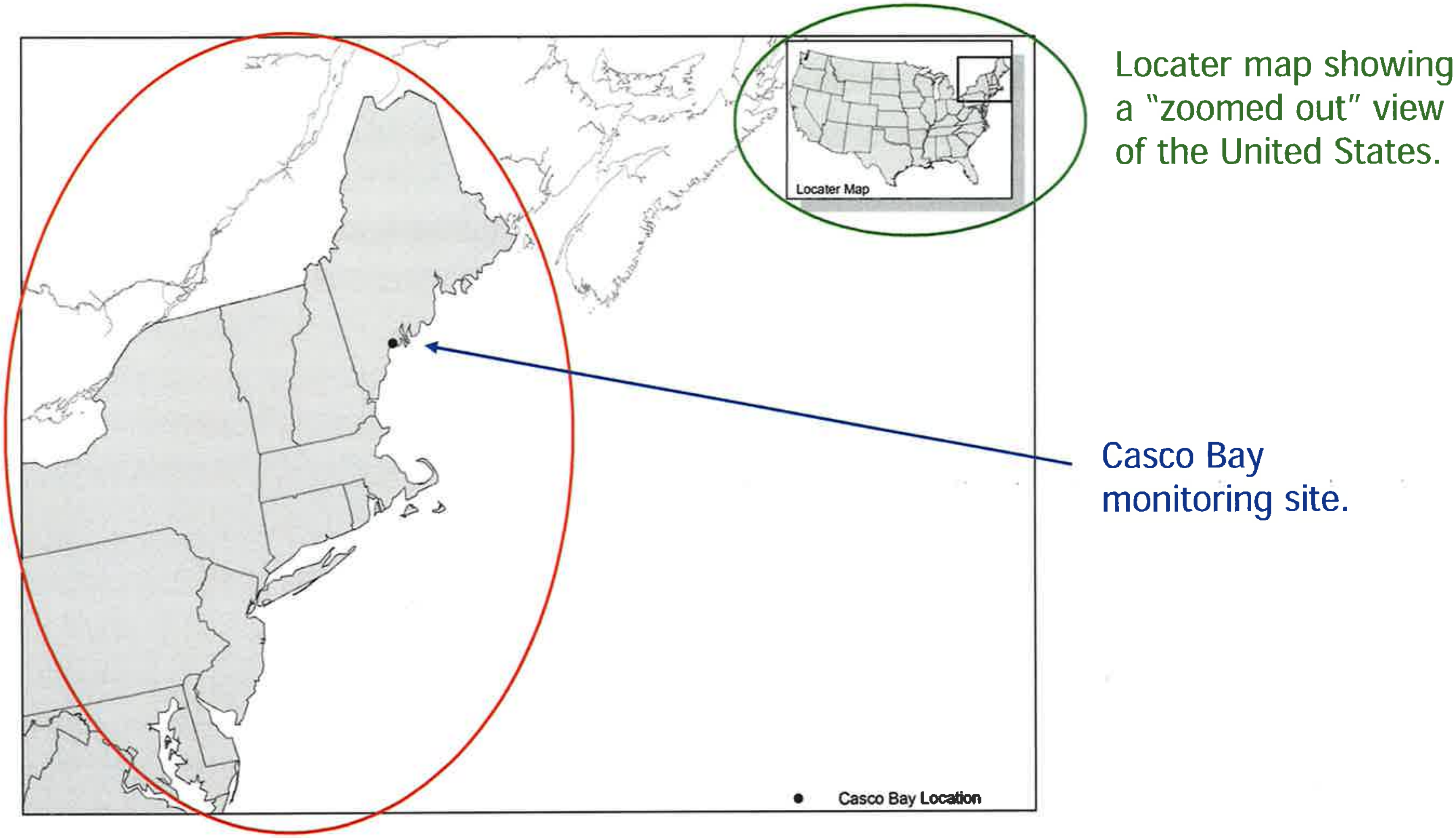
Polissar A.V., Hopke P.K., and Poirot R.L. (2001) Atmospheric aerosol over Vermont: chemical composition and sources. *Environ. Sci. Technol.* **35** (23), 4604-4621.

Case-study Ratios

- Ratios of metals in case-study days versus the seasonal average were investigated to further understand possible source influence.
- Numbers in **red and bold** are outside one standard deviation of the seasonal average.
- Numbers in red but not bold are more than twice the seasonal average, and numbers in blue but not bold are less than half the seasonal average.
- Based on these ratios
  - Mn is significantly higher in precipitation data taken 2/18/2004
  - Ni is significantly higher in precipitation data taken 8/18/2004

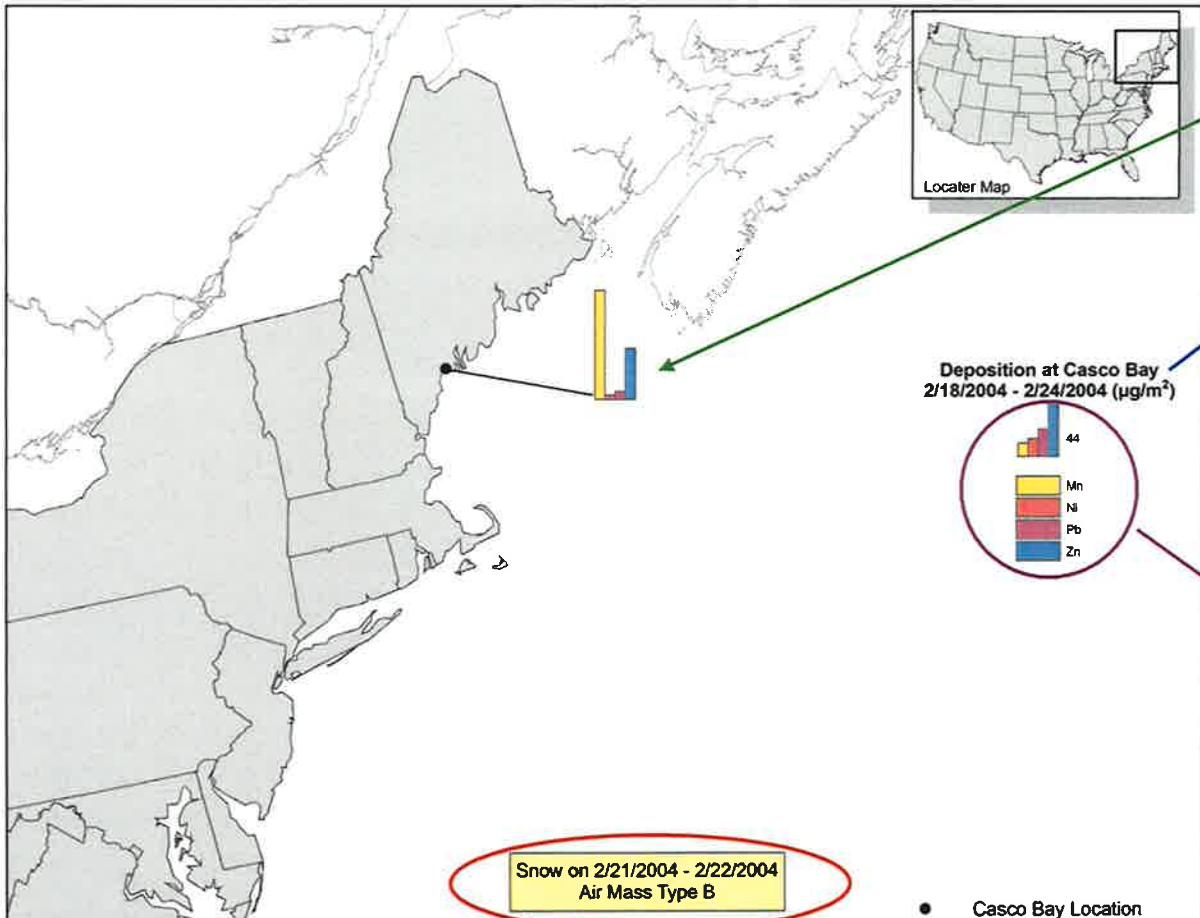
Precipitation Sample Date	Season	Mn/ Ni	Mn/ Pb	Mn/ Zn	Ni/ Pb	Ni/ Zn	Pb/ Zn
2/19/2003	Cool	4.6	1.9	0.46	0.42	0.10	0.24
2/18/2004	Cool	**24**	**13**	**2.1**	0.55	0.090	0.16
11/2/1005	Cool	9.5	5.9	**1.7**	0.62	0.18	0.29
Cool Seasonal Average		4.5	3.7	0.56	0.81	0.12	0.15
8/18/2004	Warm	2.1	8.6	**1.6**	**4.1**	**0.78**	0.19
7/20/2005	Warm	10	3.6	0.88	0.35	0.086	0.25
8/3/2005	Warm	2.2	1.5	0.35	0.66	0.16	0.23
Warm Seasonal Average		6.0	3.4	0.67	0.58	0.11	0.19

Map Interpretation - Base



A "zoomed in" view of the Northeastern United States.

Map Interpretation - Deposition



Bar chart of deposition data collected at Casco Bay.

The legend title indicates the deposition sampling time period.

The legend indicates the scale of bar chats in the map and defines bar colors.

The textbox indicates precipitation time period and air mass type. Air mass descriptions can be found in slides 23 and 24.

ATTACHMENT 1

CASCO BAY TRACE METALS VALIDATION AND PRELIMINARY ANALYSIS 2002-2005

Updated Presentation

Casco Bay Trace Metals Validation and Preliminary Analysis 2002-2005

Prepared by:
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Jessie Charrier
Steve Brown
Sonoma Technology, Inc.
Petaluma, CA

Prepared for:
U.S. Environmental Protection Agency, Region I
March 12, 2008

STI

STI-906058.02-3277

Outline

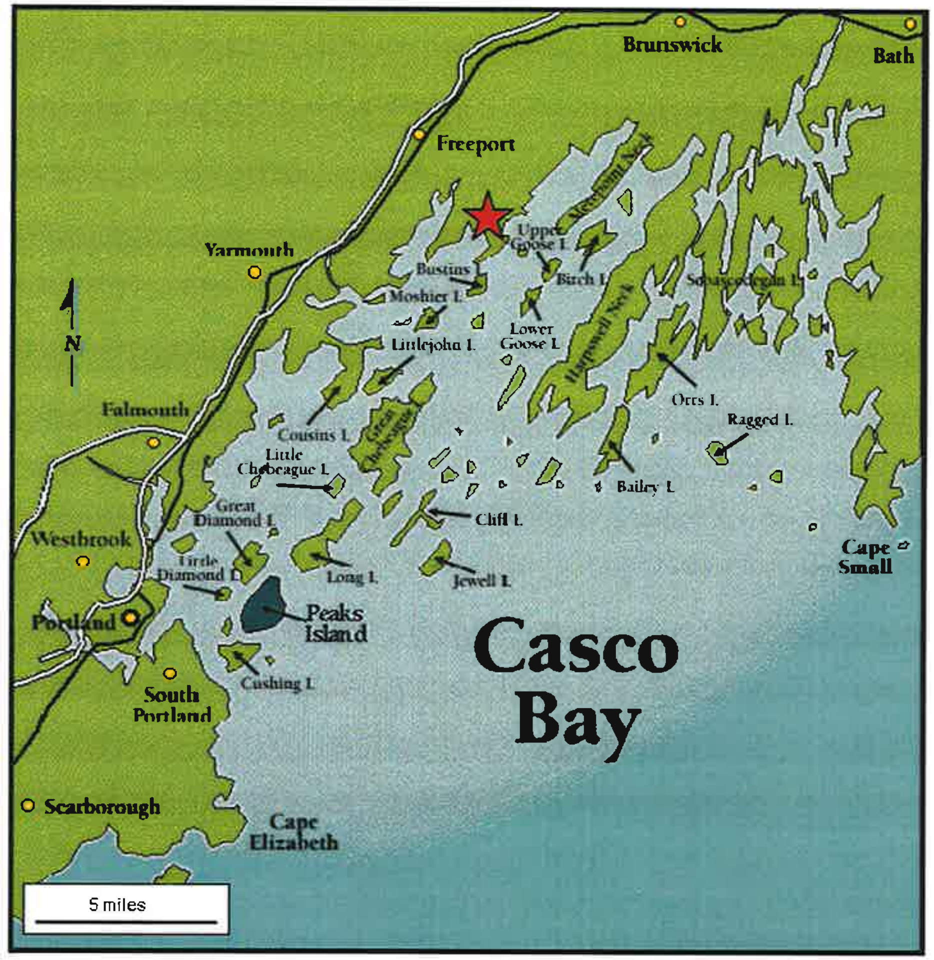
- Overview of Work Scope
- Summary of Past Analysis
- Data Validation
- Data Analyses
  - Seasonal Variations
  - Correlations
  - Scatter Plots
  - Time Series
  - Met Analysis
  - Case Studies and Ratio Analysis
- Summary
- Recommendations

Overview of Work Scope

- Update the previous analyses with 2005 data
  - Incorporate 2005 data into previous presentation and executive summary
  - Perform Level 1 validation of the data and update plots and analyses
  - Reassess the possibility of using the updated data set for source apportionment and make a recommendation in this regard
- Perform meteorological and air quality data analysis
  - Identify deposition samples impacted by a single weather system or by a combination of warm and cold fronts; classify samples with a synoptic or frontal passage pattern; compare the deposition/concentrations when these different weather types occur.
  - Identify up to five case-study events for further analysis (run back trajectories and characterize the meteorology that affected the site).
  - Examine the spatial and temporal patterns of the IMPROVE speciated $PM_{2.5}$ lead, manganese, and arsenic data on the days prior to and during the case-study events.

Data Overview

- Mercury Deposition Network (MDN) samples were collected at the Casco Bay, Maine, site (ME96) and analyzed by Frontier Geosciences for trace metals. The samples were collected from January 2002* through January 2006.
- Data were validated and then evaluated by season and year, by single events versus multiple events, and by event size and duration including trajectory analyses.



*Note that data collected prior to October 2002 were not available.

Previous Work

- Previous analyses focused on 2003-2004 data (*Wu et al., 2005*).
- Good correlations among many of the metals were found, indicating that source type or source region information may be discernible from the data set.
- Trajectory analyses were difficult to interpret because in most of the week-averaged samples, multiple precipitation events occurred.

Wu J., Brown S., and Hafner H. (2005) Casco Bay trace metal validation and preliminary analysis. Presentation prepared for the U.S. Environmental Protection Agency, Region 1, North Chelmsford, MA, by Sonoma Technology, Inc., Petaluma, CA, STI-904080.03-2883, December.

Available Data from the National Atmospheric Deposition Program (NADP)

- Weekly concentrations and depositions of Hg, AsICPMS, AsHGAFS, SeICPMS, SeAFS, Cd, Cr, Cu, Mn, Ni, Pb, Mg, and Zn from 2002 to 2005 (164 weeks).
- As and Se were measured by ICPMS and HGAFS.
- Quarterly summaries of concentrations and depositions for each species.
- Estimated detection limit (eMDL), 5*eMDL (similar to a lower quantifiable limit), and volume-weighted averages (VWA) for each species on a quarterly basis.
- Bottle capture volume, efficiency, and sample notes and observations.

ICPMS = inductively coupled plasma mass spectrometry
HGAFS = hydride generation atomic fluorescence spectrometry

Data Validation: Not Reported and Below Detection Limit Data

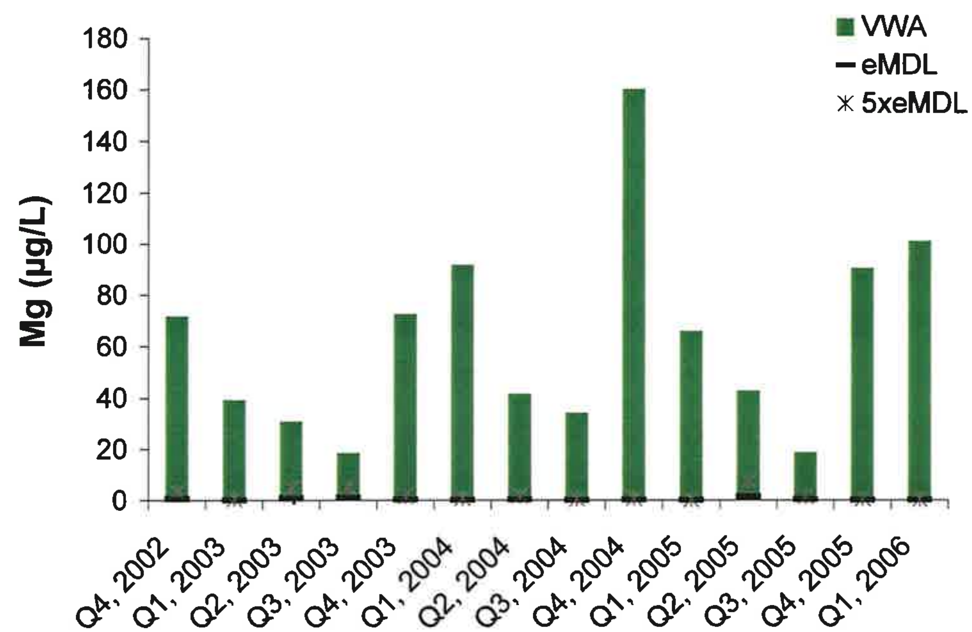
Species	Not Reported	Less than eMDL	Between eMDL and 5xeMDL	Greater than 5xeMDL	N Above eMDL
AsICPMS	1%	52%	45%	3%	62
AsHGAFS	15%	90%	10%	0%	13
SeICPMS	0%	74%	22%	5%	34
SeAFS	*51%*	*100%*	*0%*	*0%*	*0*
Cd	0%	40%	38%	22%	78
Cr	52%	81%	17%	2%	25
Cu	0%	35%	42%	24%	85
Mn	0%	24%	6%	70%	99
Ni	0%	37%	27%	36%	82
Pb	0%	18%	22%	61%	107
Mg	0%	13%	2%	85%	113
Zn	0%	25%	21%	54%	97
Be	0%	93%	7%	0%	9

Species in **bold** were not included in further analysis
Pink shading indicates the majority of samples were below the eMDL
Concentrations less than zero were treated as below the eMDL

- 130 samples were collected
- Similar to the last analysis, As, Cr, and Se were below detection most of the time
- 'Not Reported' includes dates when a sample was collected/analyzed, but a particular compound was not reported
- Cu was above detection in 65% of the samples, compared to 25% in the last analysis
- The following slides show example volume weighted averages, estimated detection limits, and 5 times the estimated detection limit by quarter; all species are shown in the appendix
- Hg VWA was not provided and was not available from MDN

Quarterly Summary

- This example shows a quarterly summary of volume weighted average Mg concentrations.
- This metal was nearly always above the eMDL and 5xeMDL.
- Q1 2004 VWA was high for most species; this quarter also had the highest number of low volume samples (5 out of 13), which could be impacting the VWA calculations.
- Quarterly summaries for all species are available at the end of this presentation.



Summary of Data Validation

- Samples with trace amounts of precipitation were flagged as “low volume” samples (*27 samples*)
- Field blanks were flagged and excluded from analysis (*7 blanks*)
- Negative sample values were treated as below the estimated detection limit (*7 samples*)
- The majority of samples of six species were below the estimated detection limit (As-ICPMS, As-AFS, Se-ICPMS, Se-AFS, Cr, and Be)
- The majority of samples of four species were greater than 5 times the eMDL (Mn, Mg, Pb, Zn)
- The majority of samples for two species were not reported (Cr and Se-AFS)
- Se-AFS had all reported data below the eMDL and will be excluded from analysis
- Other data errors observed in previous reports were not observed in the most recent data set

VWA Concentration by Quarter (1 of 2)

	High Quarter	
	Concentration	Deposition
Hg	NA	2nd
AsICPMS	1st	4th
AsHGAFS	1st	3rd
SeICPMS	1st	2nd
Cd	1st	2nd
Cr*	2nd	2nd
Cu	2nd	2nd
Mn	1st/2nd	2nd
Ni	1st	2nd
Pb	2nd	2nd
Mg	4th	4th
Zn	1st	2nd
Be*	2nd	2nd

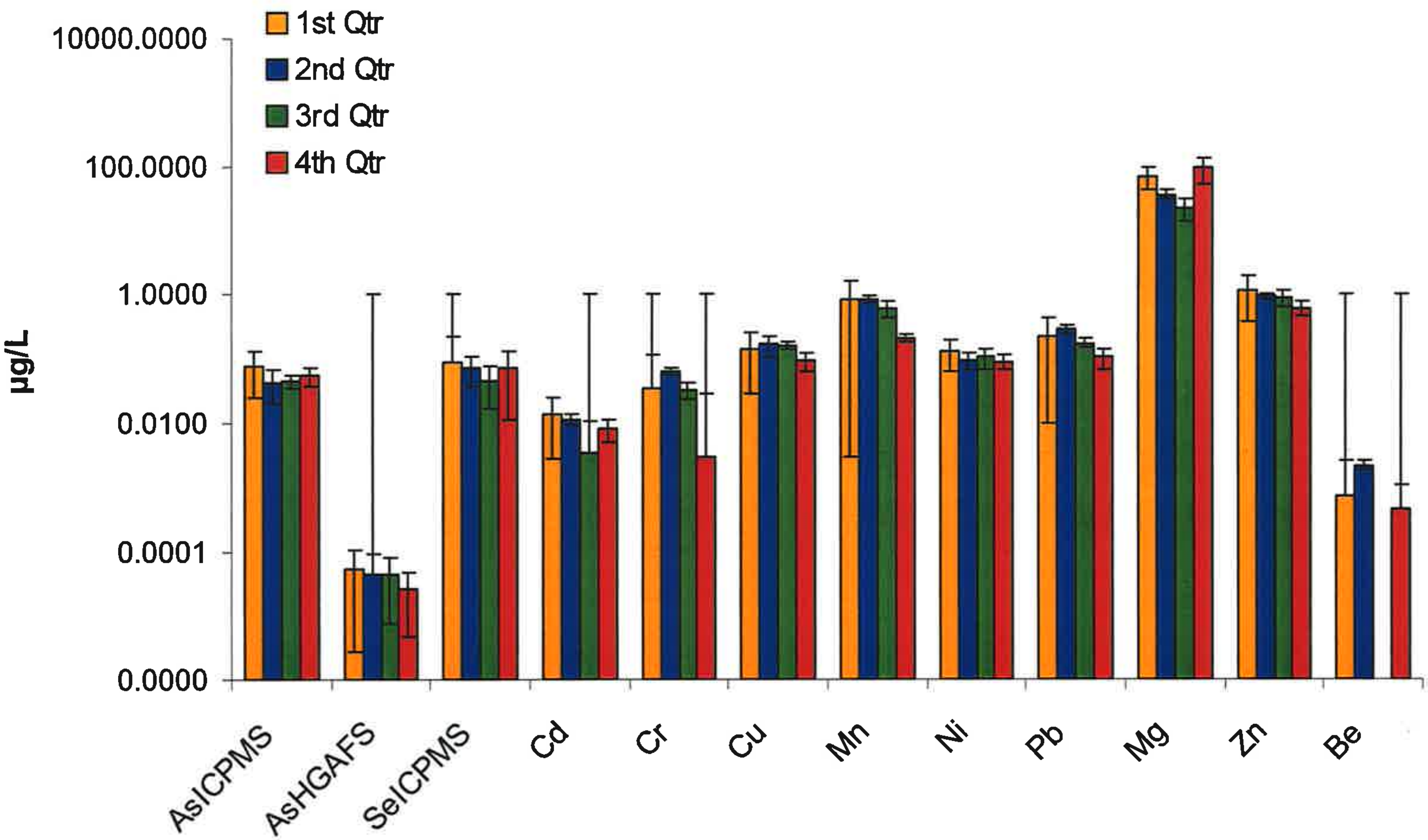
*4th quarter Cr deposition and 3rd quarter Be concentration and deposition removed due to negative values

- Similar trends were seen as with the previous analysis
- Deposition of most metals was highest in the second quarter
- Concentrations of most metals were highest in the second and/or first quarters

1st quarter = Jan – Mar, etc.

VWA Concentration by Quarter (2 of 2)

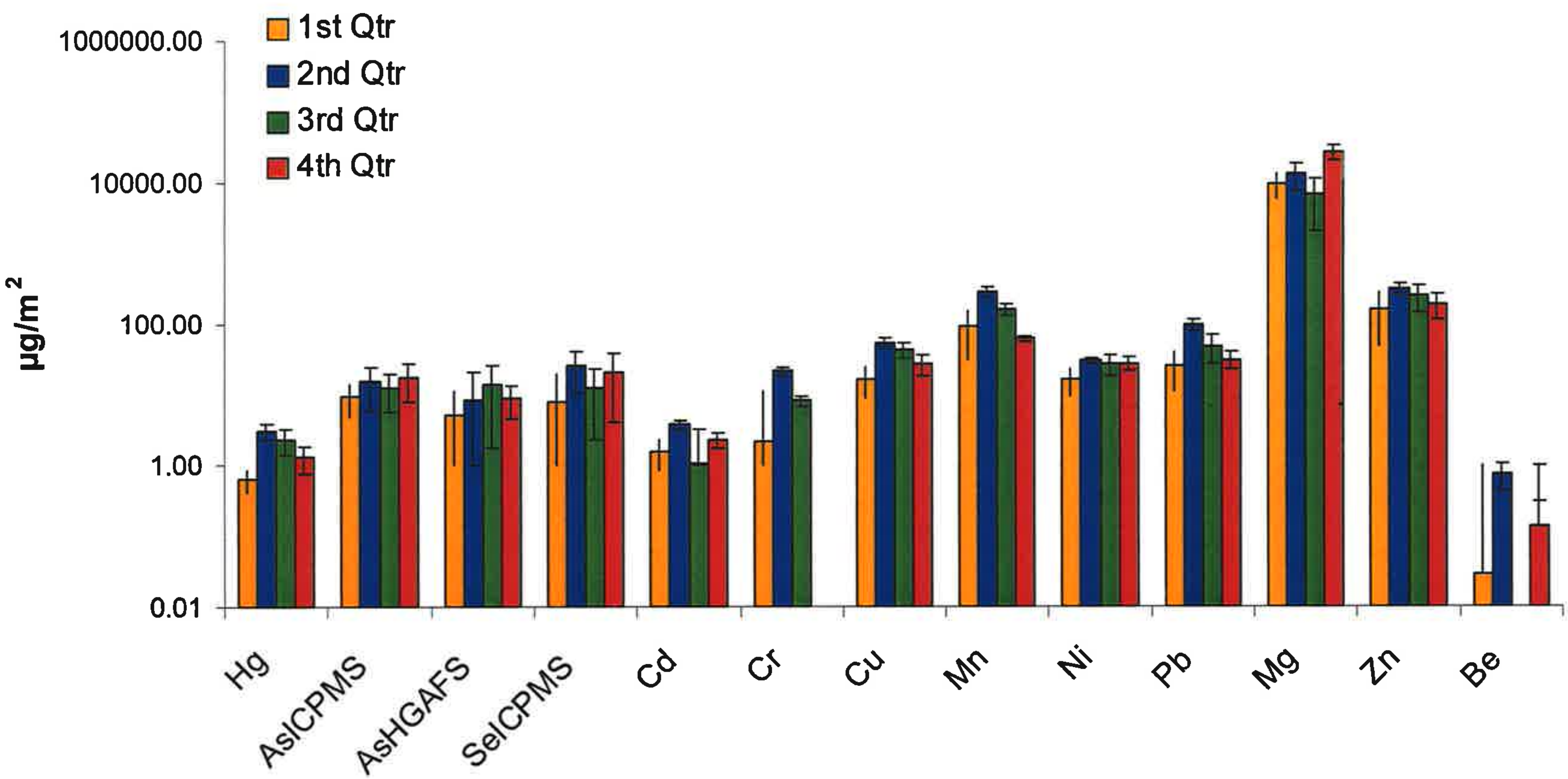
Error bars show +/- 1 standard deviation



*Quarterly averages calculated by Frontier Geosciences

Deposition by Quarter

Error bars show +/- 1 standard deviation



*Quarterly averages calculated by Frontier Geosciences

Summary of Concentration, Deposition Levels

- Concentrations of Mg are highest; next highest are Zn and Mn. Cu, Ni, and Pb have similar concentrations. Se and As (ICPMS) also have similar concentrations.
- Deposition shows similar relative patterns to concentration with Mg exhibiting the highest deposition values followed by Zn and Mn. Cu, Ni, and Pb have similar deposition values. Hg and Cd are also similar.

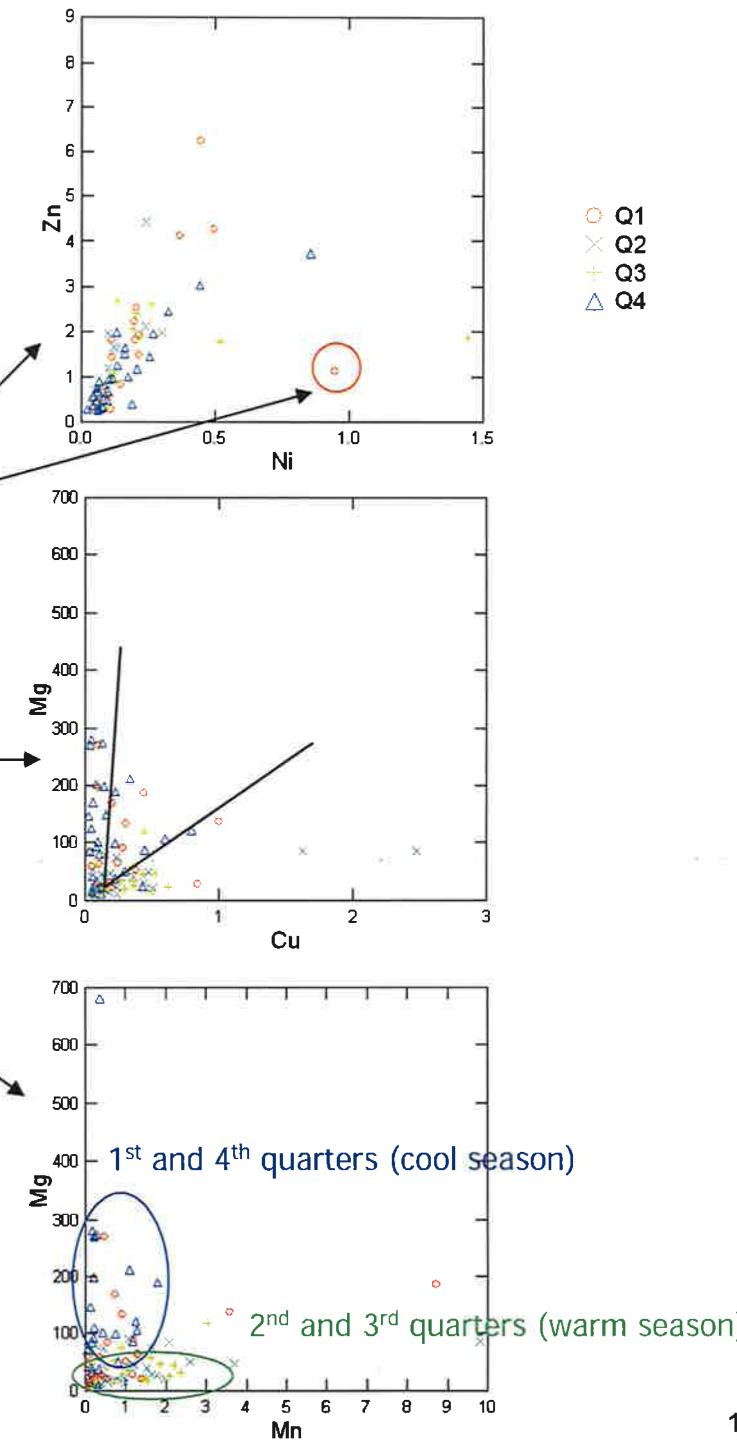
Correlations Between Species Concentrations

Period		CD	CU	HG	MG	MN	NI	PB	ZN
1st Quarter	CD	**1.0**							
	CU	**0.7**	**1.0**						
	HG	**0.8**	**0.8**	**1.0**					
	MG	0.3	0.1	0.3	**1.0**				
	MN	0.5	0.5	0.6	0.4	**1.0**			
	NI	0.5	0.3	0.3	0.1	0.2	**1.0**		
	PB	**0.9**	**0.7**	**0.9**	0.3	0.6	0.3	**1.0**	
	ZN	**1.0**	**0.7**	0.6	0.2	0.5	0.5	0.6	**1.0**
2nd Quarter	CD	**1.0**							
	CU	**0.9**	**1.0**						
	HG	0.3	0.3	**1.0**					
	MG	0.5	0.6	0.1	**1.0**				
	MN	**0.9**	**0.9**	0.4	0.4	**1.0**			
	NI	0.4	0.7	0.1	0.1	0.7	**1.0**		
	PB	**0.9**	**0.9**	0.5	0.5	**0.9**	0.6	**1.0**	
	ZN	**0.7**	**1.0**	0.1	0.5	**0.8**	**0.8**	**0.7**	**1.0**
3rd Quarter	CD	**1.0**							
	CU	0.3	**1.0**						
	HG	**-0.4**	0.1	**1.0**					
	MG	**0.6**	0.0	0.3	**1.0**				
	MN	**0.6**	**0.7**	0.5	0.4	**1.0**			
	NI	0.3	**0.3**	**0.9**	**0.8**	0.6	**1.0**		
	PB	**0.5**	**0.9**	0.1	-0.1	**0.8**	0.1	**1.0**	
	ZN	**0.9**	0.3	-0.1	0.0	0.3	0.2	0.4	**1.0**
4th Quarter	CD	**1.0**							
	CU	0.7	**1.0**						
	HG	0.6	0.7	**1.0**					
	MG	0.3	-0.1	0.0	**1.0**				
	MN	0.6	**0.8**	0.6	0.0	**1.0**			
	NI	0.6	**0.8**	**0.7**	-0.1	0.6	**1.0**		
	PB	**0.8**	**0.9**	**0.8**	0.1	**0.7**	**0.8**	**1.0**	
	ZN	0.7	**0.9**	**0.8**	0.0	**0.9**	**0.9**	**0.9**	**1.0**
All Quarters	CD	**1.0**							
	CU	**0.7**	**1.0**						
	HG	0.3	0.4	**1.0**					
	MG	0.2	0.0	-0.1	**1.0**				
	MN	0.7	**0.7**	0.4	0.0	**1.0**			
	NI	0.5	0.4	0.3	0.0	0.4	**1.0**		
	PB	**0.8**	**0.8**	0.5	0.1	**0.8**	0.4	**1.0**	
	ZN	**0.8**	0.6	0.2	0.0	0.5	0.5	0.6	**1.0**

- Correlations between species were examined to look for common sources, but this analysis is limited by the low number of samples.
- Species with <10 samples above detection were excluded, including As, Se, Cr, Cd, and Be.
- Pink shading indicates <5 pairs.
- Orange shading indicates 5-10 pairs.
- Bold indicates good correlation.
- A number of relationships between species are seen, and may suggest common sources or source areas.

Scatter Plot Analysis Concentration

- In addition to the R^2 values, scatter plots were examined by quarter to look for trends in the correlations and outlying events
- Several outliers were noted
- Some pollutants had two distinct edges, indicating more than one source
- Some species exhibited seasonal segregation, indicating source strength changes with season
- Full scatter plot analysis is available in the Appendix (attached)
- All units are µg/L

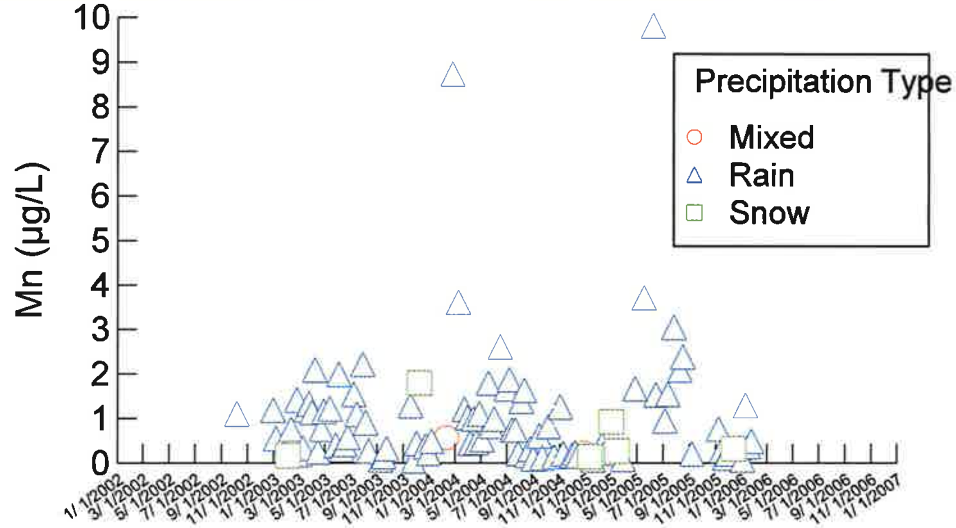


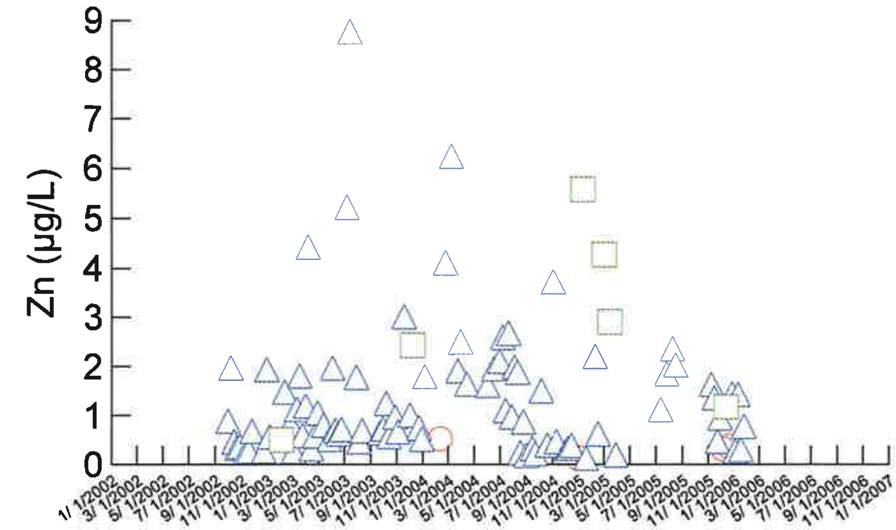
Summary of Scatter Plot Analysis

- Scatter plots showed the following relationships:
  - Hg did not correlate well with most metals overall, but did have moderate correlations with Cd, Cu, and Pb in the 1st quarter and Ni, Pb, and Zn in the 4th quarter.
  - As (ICPMS) correlated well with Cd, Pb, Cu, and Zn.
  - Cu correlated well with Pb and Zn.
  - Cd correlated well with most other metals. Its relationship with Mg indicates possible multiple sources. Cu showed a similar relationship with Mg.
  - Mn, Mg, and Se data did not strongly correlate with other metals.
  - Ni correlated well with Zn.
  - Many Pb samples correlated with Zn.
- It is difficult from these relationships to point to any single source types.
- Full scatter plot analysis is available at the end of this presentation.

Time Series Analysis

- Time series were examined by precipitation type (rain, snow, mixed) to determine if certain events were conducive to high concentrations.
- Highest concentrations of most species were during rain, which was the most common precipitation.
- Zinc concentrations were high for several samples during weeks when snow occurred.
- Full time-series analysis is available at the end of this presentation.





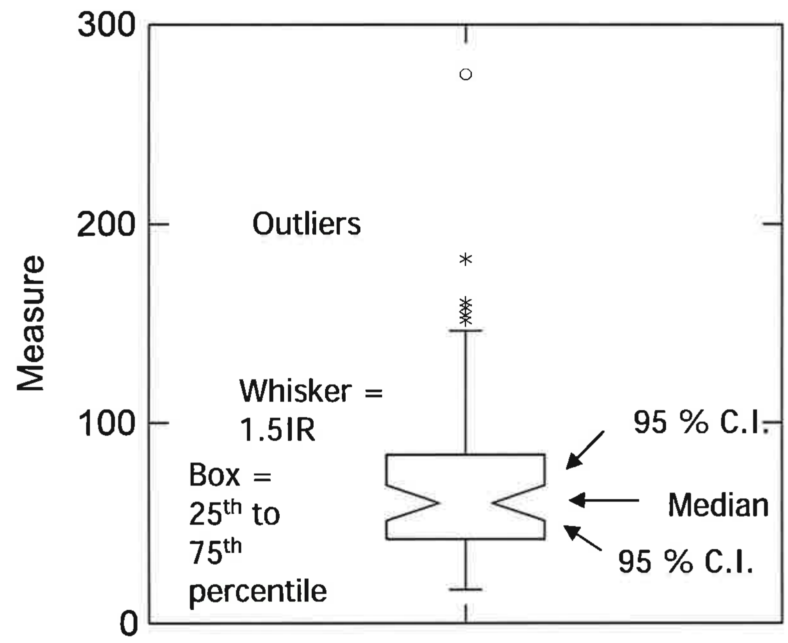
Ratio Analysis Overview

- Metals ratios in the deposition data were compared to source signatures to understand whether edges observed on scatter plots are indicative of individual source types.
- Goals were to attempt to answer the following:
  - Are ratios at Casco Bay in precipitation similar or dissimilar on a weekly basis?
  - Are ratios in precipitation the same as the aerosol?
  - Can we say anything about the source of aerosol and source of metals in precipitation?
- Source ratios from Sweet et al., 1998 were used for comparison to ambient ratios.

Clyde W. Sweet, Aaron Weiss, and Stephen J. Vermette. 1998. Atmospheric Deposition of Trace Metals at Three Sites Near the Great Lakes. *Water, Air, and Soil Pollution* **103**: 423-439.

Interpreting Notched Box Plots

Notched Box Whisker
Plots in SYSTAT



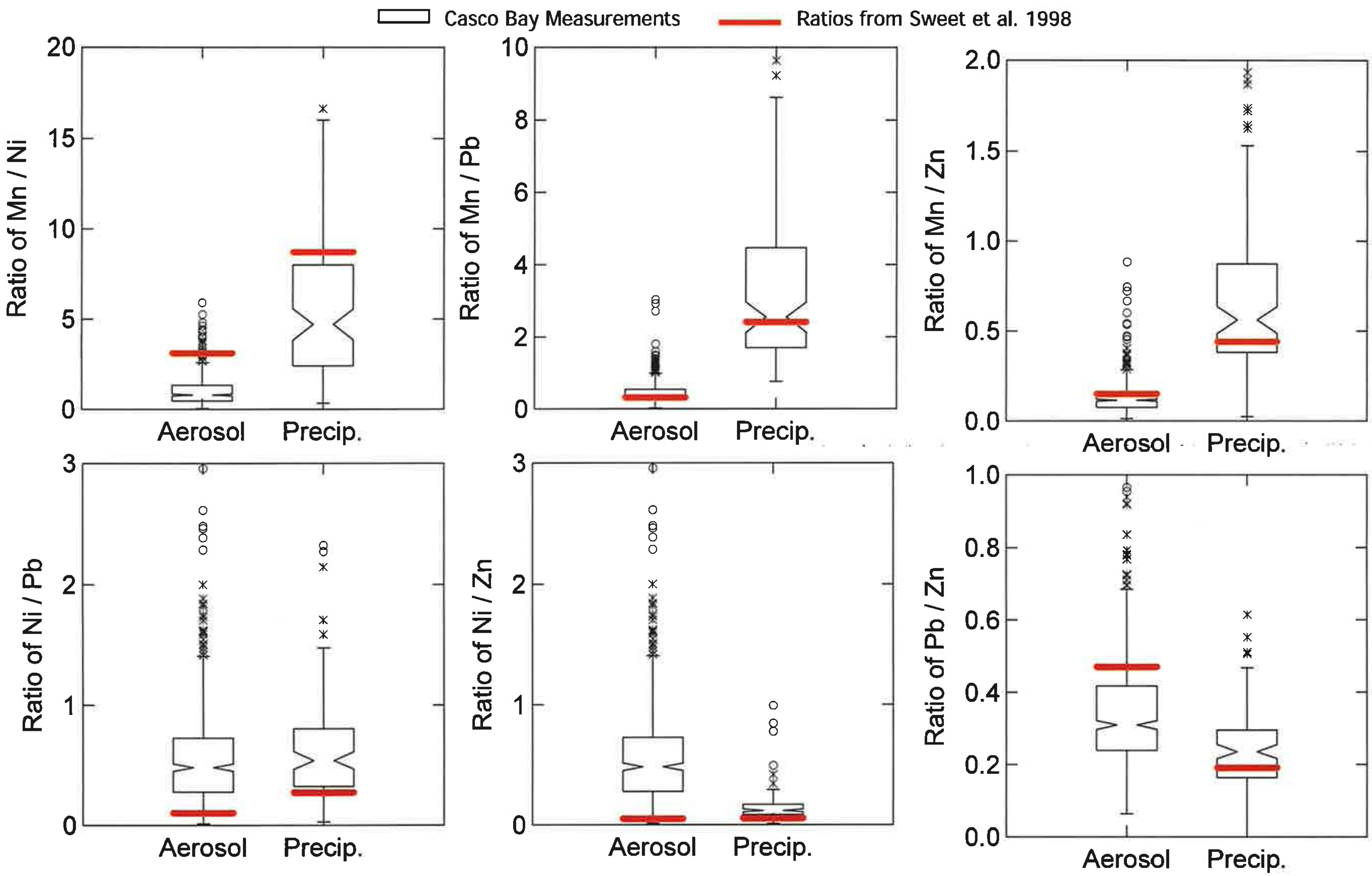
Ratios among Ni, Pb, Zn, and Mn in precipitation data were compared to ratios in collocated aerosol measurements using notched box plots.

where

IR = interquartile range

C.I. = confidence interval

Ratios in Precipitation vs. Aerosol



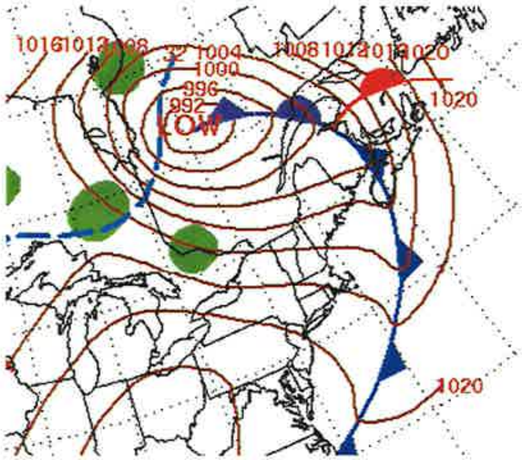
Ratios in Precipitation vs. Aerosol

- Comparing ratios in precipitation and aerosol showed the following results:
  - Mn ratios were significantly higher in Casco Bay precipitation data compared to the other metals. Ratios with Mn were also much more variable in the precipitation than in the aerosol. It is not clear why.
  - Ratios of Pb with Ni and Zn were similar in precipitation and aerosol measurements.
  - The ratio of Ni to Zn was lower and less variable in the precipitation data.
- The metals ratios were compared to deposition and aerosol data collected in Pennsylvania using similar methods (Sweet et al.,1998).
  - Precipitation ratios at Casco Bay were in relatively good agreement with the results in Sweet et al.
  - Aerosol ratios at Casco Bay were not always in agreement with results in Sweet et al. This is probably due to spatial and temporal differences of the aerosol measurements.
  - Concentrations of trace metals in precipitation may be influenced by longer and/or larger scale transport than aerosol concentrations.
  - Most of the ratios observed at Casco Bay are different than the what was seen in the earlier Pennsylvania data, suggesting there may be different sources impacting Casco Bay or source mixture has changed.

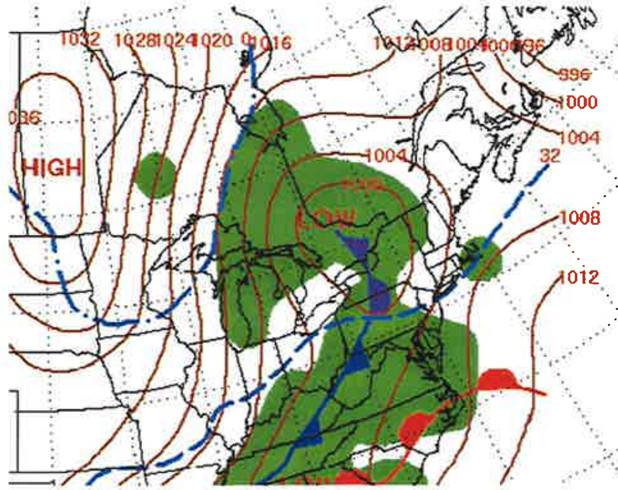
Meteorological Analyses

- Trace metal concentration and deposition data were analyzed by meteorological regime.
- Based on weather maps and local observations in Portland, Maine, six different weather patterns were identified for weekly samples with a single precipitation event occurring during that week; samples were also classified by rain, snow, or mixed precipitation. The next two slides show examples of the six patterns.
- Case study events for different weather patterns were also examined with IMPROVE and trajectory data to look for common patterns in the relative concentrations of the metals.

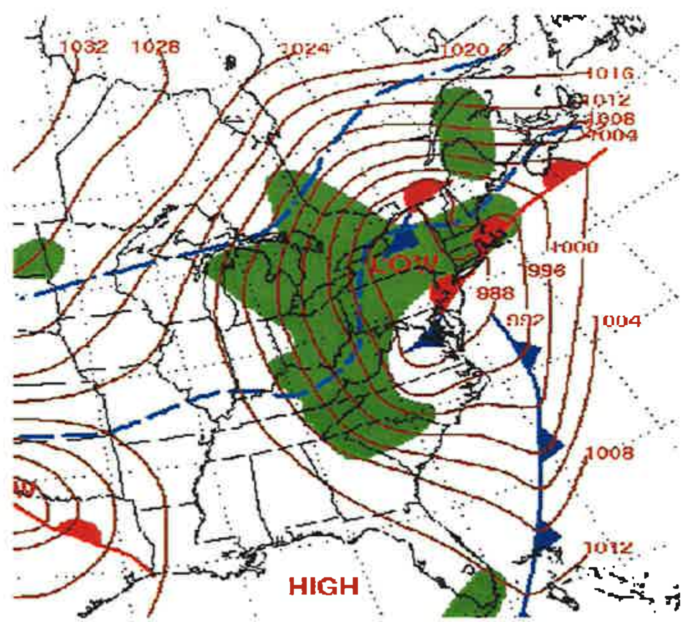
Meteorological Typing (1 of 2)



Pattern A: cold frontal passage. Example shown is November 7, 2005



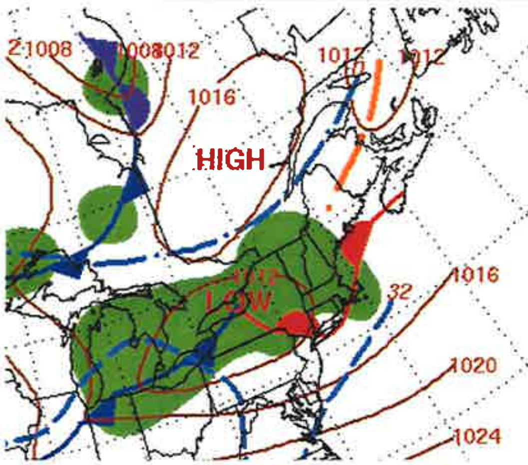
Pattern B:
low pressure system moving through from west to east. Example shown is January 17-19, 2004



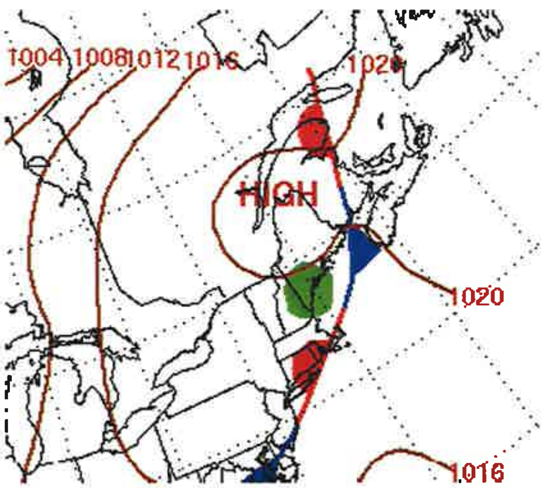
Pattern C : low pressure system moving up the coast. Example shown is February 22-24, 2003

The examples shown in this and the next slide provide representative days – not all weekly samples are shown. All sample designations are listed in the supplementary material.

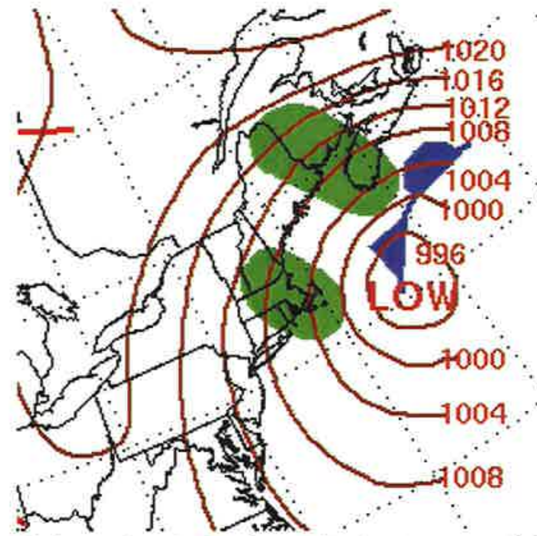
Meteorological Typing (2 of 2)



Pattern D: warm front approaching or moving through. Example shown is January 12, 2004



Pattern E: stationary front near the region. Example shown is September 26, 2003



Pattern F: low pressure system offshore. Example shown is May 8, 2005

Comparisons by Typing

- Trends were examined by season (summer and winter) to understand seasonal differences – i.e., were concentrations or depositions consistently higher or lower under certain types of weather patterns?
- Summer was defined as May through September; winter as November through February.
- In the following graphs, no consistent trend was observed among species or typings, possibly due to the low amount of data.
- Examples are shown in the next slides; more examples are provided in the technical memo (Attachment 2).

Box Plot Interpretation

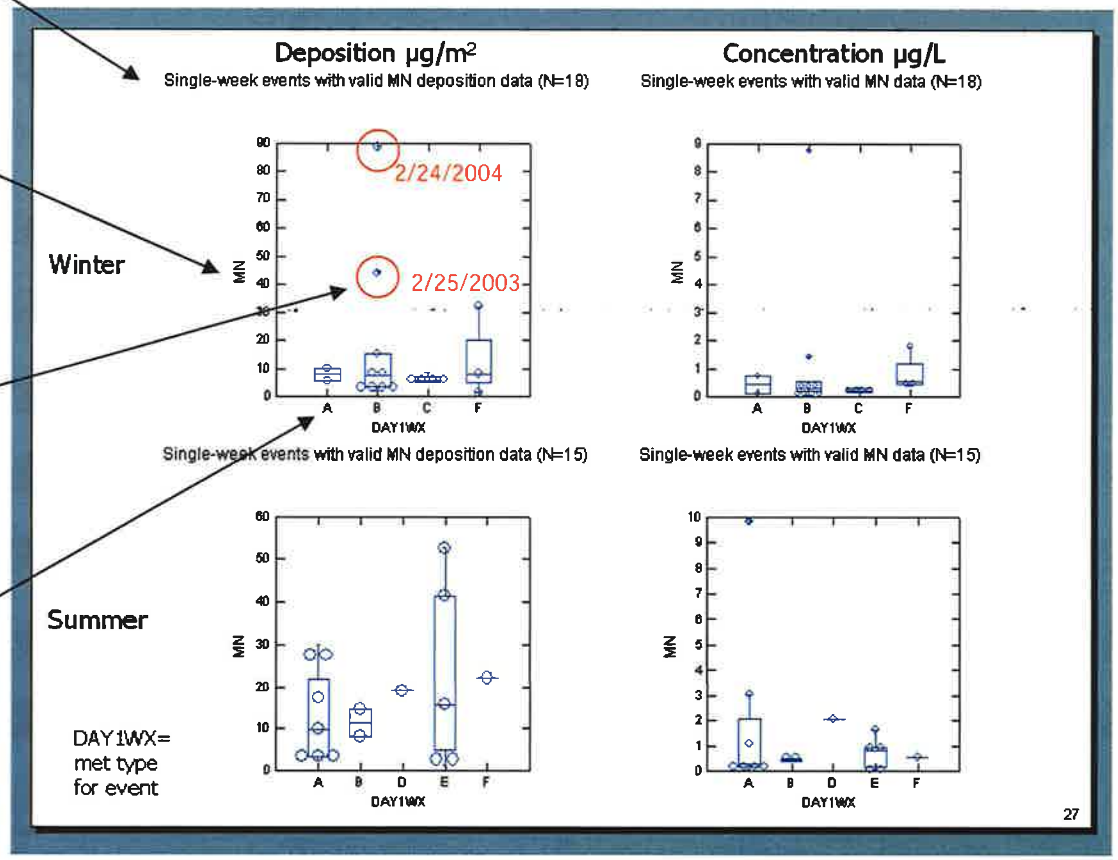
The description above each graph indicates what is plotted and how many data points were plotted. Overall, the number of data points was too low for robust interpretation of statistical differences.

The y-axis title indicates which metal is plotted as well as the observed deposition or concentration values.

Outlier concentrations are circled in red and marked with the date the outlier occurred.

The x-axis groups data by air mass type in order to investigate differences in observed concentrations due to the air mass type.

Figures for a single metal are organized in a matrix to show deposition and concentration for both winter and summer.

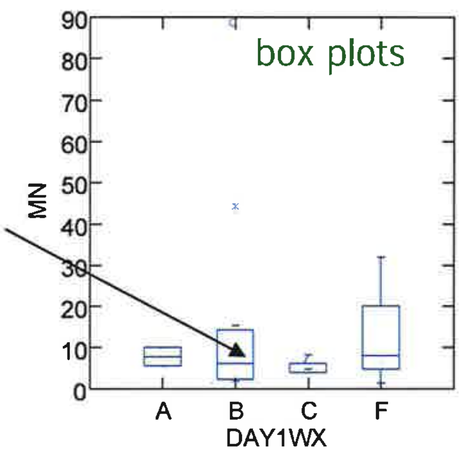


Box Plot Interpretation

Because of the low number of data points box plots and dot densities are combined in the figures.

Box plots are almost identical to notched box plots (see slide 19 for interpretation).

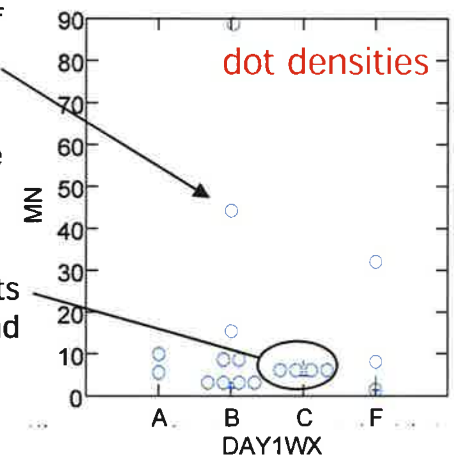
The only difference is that the median value is indicated by a vertical line in the middle of the box.



Dot densities show the value of each data point as indicated by the circles.

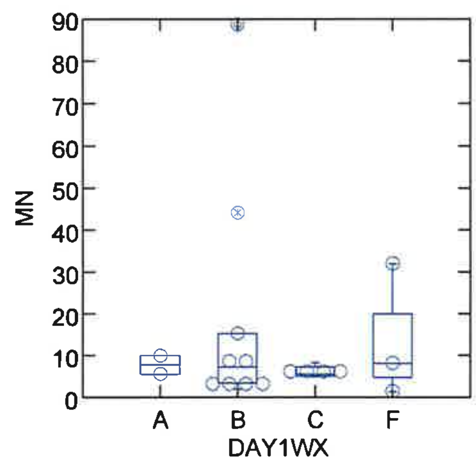
Data points that have the same value are placed next to each other in a horizontal line.

All four of the circled data points were from air mass type "C" and have the same value.



Combination of box plots and dot densities

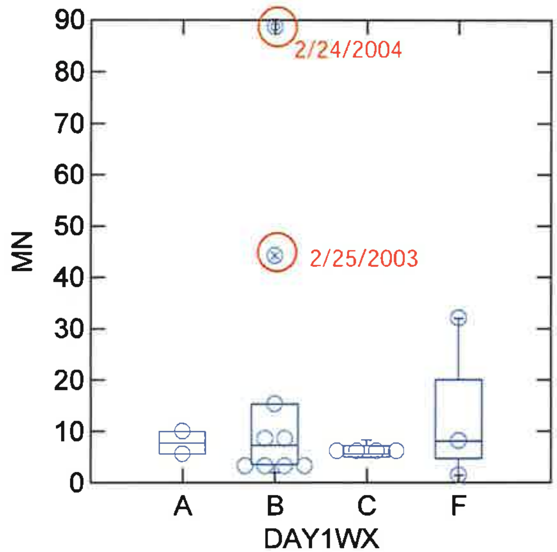
The combination of the two figure types provides the advantage of summary statistics (box plots) and the distribution of individual data points (dot densities).



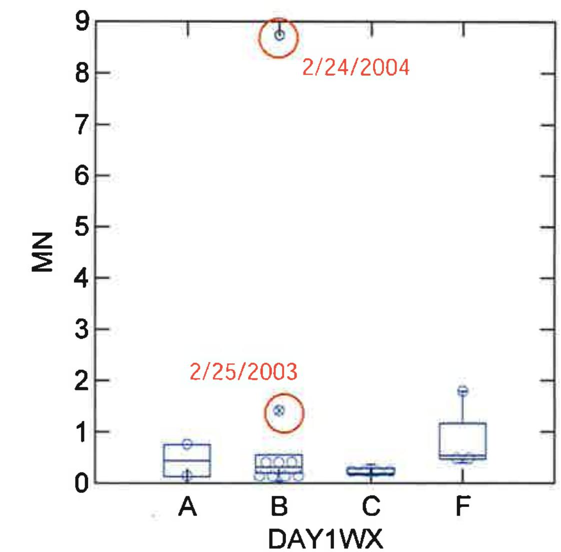
Deposition $\mu g/m^2$ / Concentration $\mu g/L$

Winter

Single-week events with valid MN deposition data (N=18)

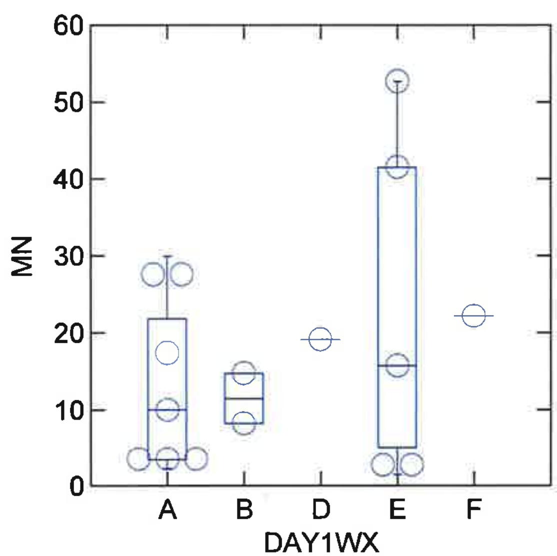


Single-week events with valid MN data (N=18)

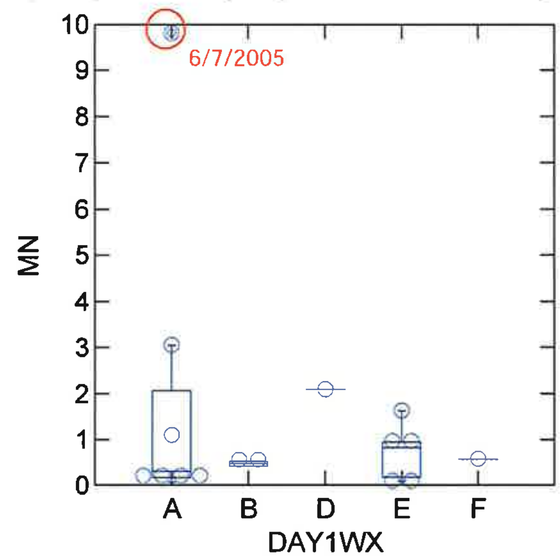


Summer

Single-week events with valid MN deposition data (N=15)



Single-week events with valid MN data (N=15)



DAY1WX= met type for event

Deposition µg/m²

Concentration µg/L

Winter

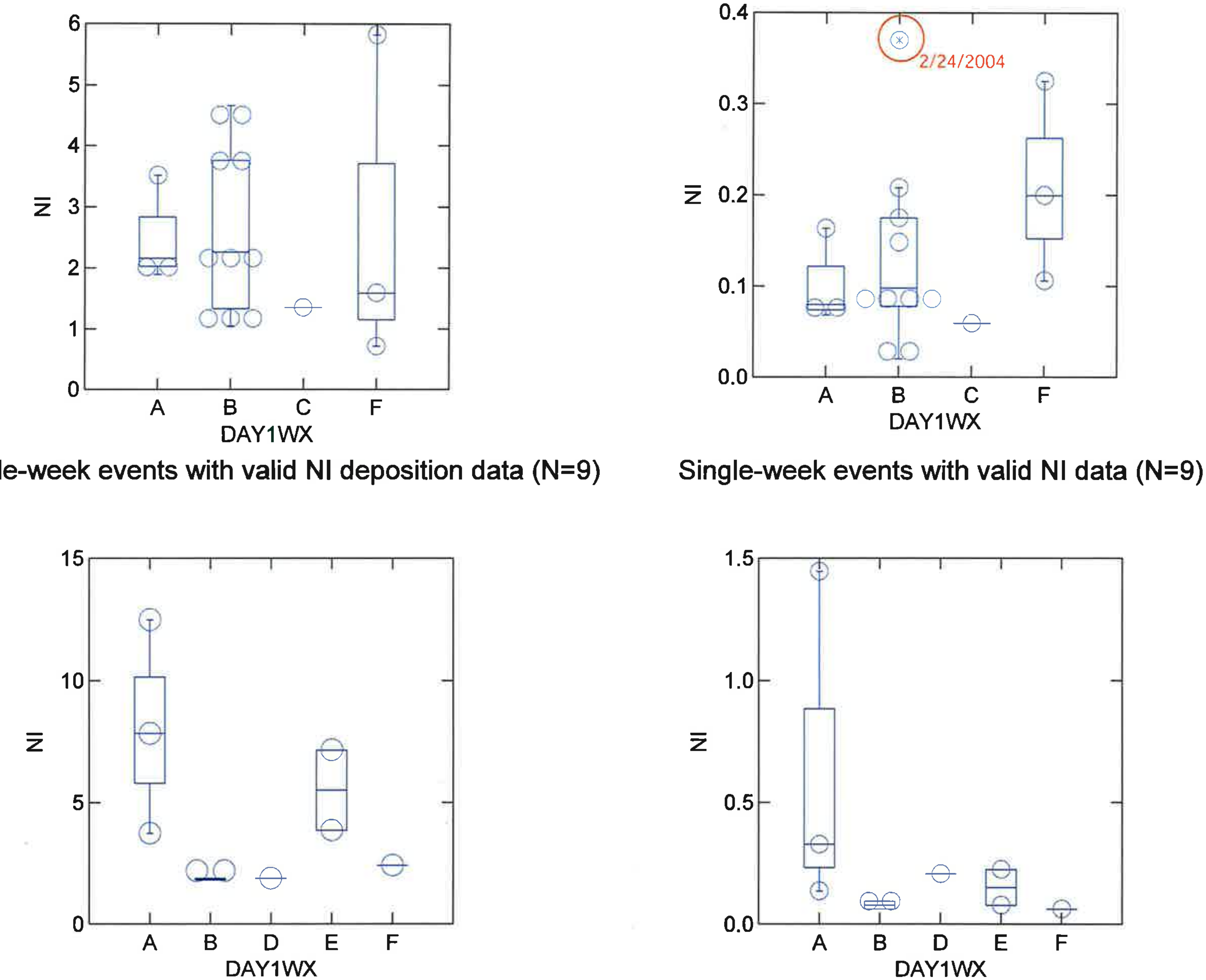
Single-event weeks with valid NI deposition data (N=17)

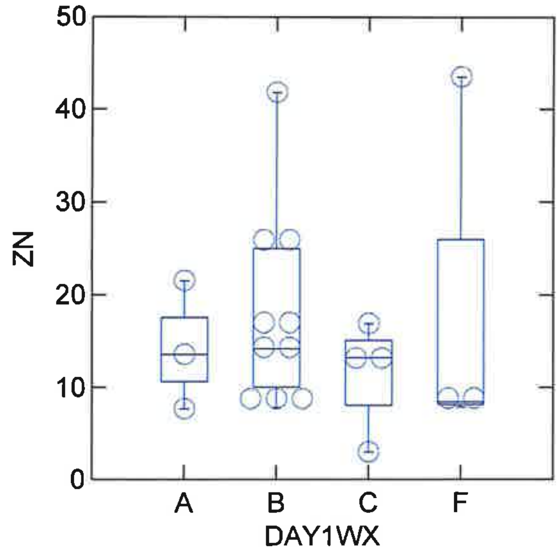
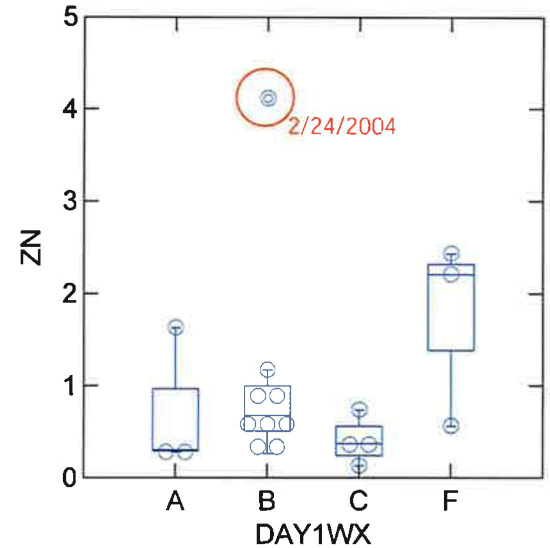
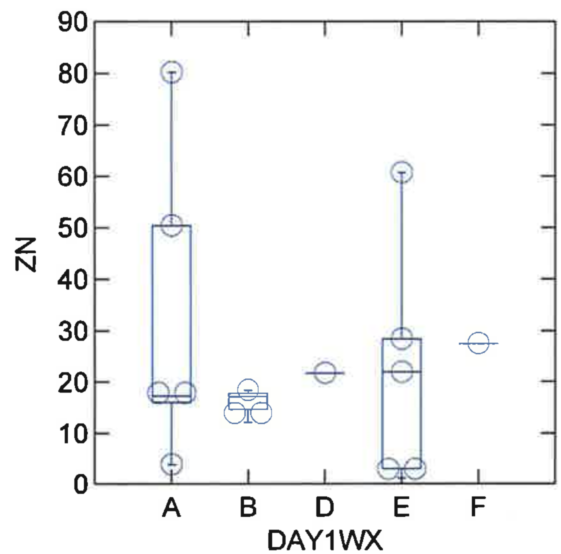
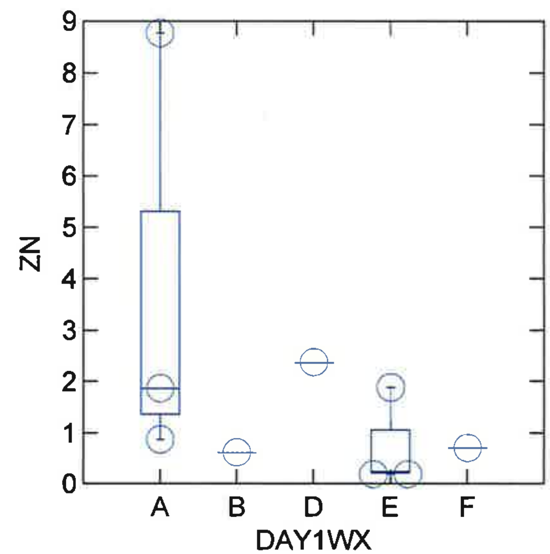
Single-event weeks with valid NI data (N=17)

Summer

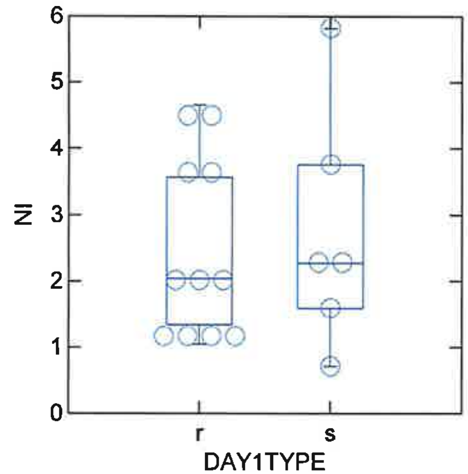
Single-week events with valid NI deposition data (N=9)

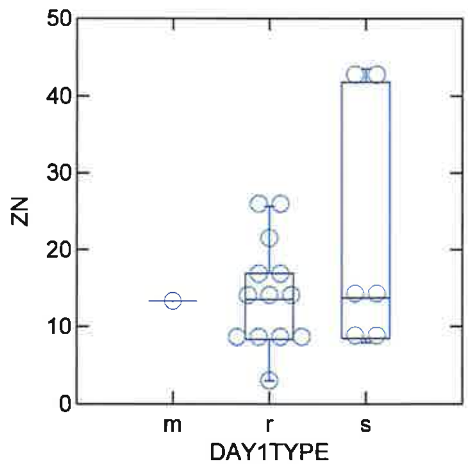
Single-week events with valid NI data (N=9)

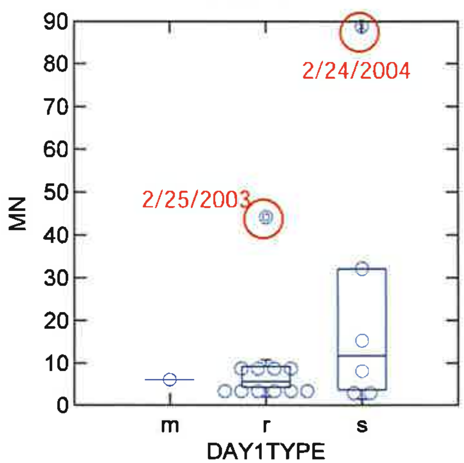


	Deposition μg/m²	Concentration μg/L
	Single-event weeks with valid ZN deposition data (N=19)	Single-event weeks with valid ZN data (N=19)
Winter		
	Single-week events with valid ZN deposition data (N=8)	Single-week events with valid ZN data (N=8)
Summer		

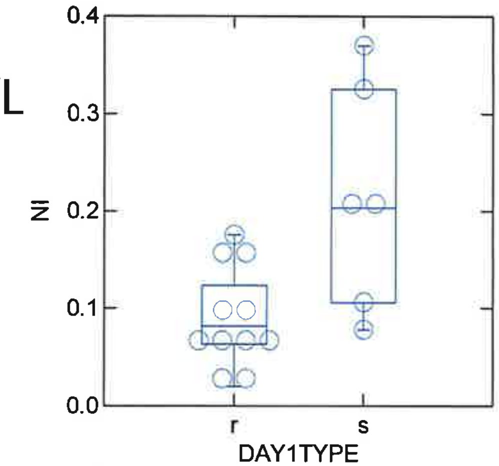
Deposition μg/m² Concentration μg/L

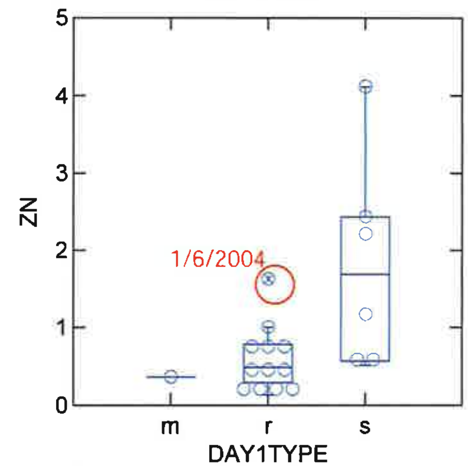


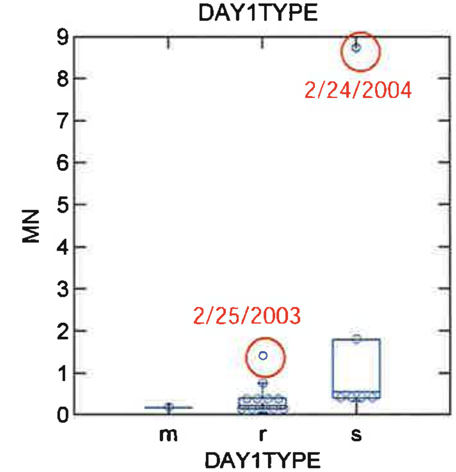




- Only a handful of snow events occurred, so while snow events had higher deposition and concentration for Zn and Mn (and concentration for Ni), there is an insufficient number to be conclusive
- Lead showed no difference between rain and snow







Case Studies

- For six weekly samples with a single precipitation event (events can be more than one day in duration), trajectories were run from the date of the precipitation event. The case studies were chosen to cover a range of meteorological types and seasons.
- These trajectories were overlaid with nearby IMPROVE $PM_{2.5}$ aerosol data to understand if there is a relationship between $PM_{2.5}$ composition/concentration and deposition or if different regional patterns are evident when there are differences in deposition between events.
- The following slides orient the reader to the full case-study summary pages.

Sources in the Literature

- PMF results of $PM_{2.5}$ data in Vermont were presented by Polissar et al. in 2001. Back trajectories of the resulting factors were also investigated, making this work an excellent comparison to Casco Bay case-study data.
- The following source results were described by Polissar et al.:
  - Zn had two major sources:
    - Cu smelting → from Midwest and East Coast
    - Zn/Pb factor from a mixture of sources → from Midwest
  - Pb had two major sources:
    - Canadian smelting and mobile sources → from Canada
    - Zn/Pb factor from a mixture of sources → from Midwest
  - Ni had one major source:
    - Oil fueled power plants → from East Coast
  - Mn had one major source:
    - Canadian smelting and mobile sources → from Canada

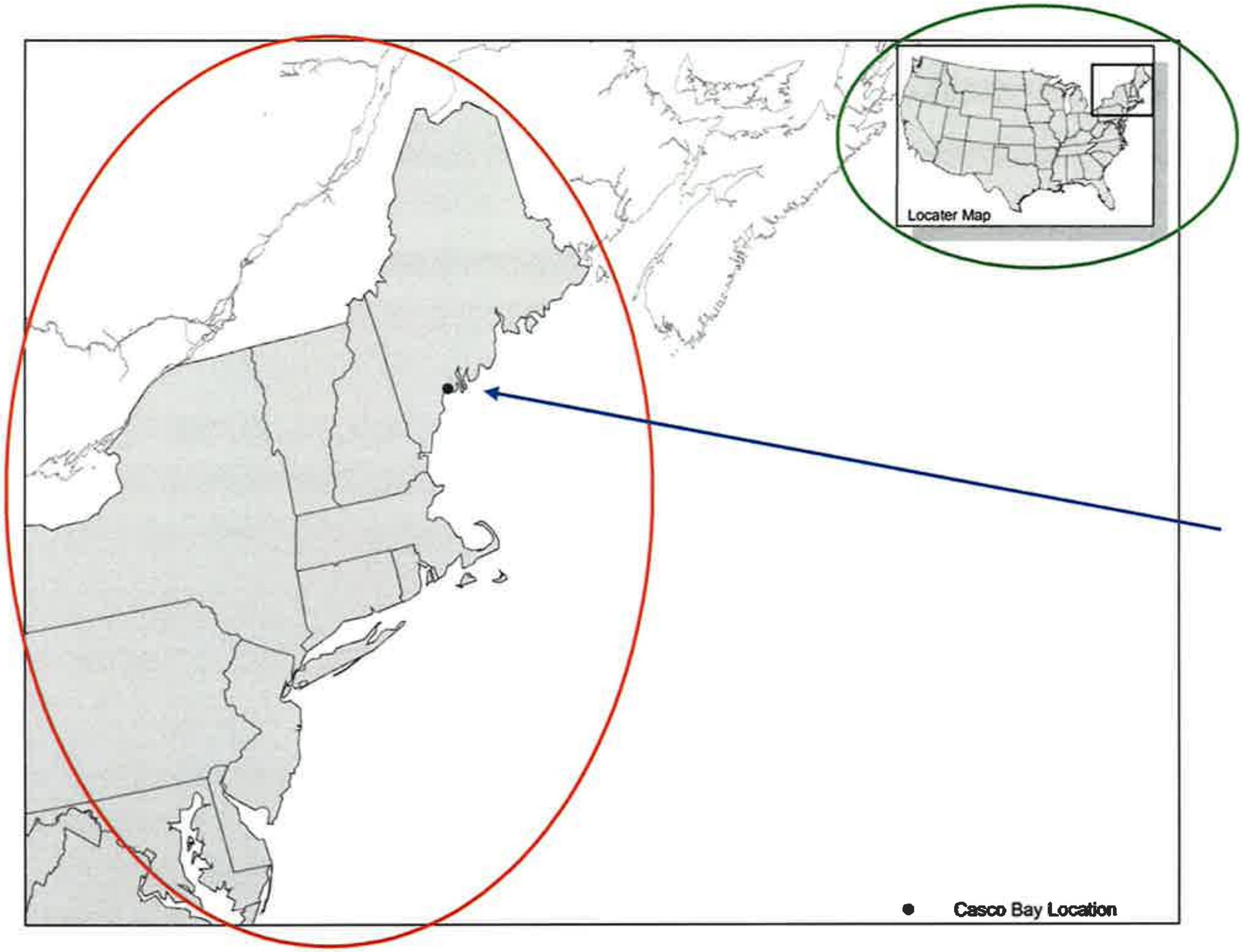
Polissar A.V., Hopke P.K., and Poirot R.L. (2001) Atmospheric aerosol over Vermont: chemical composition and sources. *Environ. Sci. Technol.* **35** (23), 4604-4621.

Case-study Ratios

- Ratios of metals in case-study days versus the seasonal average were investigated to further understand possible source influence.
- Numbers in **red and bold** are outside one standard deviation of the seasonal average.
- Numbers in red but not bold are more than twice the seasonal average, and numbers in blue but not bold are less than half the seasonal average.
- Based on these ratios
  - Mn is significantly higher in precipitation data taken 2/18/2004
  - Ni is significantly higher in precipitation data taken 8/18/2004

Precipitation Sample Date	Season	Mn/ Ni	Mn/ Pb	Mn/ Zn	Ni/ Pb	Ni/ Zn	Pb/ Zn
2/19/2003	Cool	4.6	1.9	0.46	0.42	0.10	0.24
2/18/2004	Cool	**24**	**13**	**2.1**	0.55	0.090	0.16
11/2/1005	Cool	9.5	5.9	**1.7**	0.62	0.18	0.29
Cool Seasonal Average		4.5	3.7	0.56	0.81	0.12	0.15
8/18/2004	Warm	2.1	8.6	**1.6**	**4.1**	**0.78**	0.19
7/20/2005	Warm	10	3.6	0.88	0.35	0.086	0.25
8/3/2005	Warm	2.2	1.5	0.35	0.66	0.16	0.23
Warm Seasonal Average		6.0	3.4	0.67	0.58	0.11	0.19

Map Interpretation - Base

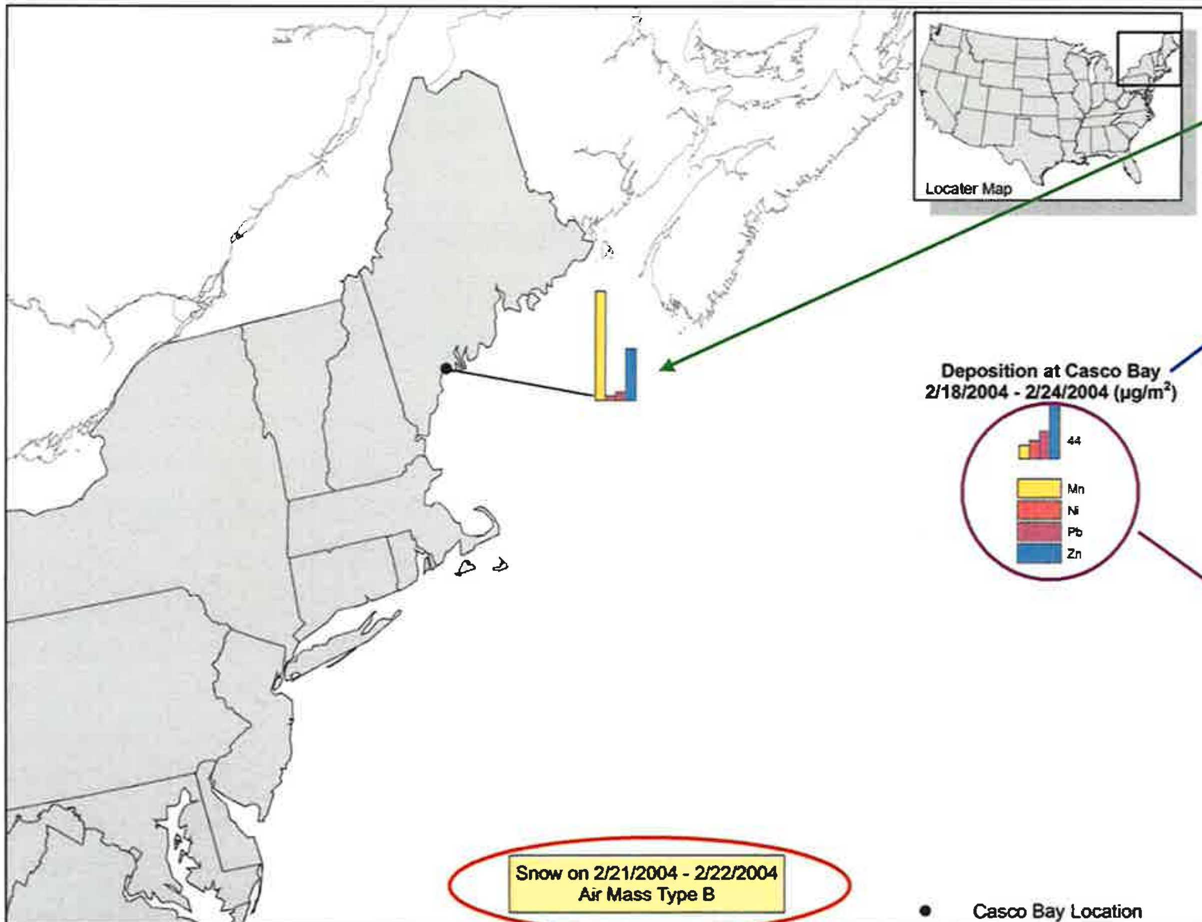


Locater map showing a "zoomed out" view of the United States.

Casco Bay monitoring site.

A "zoomed in" view of the Northeastern United States.

Map Interpretation - Deposition



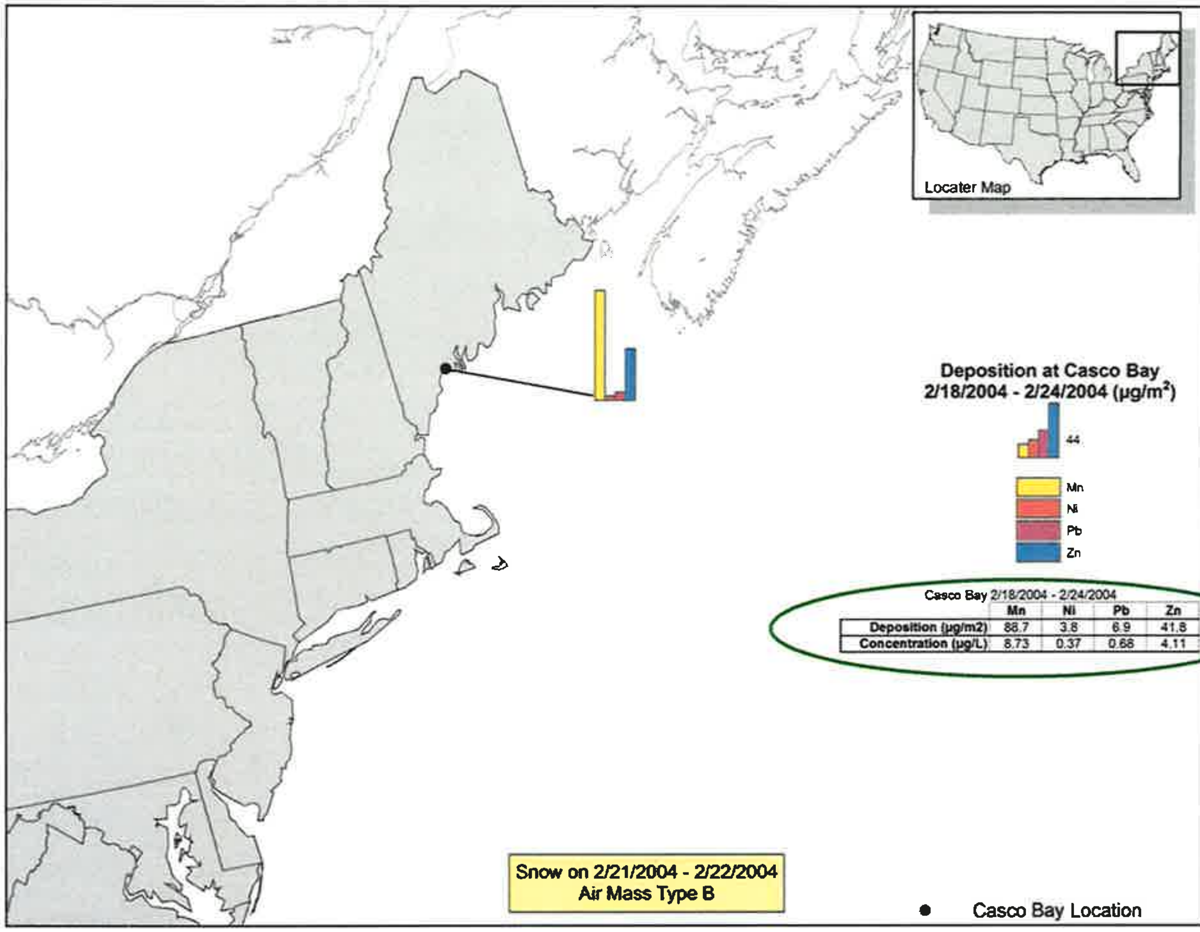
Bar chart of deposition data collected at Casco Bay.

The legend title indicates the deposition sampling time period.

The legend indicates the scale of bar chats in the map and defines bar colors.

The textbox indicates precipitation time period and air mass type. Air mass descriptions can be found in slides 23 and 24.

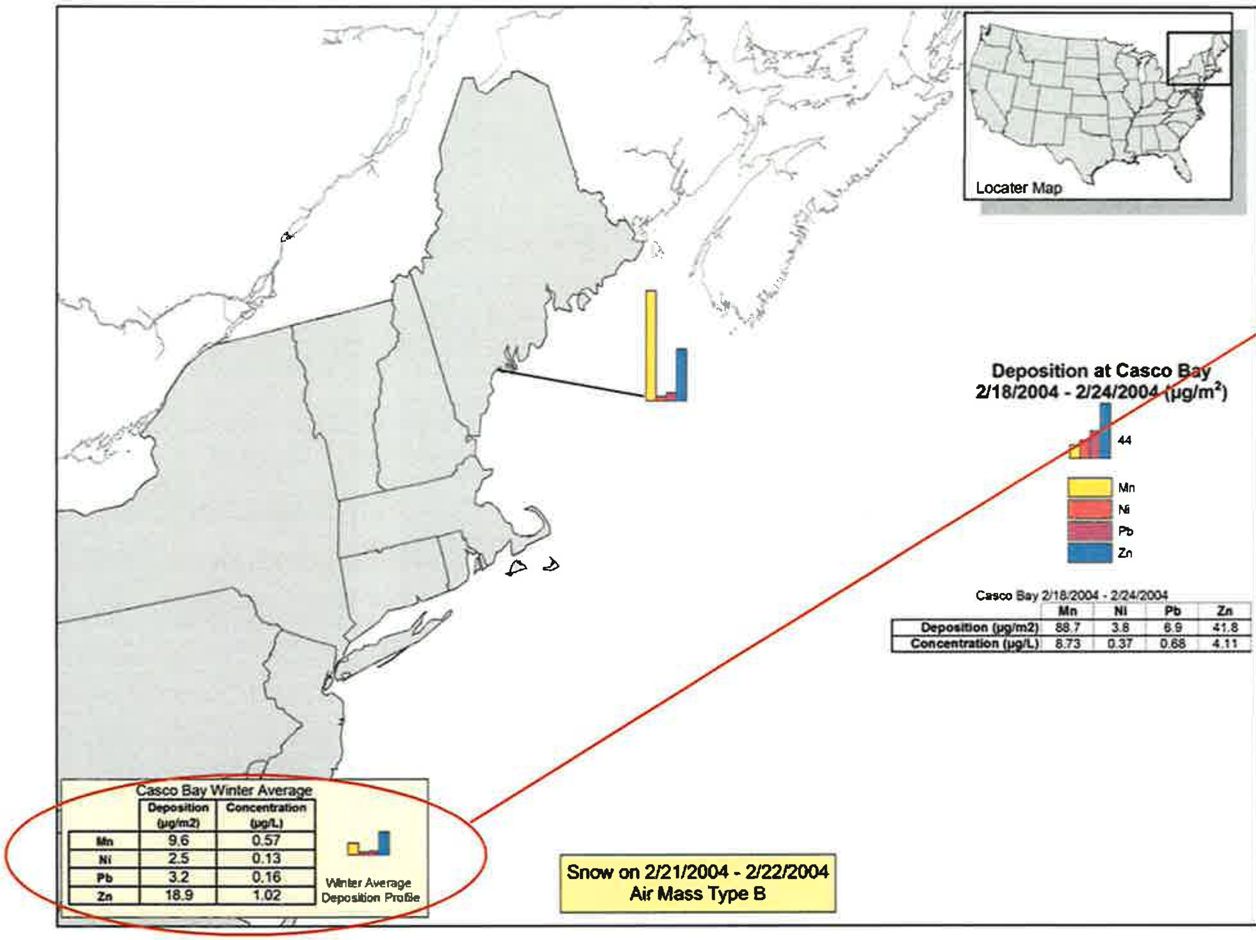
Map Interpretation - Deposition



Casco Bay 2/18/2004 - 2/24/2004	Mn	Ni	Pb	Zn
Deposition (µg/m2)	88.7	3.8	6.9	41.8
Concentration (µg/L)	8.73	0.37	0.68	4.11

The table provides deposition and concentration values measured at Casco Bay. Deposition data corresponds to the bar chart, concentration data are not graphed.

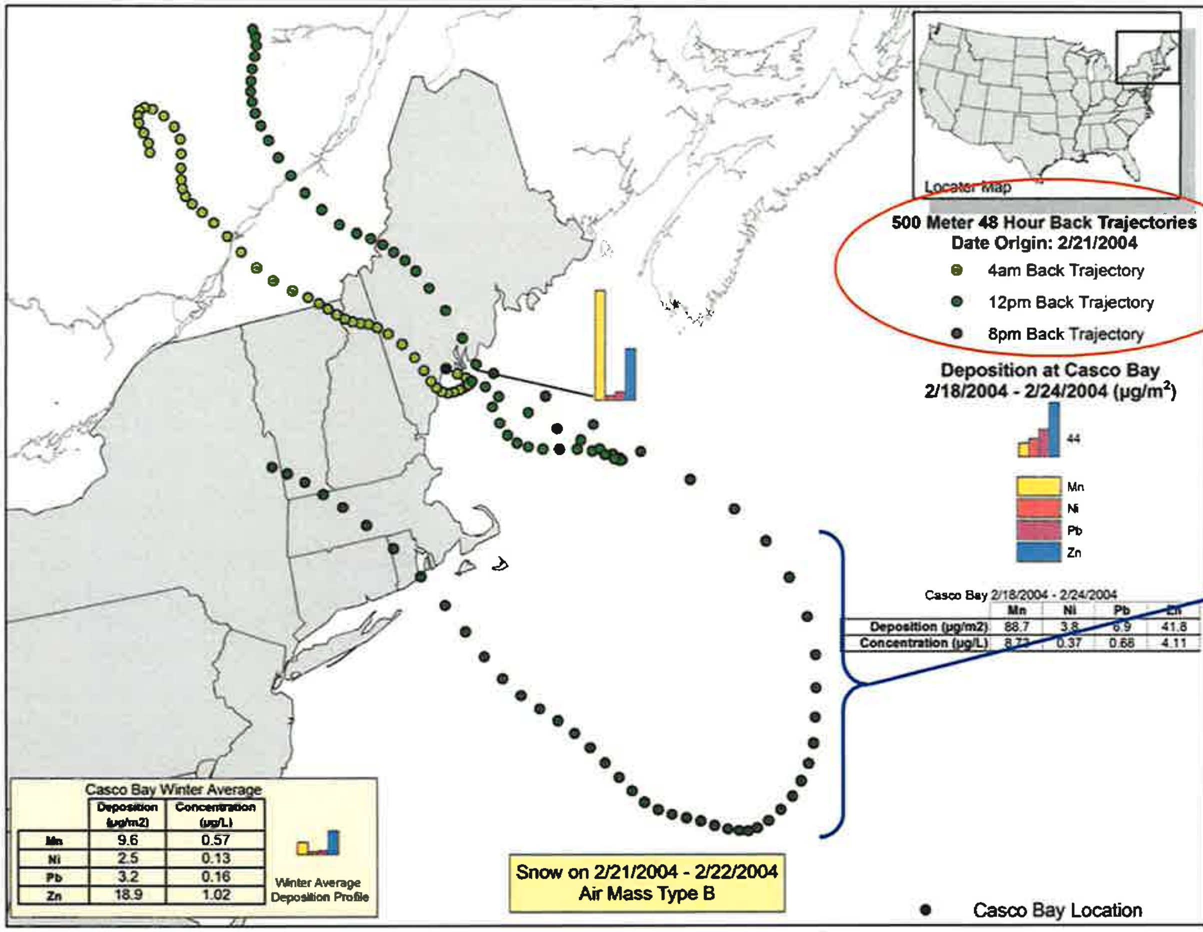
Map Interpretation - Deposition



The pale yellow table provides seasonal average deposition and concentration data. The bar chart shows the seasonal average deposition, and is on the same scale as the map data to allow direct comparison.

Interpretation of comparison to seasonal average: *The deposition measured at Casco Bay between 2/18/2004 and 2/24/2004 had much higher Mn concentrations than the seasonal average, and the ratio of Mn to Ni is different than that observed in the seasonal average. This may indicate an unusual source.*

Map Interpretation – Back Trajectories

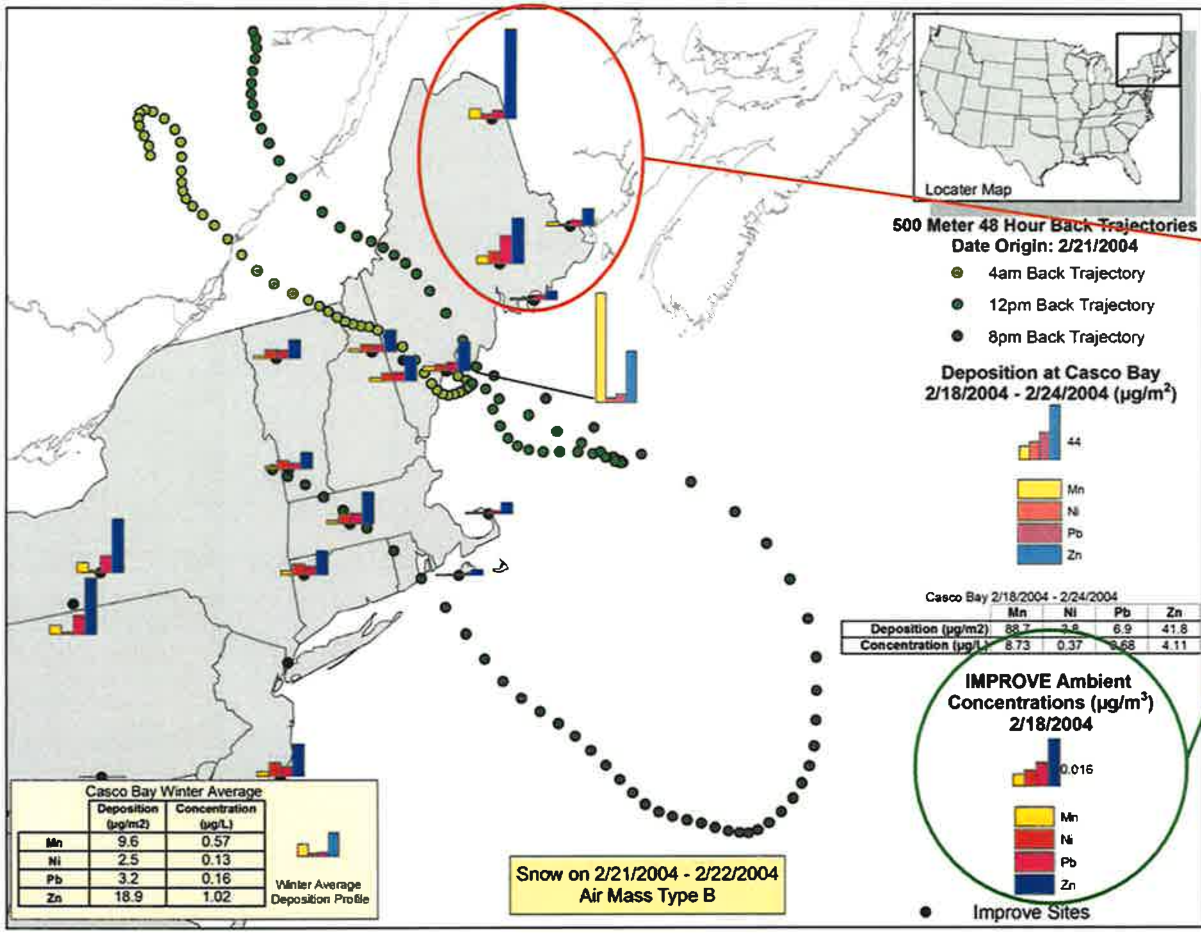


The legend title indicates the date from which back trajectories were calculated. Trajectories begin the first day of measured precipitation to understand the source of the air mass.

Green dots indicate the back trajectory path. Starting from the Casco Bay monitoring location, each dot indicates one hour backwards in time. Three back trajectories were calculated, indicated by the 3 shades of green, each has a different begin hour.

Interpretation of back trajectories: *If snow at Casco Bay occurred before 12pm on 2/21/2004, the air mass traveled from Canada. If snow occurred in the evening on 2/21/2004, the air mass traveled from Northeastern New York over the ocean and back to Casco Bay. Polissar et. al attributed high measured Mn events to Canada based on back trajectory analyses, in agreement with this case study if snow occurred in the first half of the day.*

Map Interpretation – IMPROVE Data



Casco Bay 2/18/2004 - 2/24/2004	Mn	Ni	Pb	Zn
Deposition (μg/m2)	88.7	3.8	6.9	41.8
Concentration (μg/L)	8.73	0.37	0.68	4.11

Casco Bay Winter Average	Deposition (μg/m2)	Concentration (μg/L)
Mn	9.6	0.57
Ni	2.5	0.13
Pb	3.2	0.16
Zn	18.9	1.02

Brightly colored bar charts represent air concentrations of the four metals at IMPROVE monitors in the Northeast.

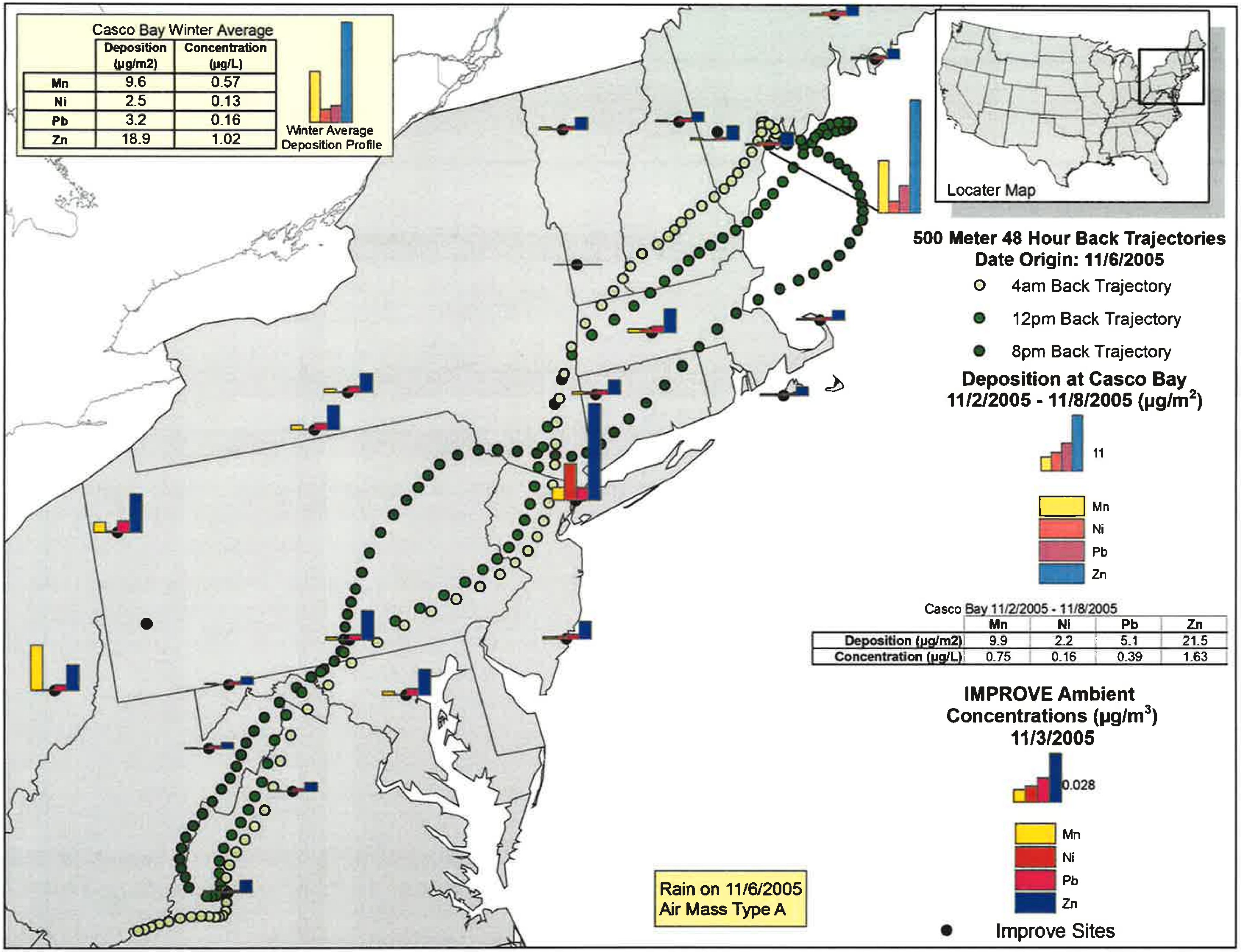
The legend title indicates the monitoring date of IMPROVE data. The date is 1-3 days before the precipitation event, based on data availability. This allows comparison of chemical composition that the precipitation air mass moved through. The legend also indicates the scale of bar chats in the map and defines bar colors.

Interpretation of IMPROVE data: *Mn concentrations at sites that the air mass moved through do not account for the high Mn deposition observed at Casco Bay. This provides more evidence for Mn transport from Canada (or a local source?). Ratios of other species are in agreement with those observed in IMPROVE data.*

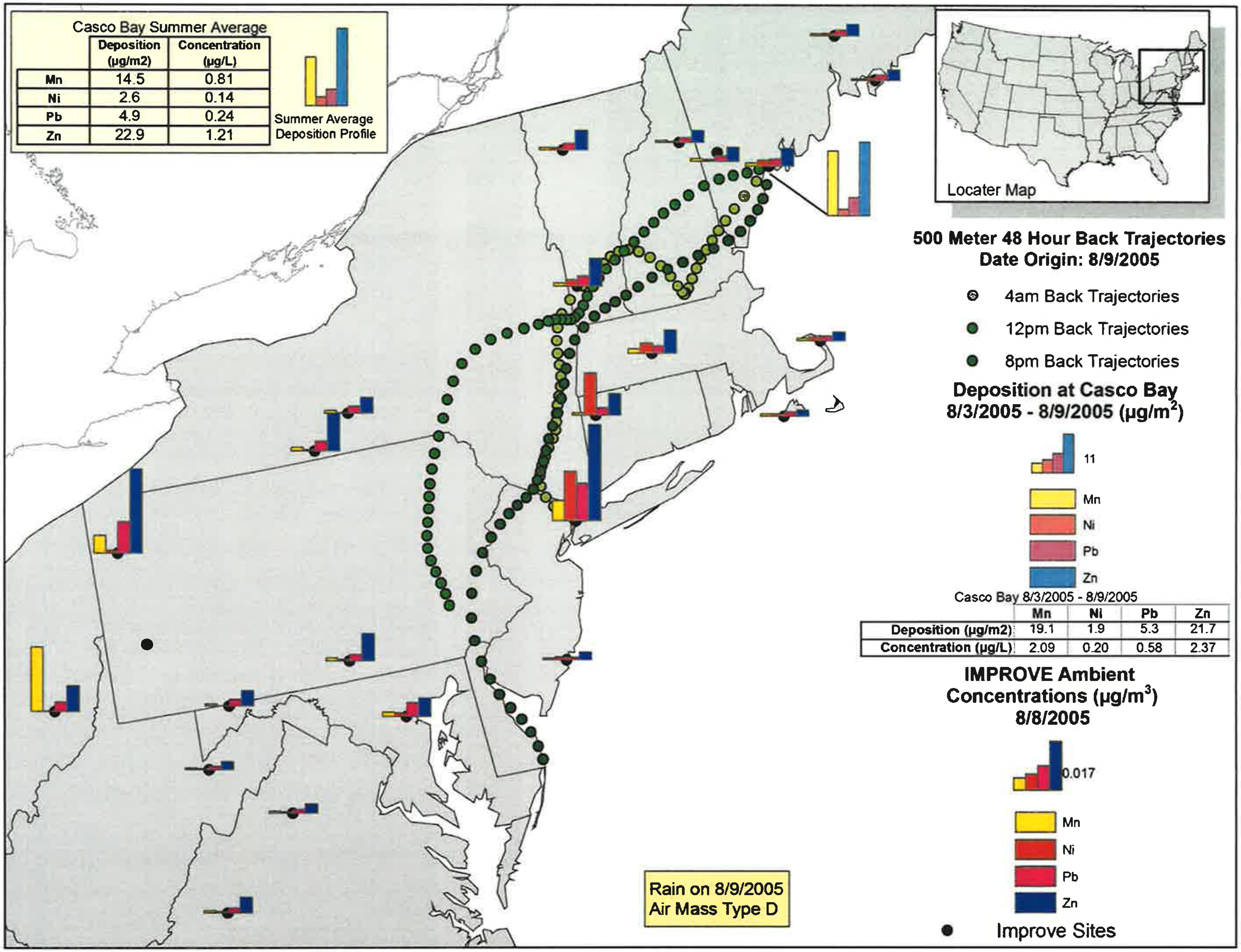
Case Studies

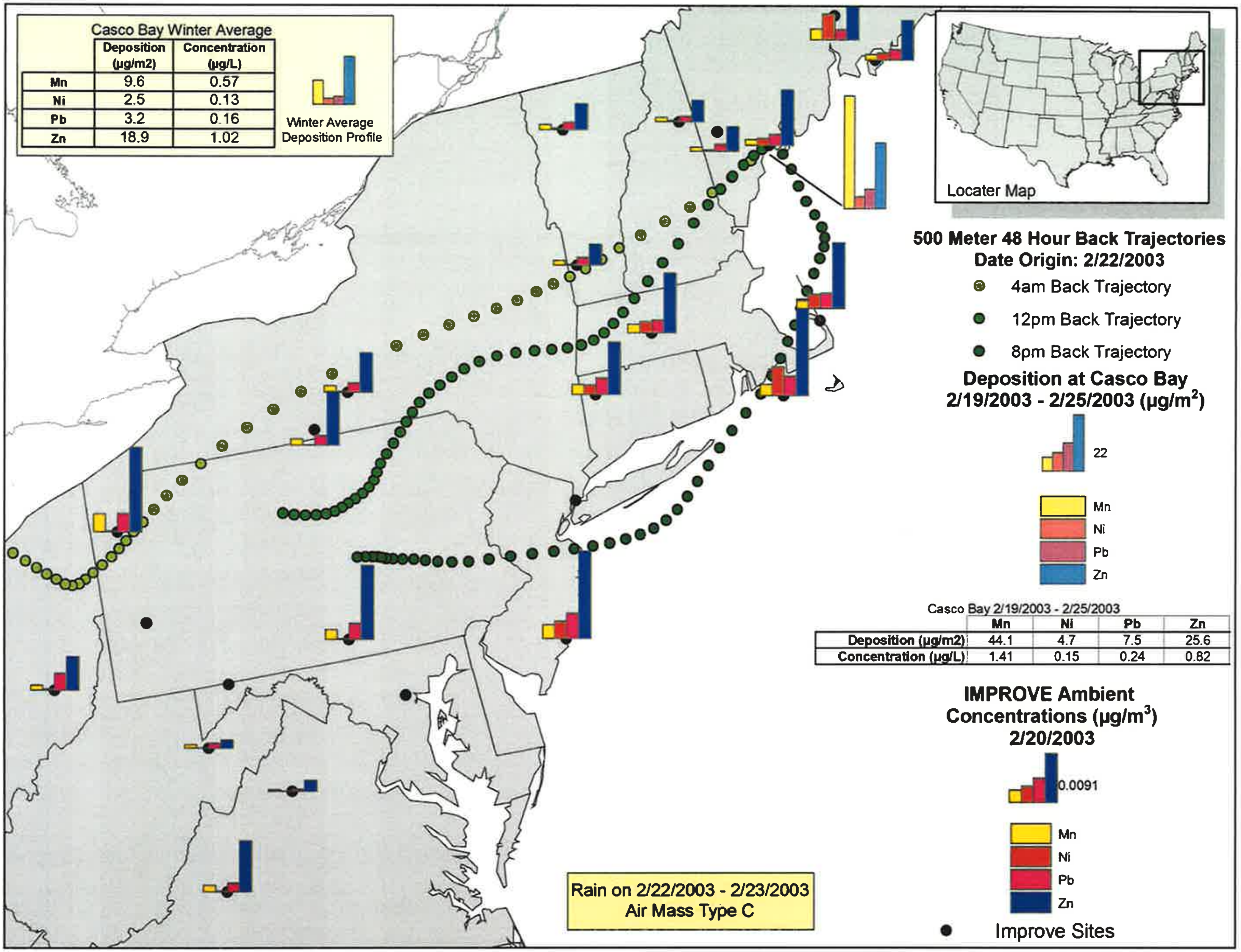
The next slides show maps for a series of case studies.

The first set have air mass trajectories from the southwest, during both summer and winter (11/6/05, 8/9/05, 2/22/03).



Casco Bay Winter Average
Deposition (µg/m2)
Concentration (µg/L)
Mn 9.6 0.57
Ni 2.5 0.13
Pb 3.2 0.16
Zn 18.9 1.02
Winter Average Deposition Profile
Locater Map
500 Meter 48 Hour Back Trajectories
Date Origin: 11/6/2005
4am Back Trajectory
12pm Back Trajectory
8pm Back Trajectory
Deposition at Casco Bay
11/2/2005 - 11/8/2005 (µg/m²)
11
Mn
Ni
Pb
Zn
Casco Bay 11/2/2005 - 11/8/2005
Mn Ni Pb Zn
Deposition (µg/m2) 9.9 2.2 5.1 21.5
Concentration (µg/L) 0.75 0.16 0.39 1.63
IMPROVE Ambient
Concentrations (µg/m³)
11/3/2005
0.028
Mn
Ni
Pb
Zn
Improve Sites
Rain on 11/6/2005
Air Mass Type A


Casco Bay Summer Average
Deposition (µg/m2) | Concentration (µg/L)
Mn 14.5 0.81
Ni 2.6 0.14
Pb 4.9 0.24
Zn 22.9 1.21
Summer Average Deposition Profile
Locater Map
500 Meter 48 Hour Back Trajectories
Date Origin: 8/9/2005
4am Back Trajectories
12pm Back Trajectories
8pm Back Trajectories
Deposition at Casco Bay
8/3/2005 - 8/9/2005 (µg/m2)
11
Mn
Ni
Pb
Zn
Casco Bay 8/3/2005 - 8/9/2005
Mn Ni Pb Zn
Deposition (µg/m2): 19.1 1.9 5.3 21.7
Concentration (µg/L): 2.09 0.20 0.58 2.37
IMPROVE Ambient
Concentrations (µg/m3)
8/8/2005
0.017
Mn
Ni
Pb
Zn
Improve Sites
Rain on 8/9/2005
Air Mass Type D



Casco Bay Winter Average

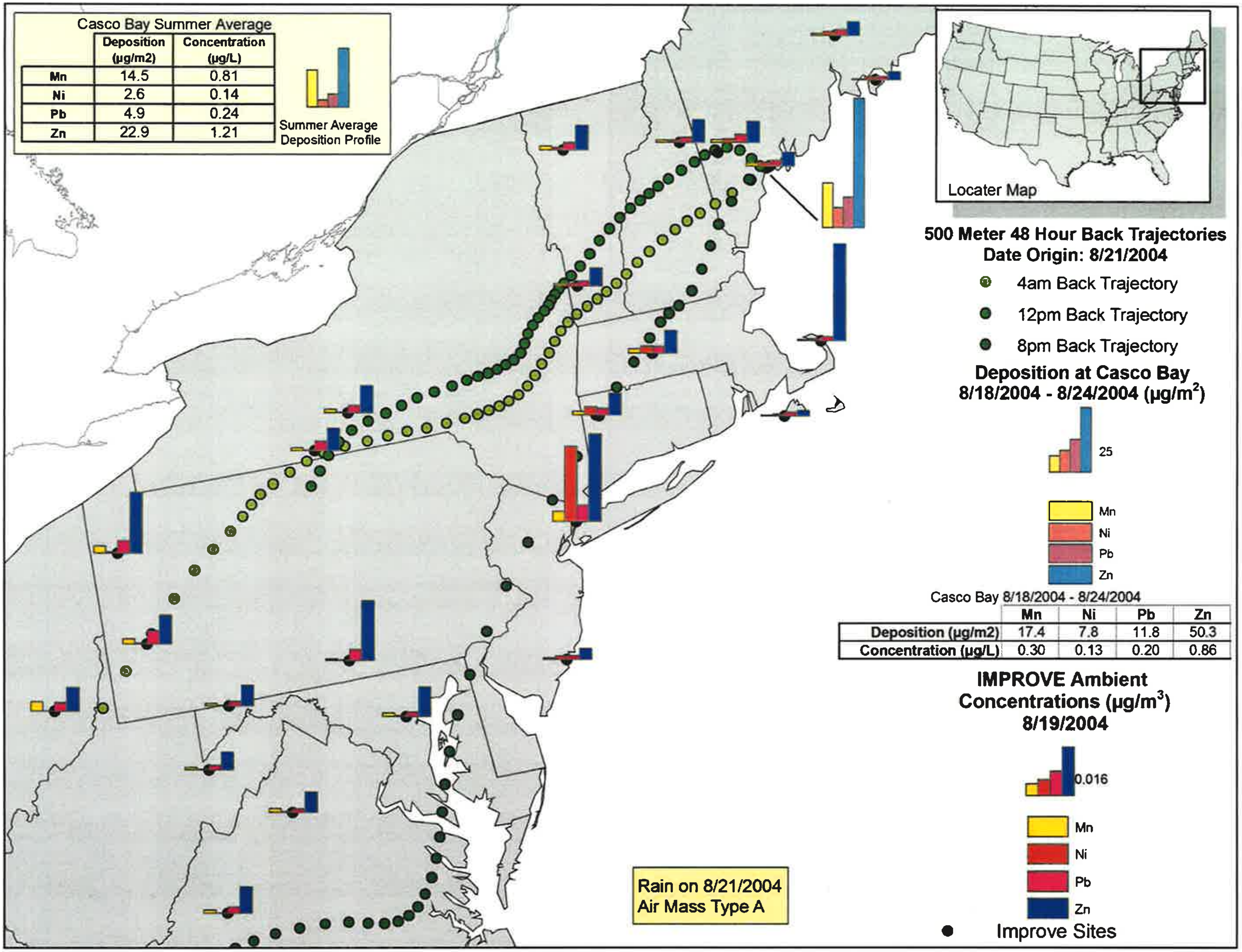
	Deposition (µg/m2)	Concentration (µg/L)
Mn	9.6	0.57
Ni	2.5	0.13
Pb	3.2	0.16
Zn	18.9	1.02

Casco Bay 2/19/2003 - 2/25/2003

	Mn	Ni	Pb	Zn
Deposition (µg/m2)	44.1	4.7	7.5	25.6
Concentration (µg/L)	1.41	0.15	0.24	0.82

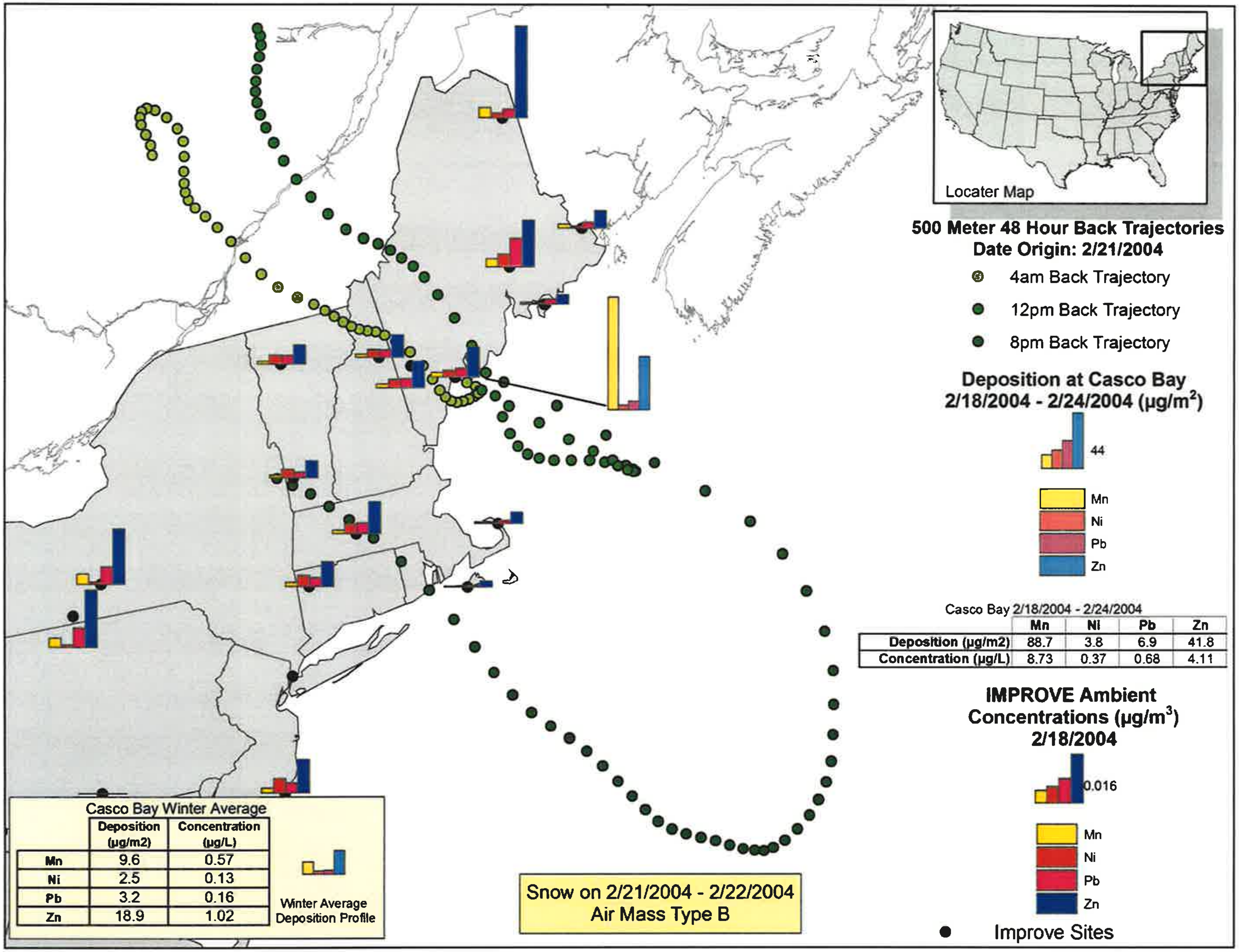
Transport from the Northeastern Metropolitan Corridor

- These three case study days (11/6/05, 8/9/05, 2/22/03) had fairly similar transport patterns, but showed Mn deposition.
- While similar in general transport pattern, the synoptic patterns were different, which may help explain differences in deposition.
- IMPROVE concentrations do not typically reflect what is seen in the deposition data, perhaps indicating local sources are important in either the deposition or IMPROVE aerosol levels.


Casco Bay Summer Average
	Deposition (µg/m2)	Concentration (µg/L)
Mn	14.5	0.81
Ni	2.6	0.14
Pb	4.9	0.24
Zn	22.9	1.21
Summer Average Deposition Profile
Locater Map
500 Meter 48 Hour Back Trajectories
Date Origin: 8/21/2004
4am Back Trajectory
12pm Back Trajectory
8pm Back Trajectory
Deposition at Casco Bay
8/18/2004 - 8/24/2004 (µg/m²)
25
Mn
Ni
Pb
Zn
Casco Bay 8/18/2004 - 8/24/2004
	Mn	Ni	Pb	Zn
Deposition (µg/m2)	17.4	7.8	11.8	50.3
Concentration (µg/L)	0.30	0.13	0.20	0.86
IMPROVE Ambient
Concentrations (µg/m³)
8/19/2004
0.016
Mn
Ni
Pb
Zn
Improve Sites
Rain on 8/21/2004
Air Mass Type A

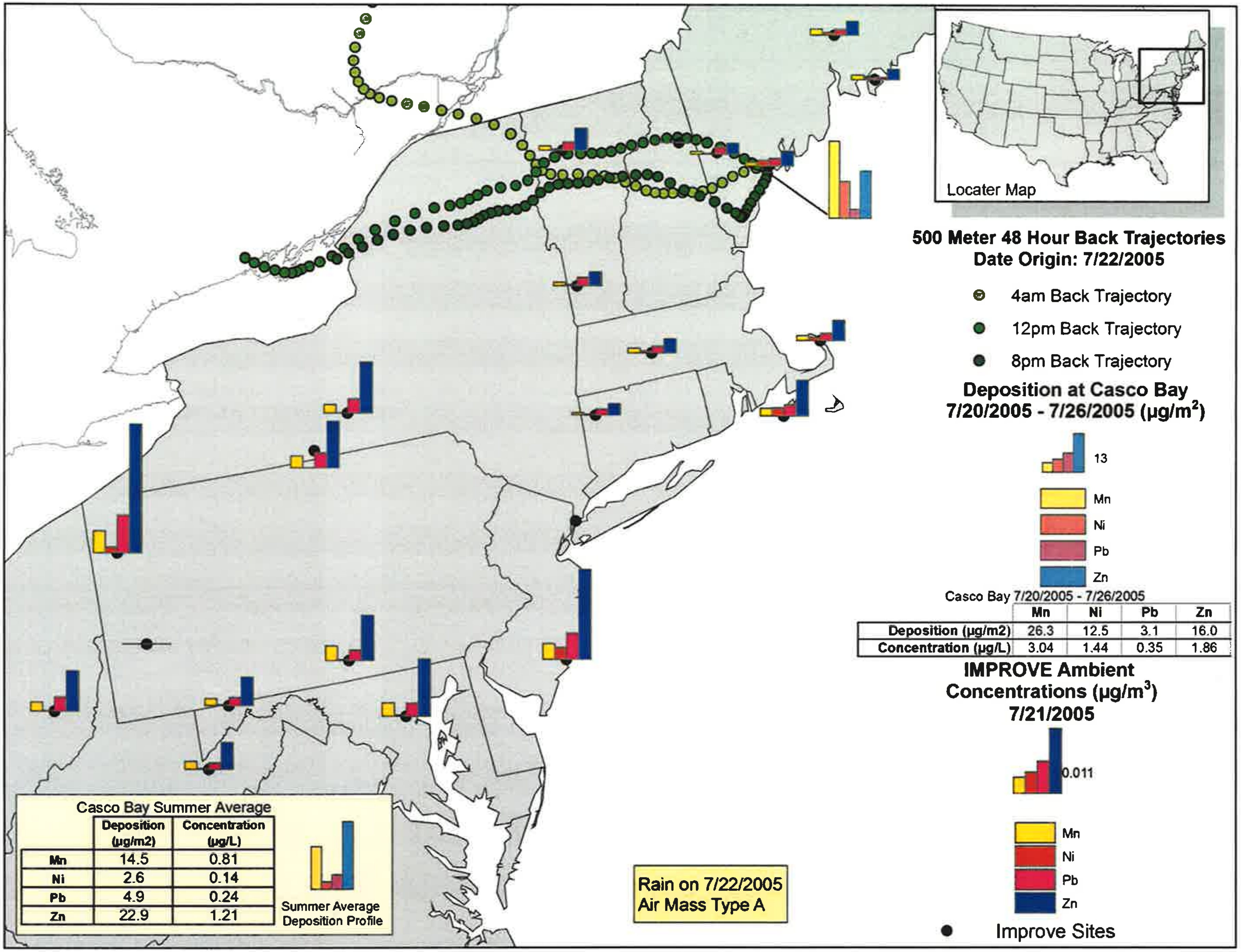
8/21/2004 Interpretation

- Significant Ni and Zn enrichment is observed in precipitation based on ratio analysis.
- Ni enrichment is not significant in the aerosol except at the New York, NY, site.
- The 8:00 p.m. back trajectory points toward New York, therefore the northeastern metropolitan corridor may be the source of Ni in precipitation.
- Polissar et al. found oil-fueled East Coast power plants to be the major source of Ni aerosol in Vermont; back trajectories of 8/18/2004 precipitation data points are consistent with this finding.


Locater Map
500 Meter 48 Hour Back Trajectories
Date Origin: 2/21/2004
4am Back Trajectory
12pm Back Trajectory
8pm Back Trajectory
Deposition at Casco Bay
2/18/2004 - 2/24/2004 (µg/m²)
44
Mn
Ni
Pb
Zn
Casco Bay 2/18/2004 - 2/24/2004
	Mn	Ni	Pb	Zn
Deposition (µg/m2)	88.7	3.8	6.9	41.8
Concentration (µg/L)	8.73	0.37	0.68	4.11
IMPROVE Ambient
Concentrations (µg/m³)
2/18/2004
0.016
Mn
Ni
Pb
Zn
Improve Sites
Snow on 2/21/2004 - 2/22/2004
Air Mass Type B
Casco Bay Winter Average
	Deposition (µg/m2)	Concentration (µg/L)
Mn	9.6	0.57
Ni	2.5	0.13
Pb	3.2	0.16
Zn	18.9	1.02
Winter Average
Deposition Profile

2/18/2004 Interpretation

- Concentrations of Mn are significantly higher based on ratio analyses; Zn concentrations are high compared to the average.
- Back trajectories point towards Canada.
- Results are in agreement with findings from Polissar et al. who observed significant Mn sources from Canadian smelting and mobile emissions.
- At that time, Canada used a unique gasoline additive methylcyclopentadienyl manganesetricarbonyl (MMT) that causes mobile emissions of Mn.


Locater Map
500 Meter 48 Hour Back Trajectories
Date Origin: 7/22/2005
4am Back Trajectory
12pm Back Trajectory
8pm Back Trajectory
Deposition at Casco Bay
7/20/2005 - 7/26/2005 (µg/m²)
13
Mn
Ni
Pb
Zn
Casco Bay 7/20/2005 - 7/26/2005

	Mn	Ni	Pb	Zn
Deposition (µg/m2)	26.3	12.5	3.1	16.0
Concentration (µg/L)	3.04	1.44	0.35	1.86

IMPROVE Ambient
Concentrations (µg/m³)
7/21/2005
0.011
Mn
Ni
Pb
Zn
Improve Sites
Rain on 7/22/2005
Air Mass Type A
Casco Bay Summer Average

	Deposition (µg/m2)	Concentration (µg/L)
Mn	14.5	0.81
Ni	2.6	0.14
Pb	4.9	0.24
Zn	22.9	1.21

Summer Average
Deposition Profile

7/22/05 Interpretation

- This rain event was associated with a slow moving air mass from the east, and saw elevated Ni deposition.
- This may be caused by oil combustion or other sources in Canada or the Northeast.
- Mn was also higher than average, observed in a number of other case studies, and could be indicative of local sources.

Summary of Findings from Case Studies

- In the six case studies performed, there were few repeated patterns from which to draw conclusions. This may be a limitation in the number of case studies conducted and that there are not very many single precipitation event weeks.
- In general, the Mn deposition was high relative to the other metals (Ni, Pb, Zn) and the aerosol data did not show higher Mn relative to Ni or Pb. In contrast, Zn is relatively high in both the deposition and in the aerosol. Canadian Mn sources may contribute to the observed enrichment in Mn precipitation.
- A similar observation can be made for the Ni measured at Casco Bay on the 2/22-2/23 2003 rain event – Ni is seen in the deposition data but not in the aerosol. *What is the source of the enriched Ni in the precipitation?*

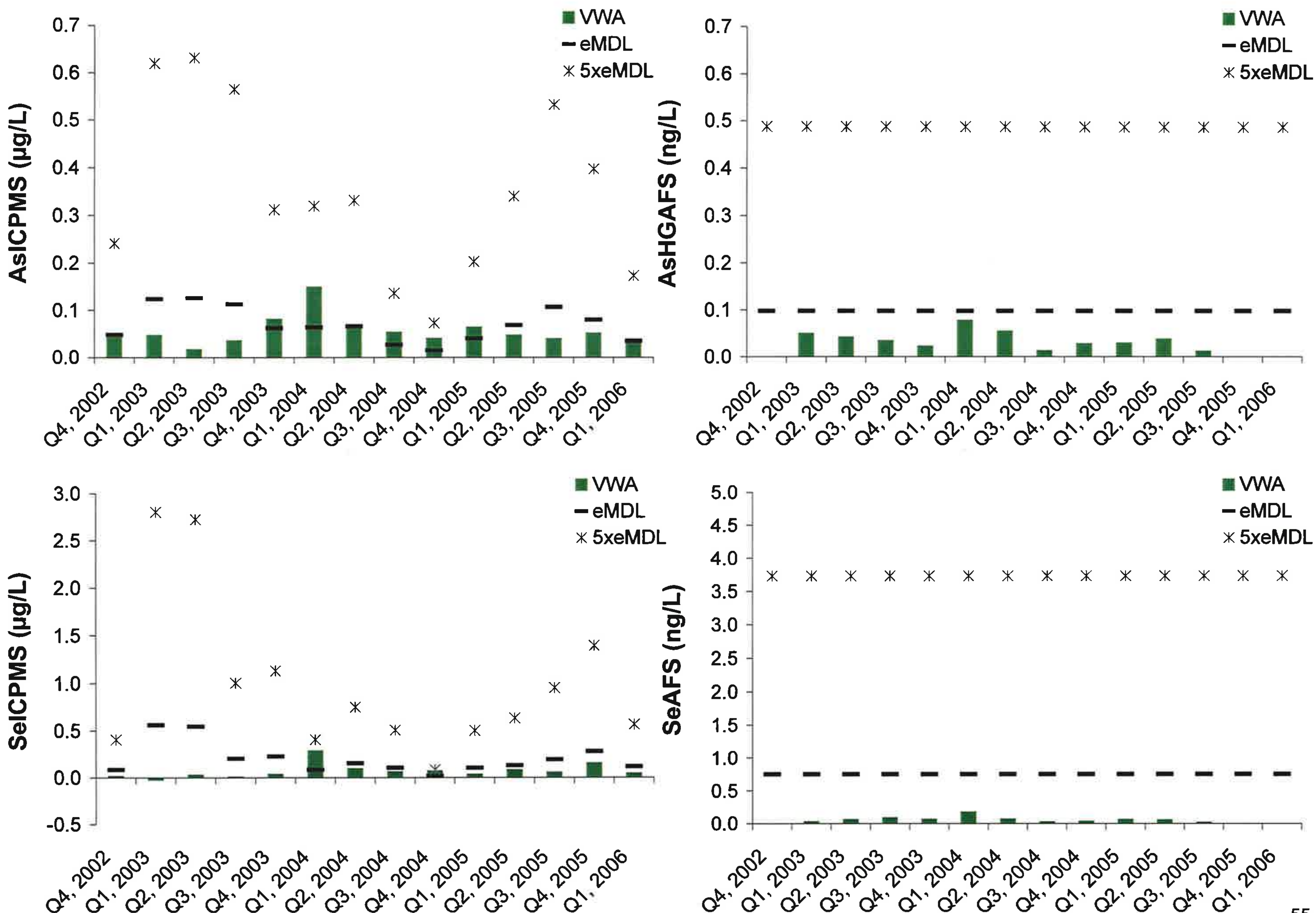
Summary/Conclusions

- Data quality was improved from the prior analysis (e.g., more data above detection, fewer reporting errors).
- With increased data, prior analyses were made more robust, and additional meteorological-oriented analyses (i.e., meteorological typing analysis, plus case-study trajectory and regional signature analysis) were conducted.
- We hoped that source type/region information would be discernable with this larger data set. While we continued to observe a number of good correlations between metals, there were not enough single-event weeks to show clear patterns of repeated source transport and signatures.

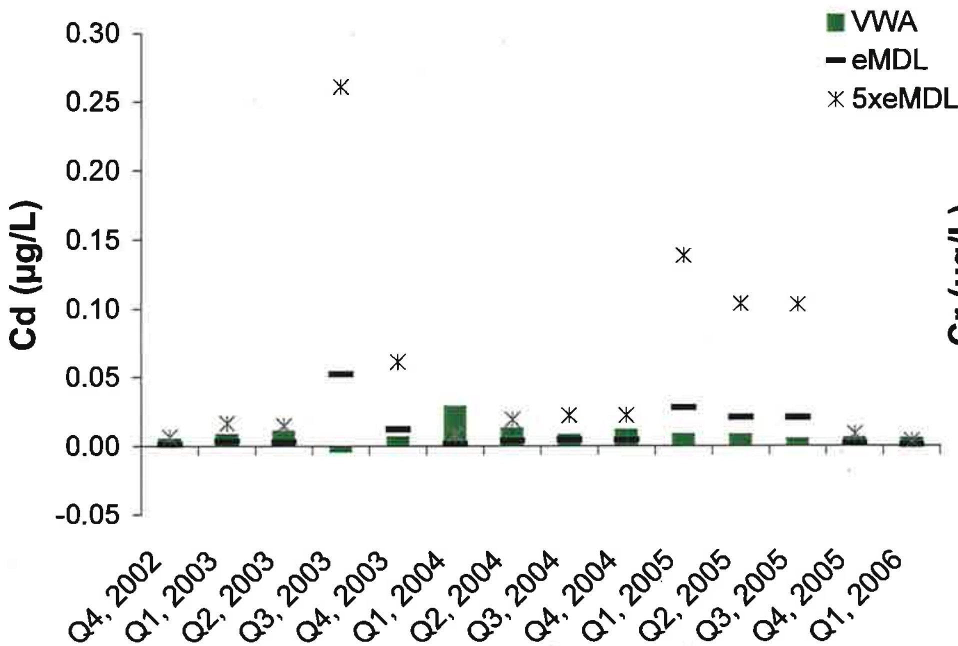
Appendix
VWA by Quarter

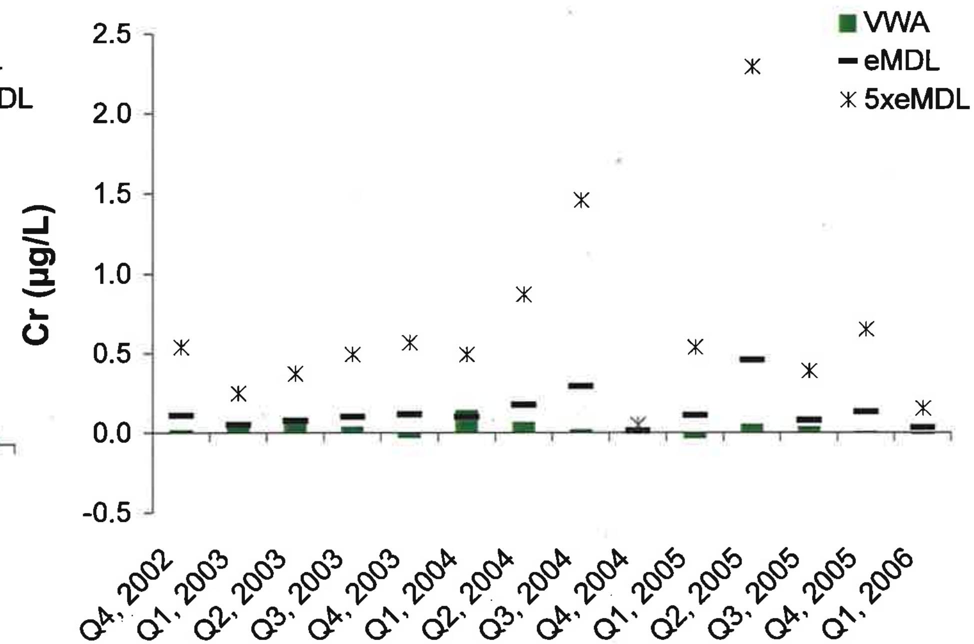
- Samples collected between January 2002 and January 2006
- Note scales are not constant among graphs
- The majority of samples of six species were below the estimated detection limit (As-ICPMS, As-AFS, Se-ICPMS, Se-AFS, Cr, and Be)
- The majority of samples of four species were greater than 5 times the eMDL (Mn, Mg, Pb, Zn)
- The majority of samples for two species were not reported (Cr and Se-AFS)

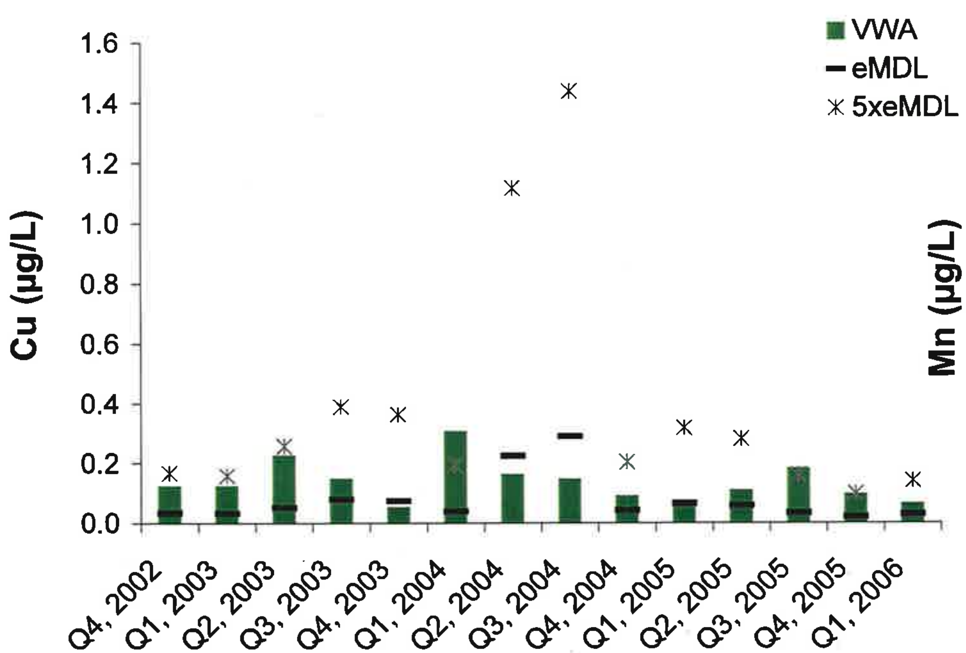
Summary by Quarter

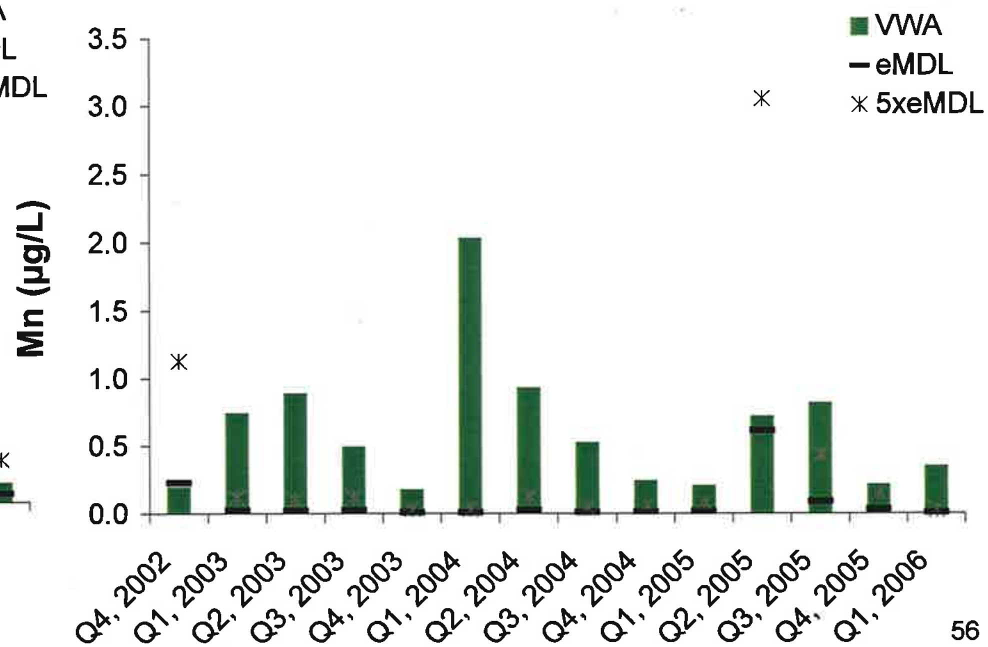


Summary by Quarter

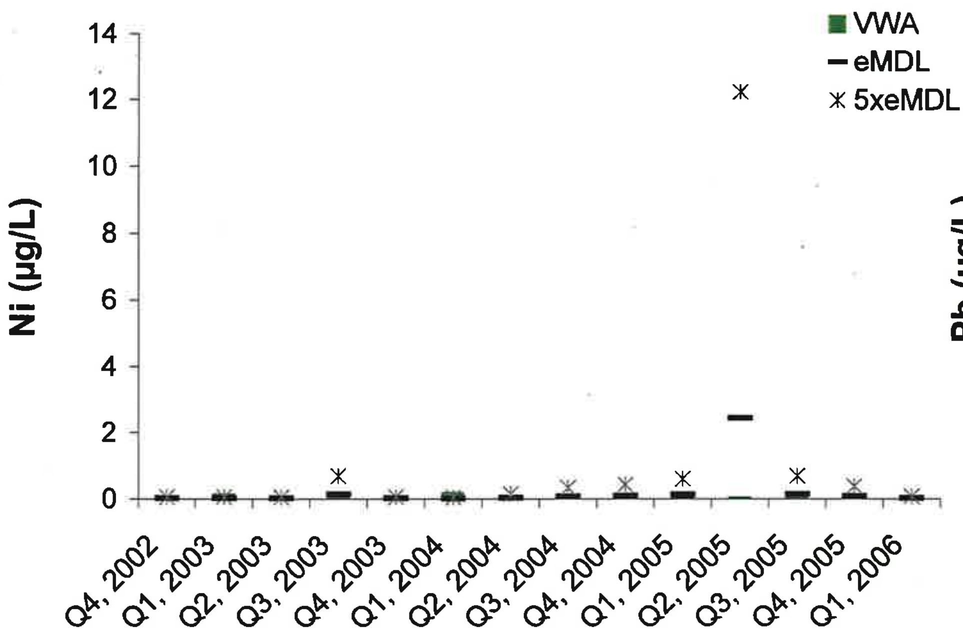


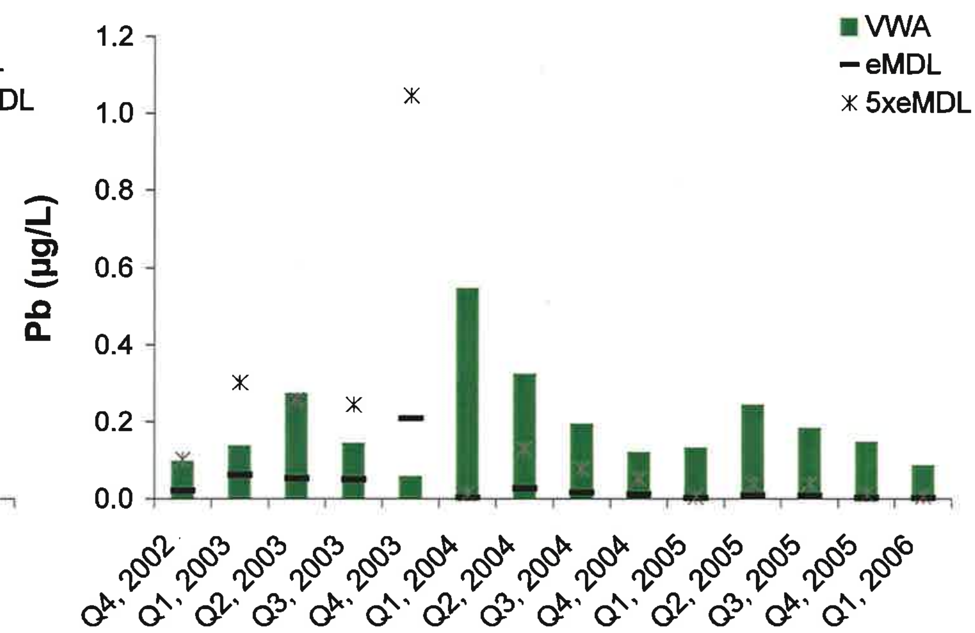


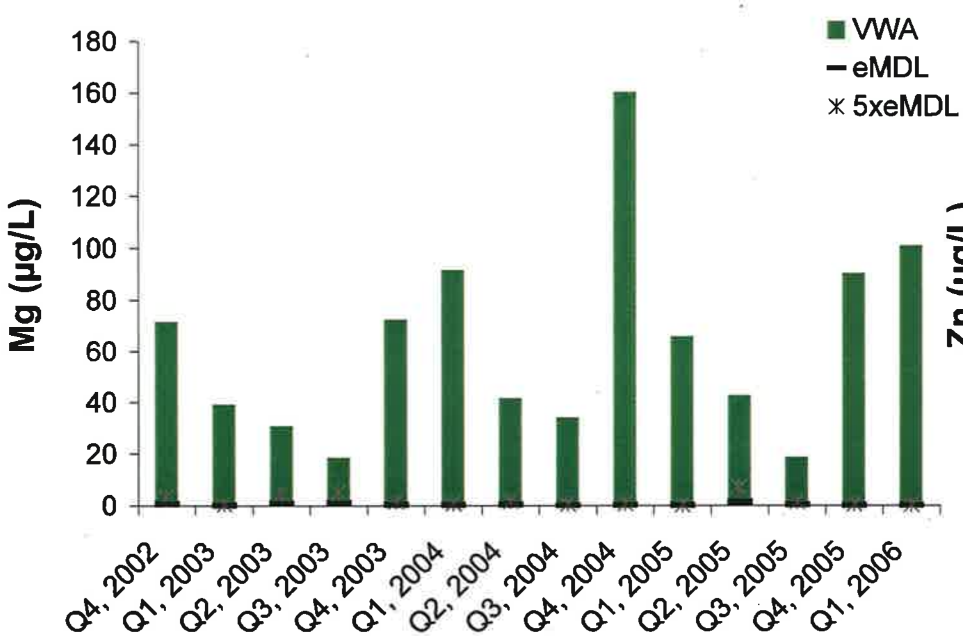


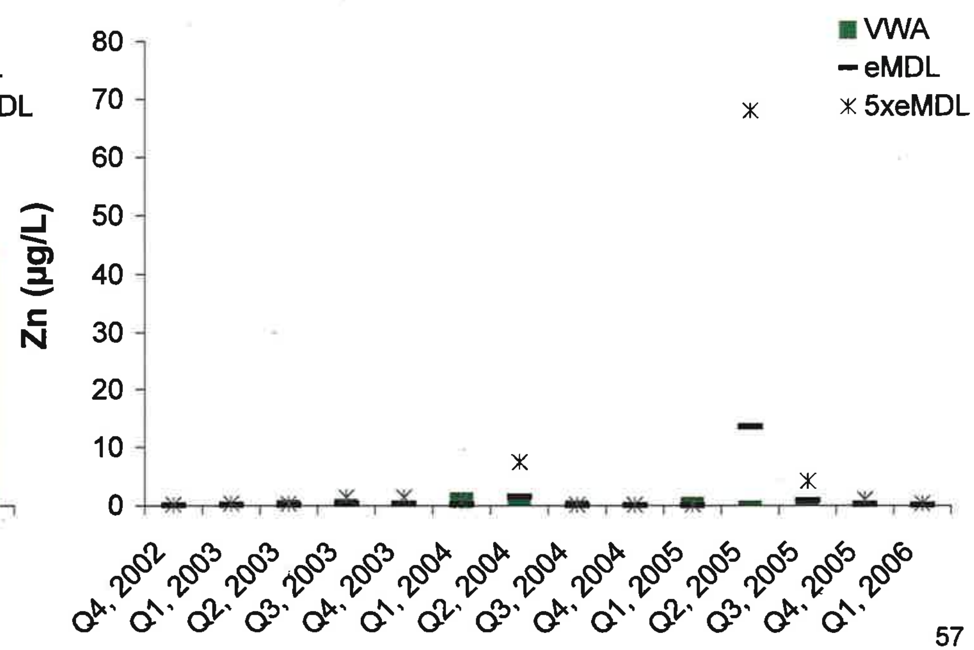


Summary by Quarter



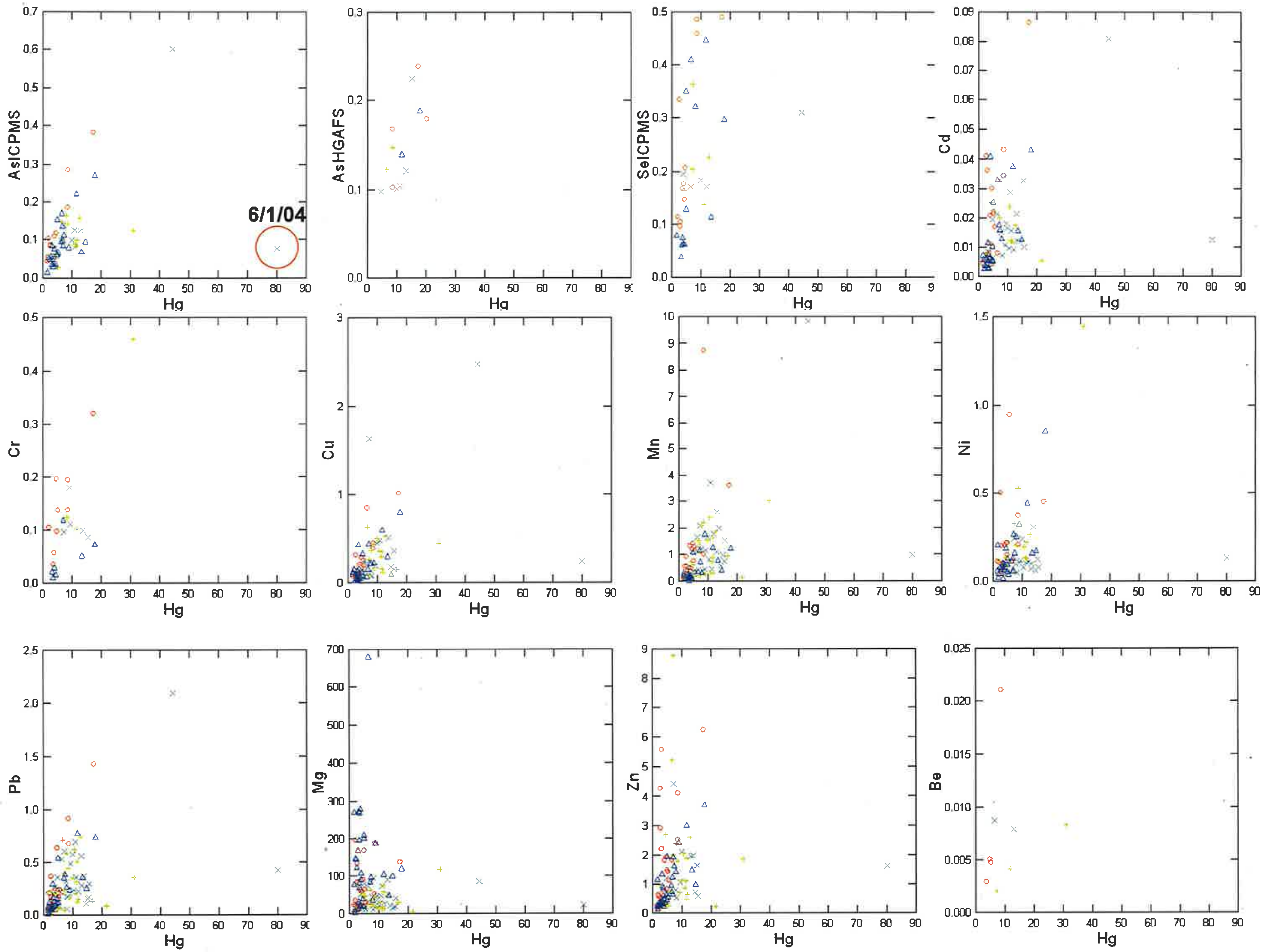


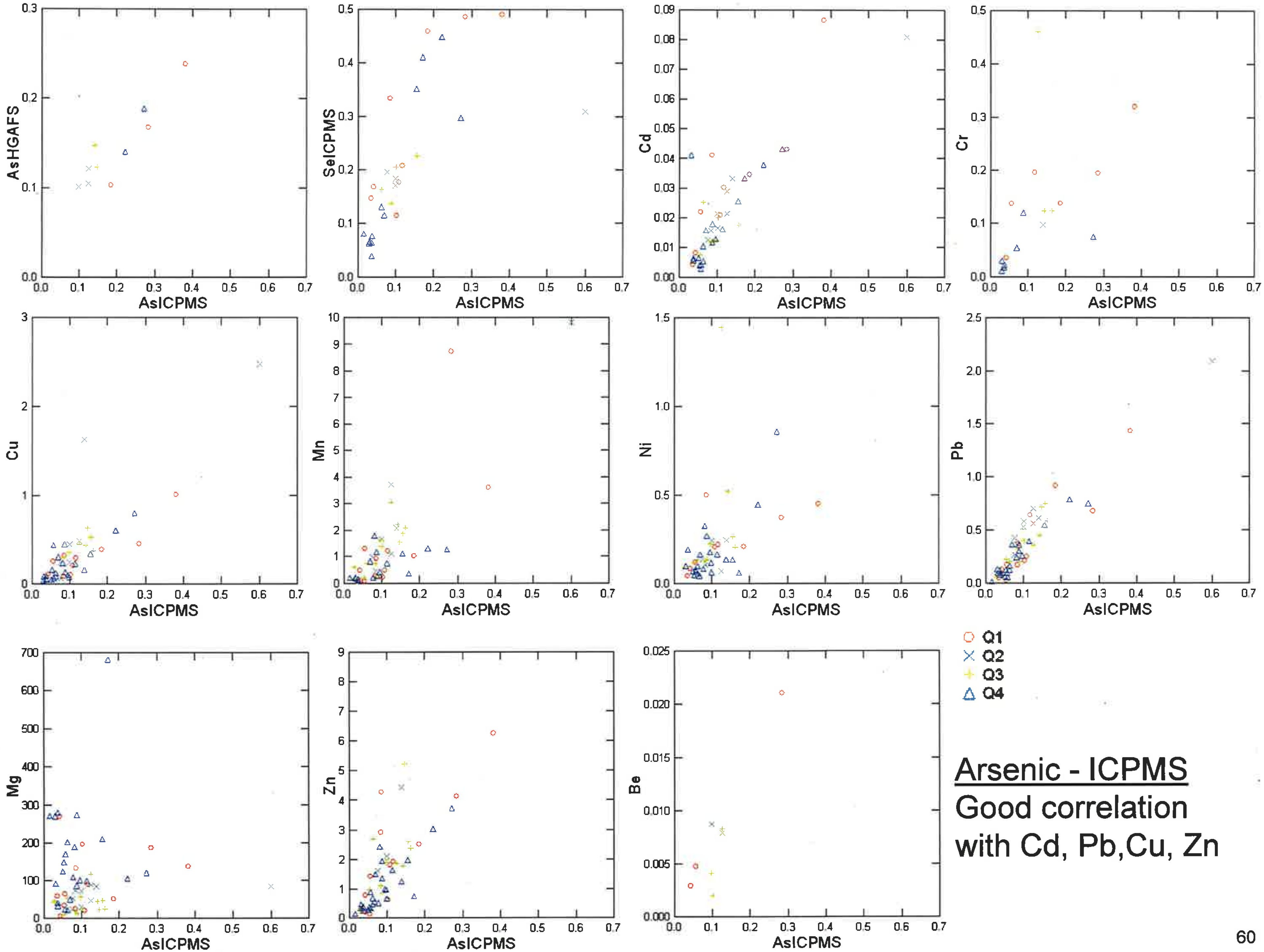




Appendix
Scatter Plot Analysis Graphs

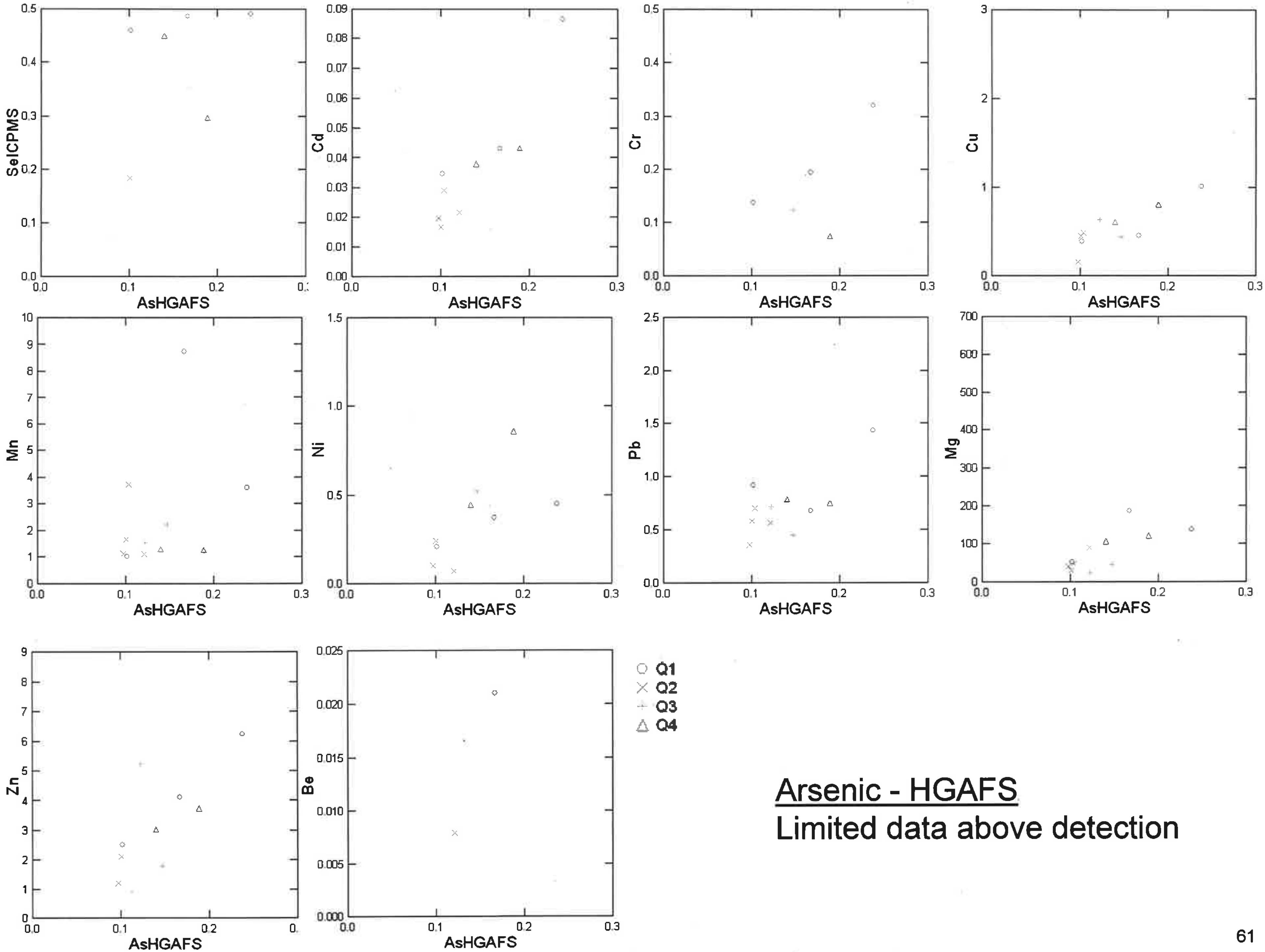
- The scatter plots show concentrations in µg/L for most species. Hg, AsHGAFS, SeAFS are in ng/L.
- Samples were collected between January 2002 and January 2005
- Only data above detection were used
- Some outliers and possible trends are noted – all data are provided separately and outliers have been flagged in that data set.


AsICPMS
Hg
6/1/04
AsHGAFS
SeICPMS
Cd
Cr
Cu
Mn
Ni
Pb
Mg
Zn
Be



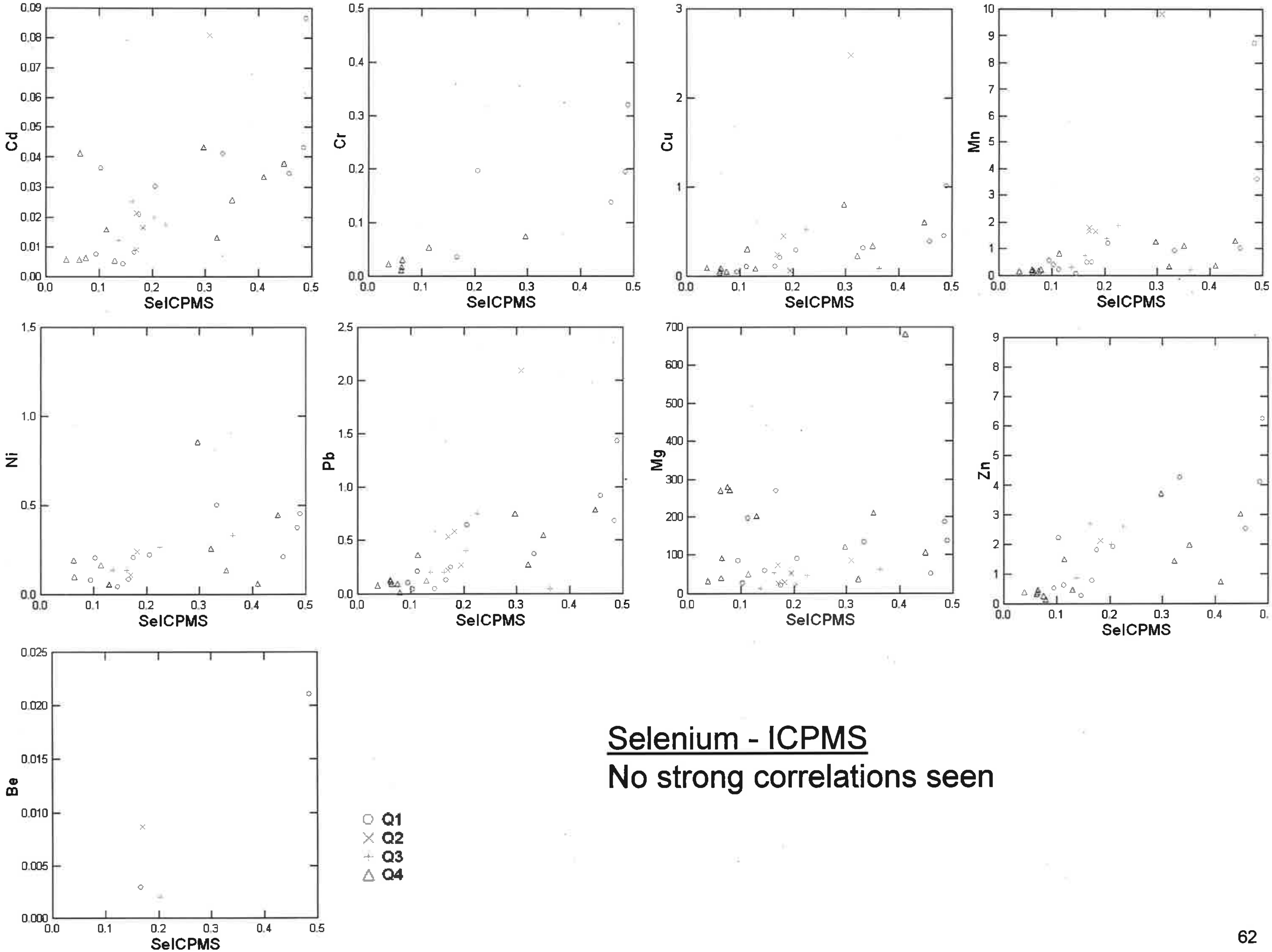
Arsenic - ICPMS

Good correlation with Cd, Pb,Cu, Zn



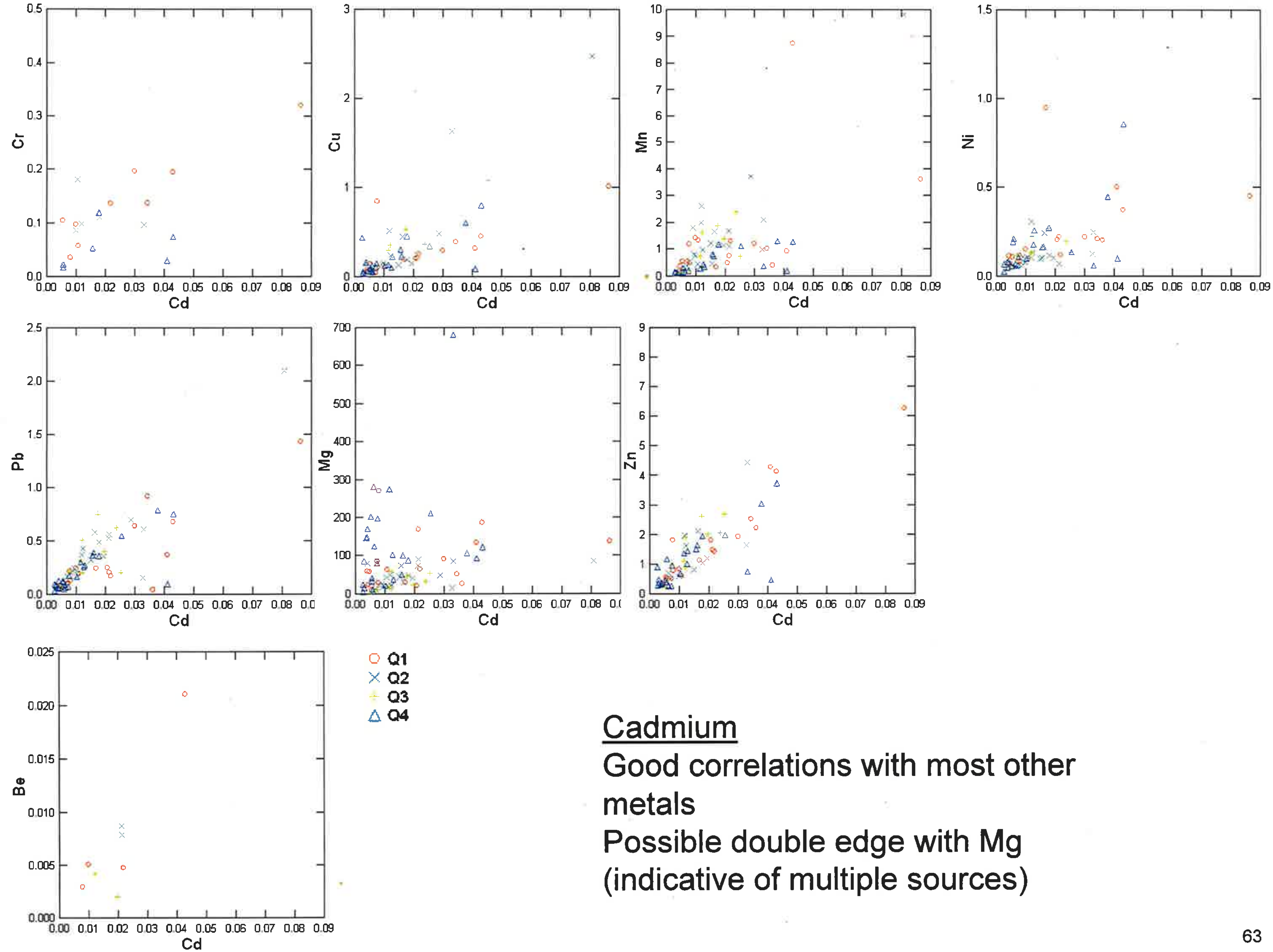
Arsenic - HGAFS

Limited data above detection



Selenium - ICPMS

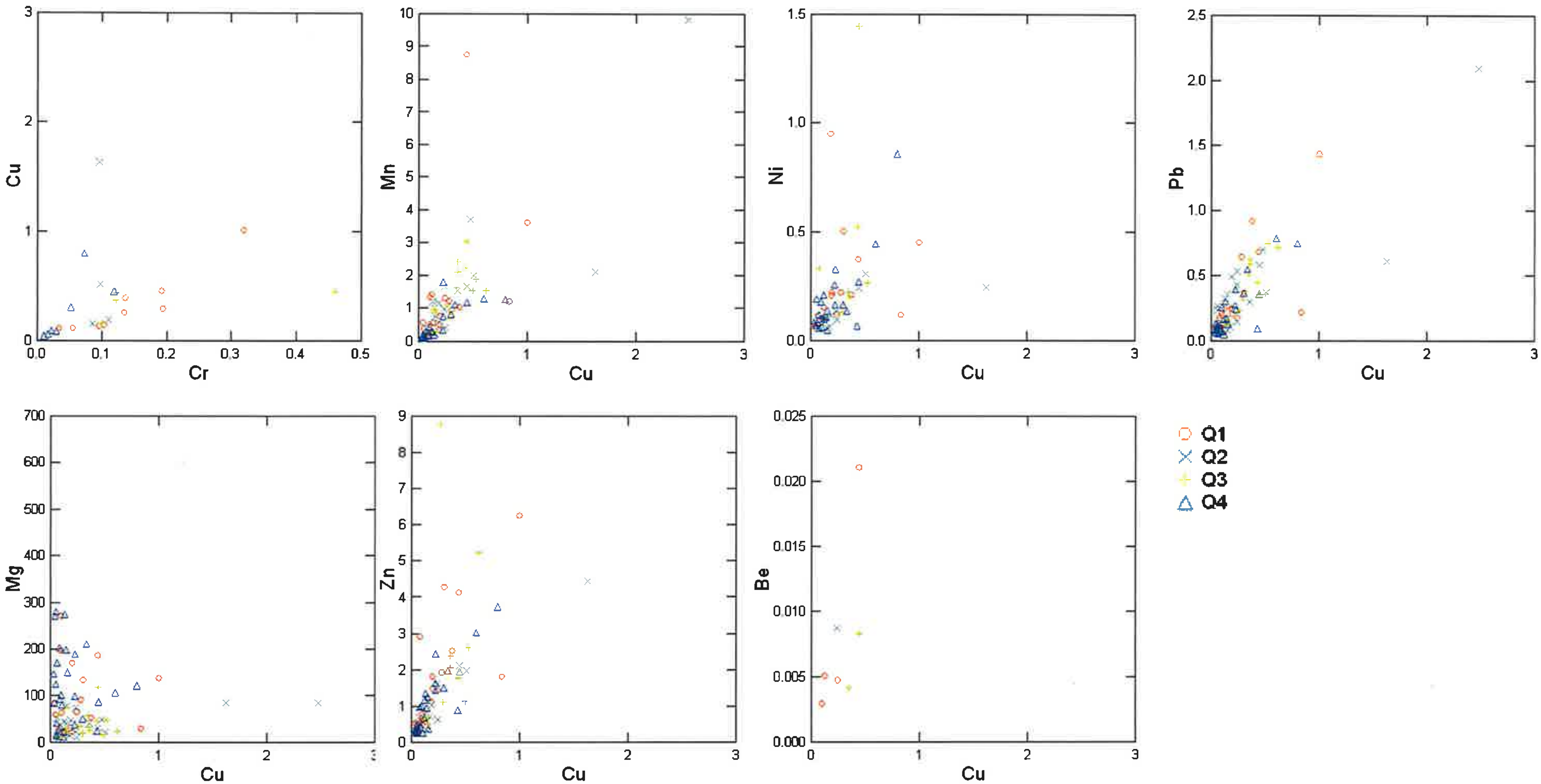
No strong correlations seen



Cadmium

Good correlations with most other metals

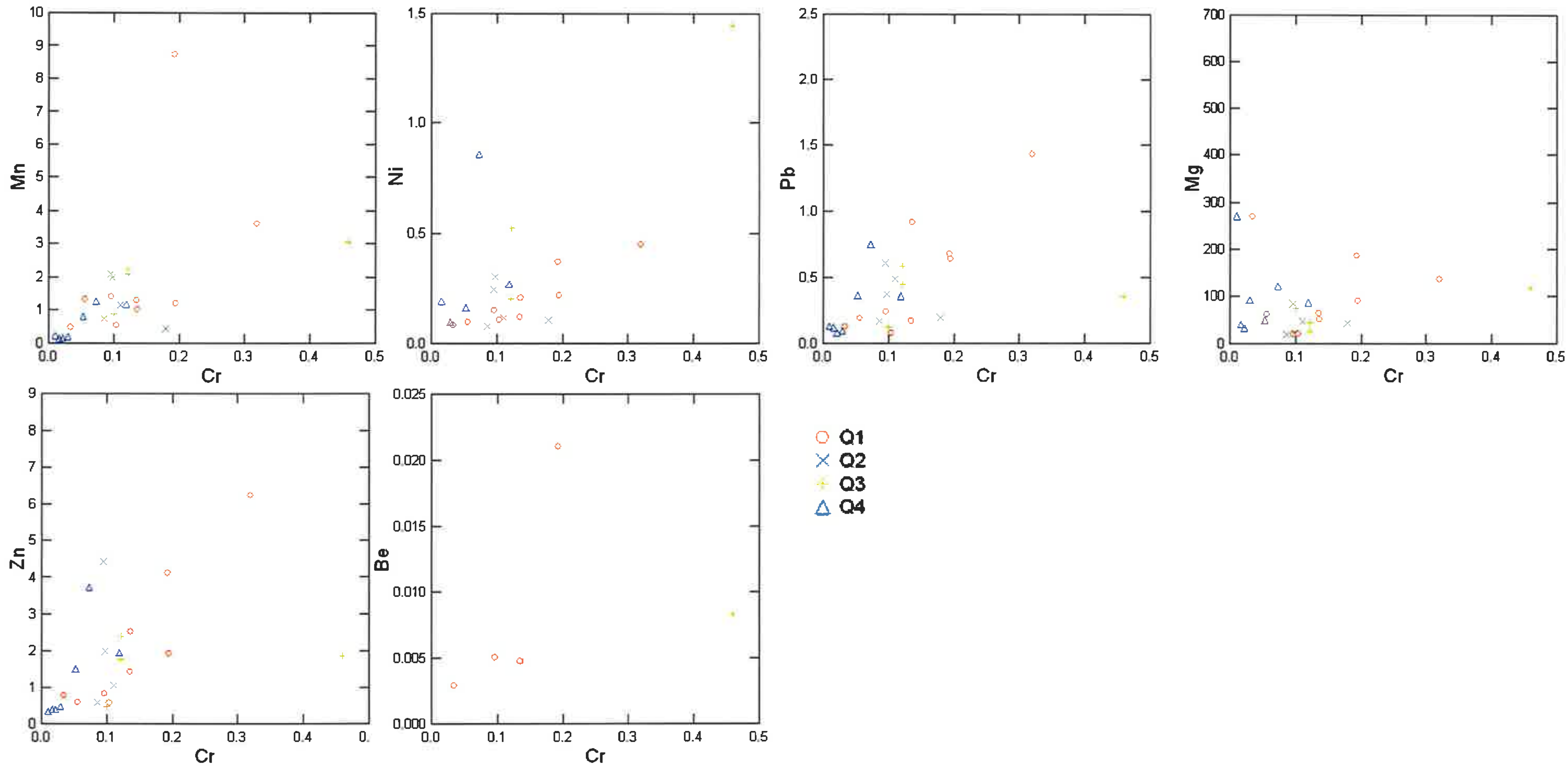
Possible double edge with Mg (indicative of multiple sources)



<u>Copper</u>

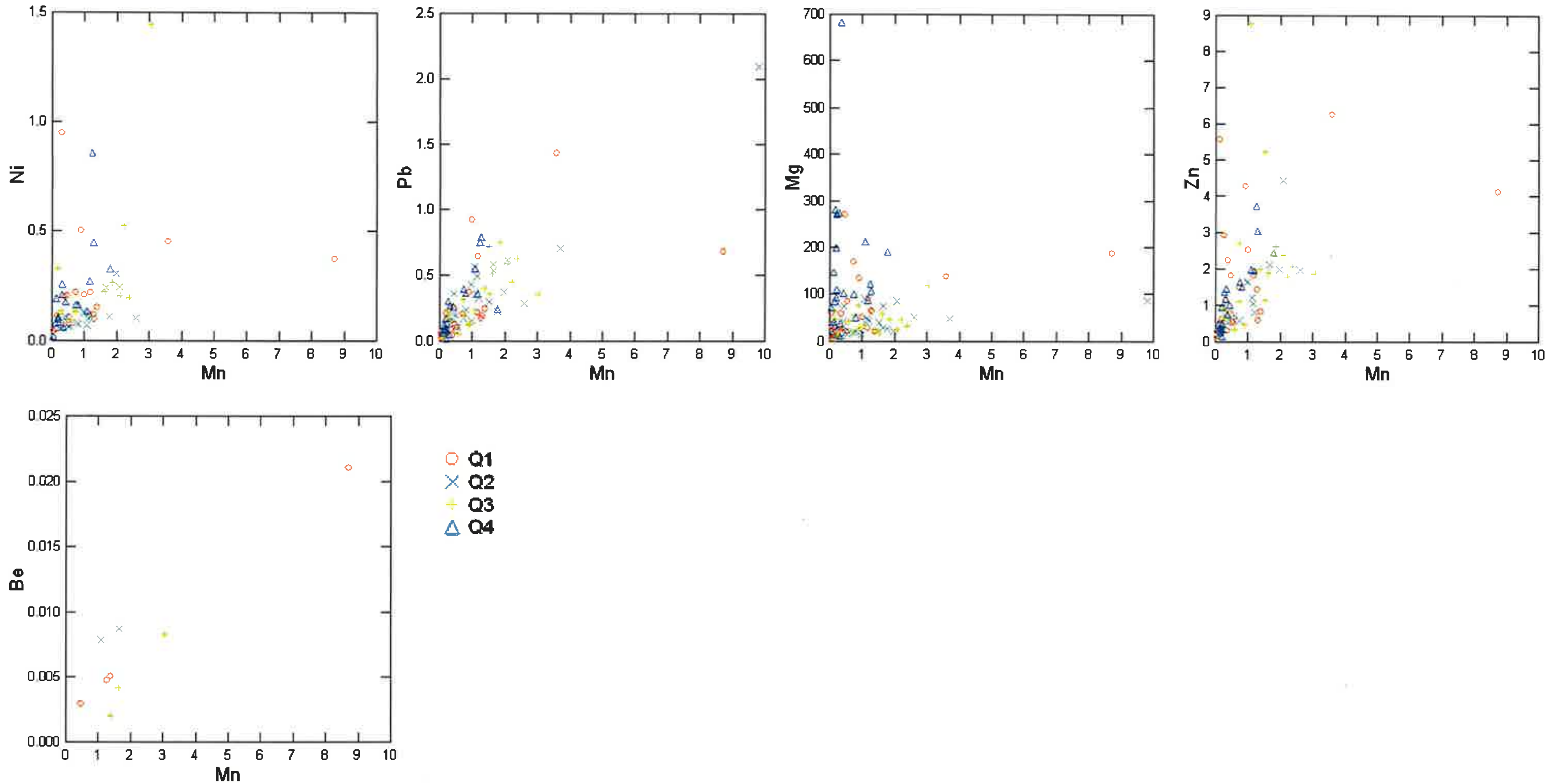
Good correlation with Pb, Zn

Double edge with Mg



<u>Chromium</u>

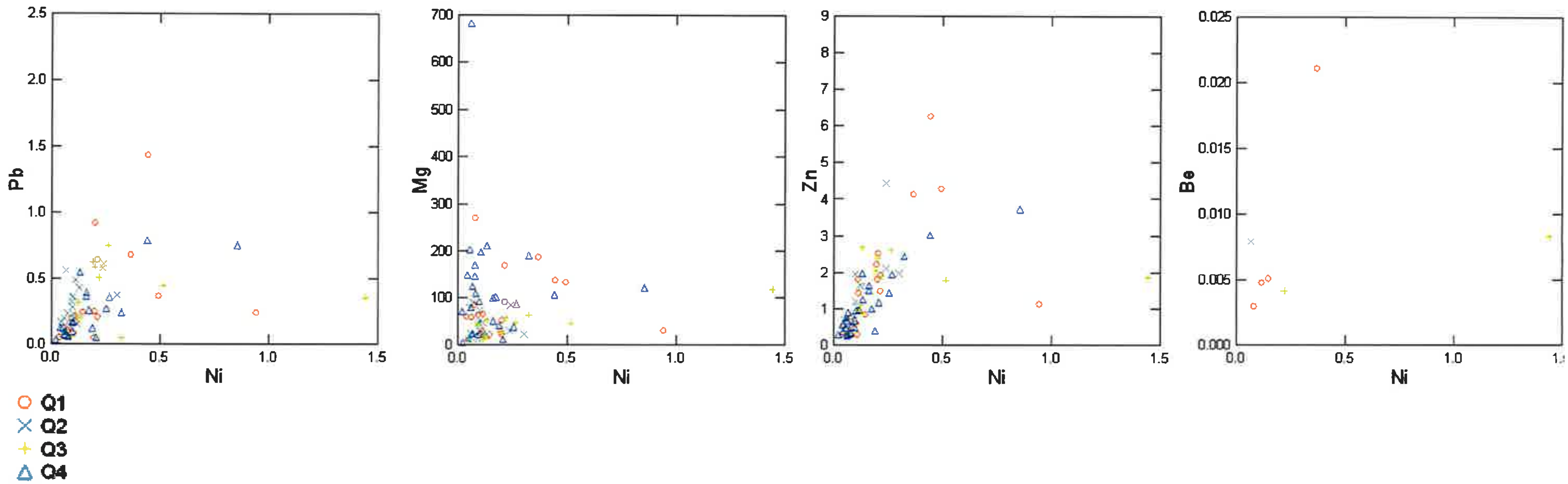
Limited data above detection limit



<u>Manganese</u>

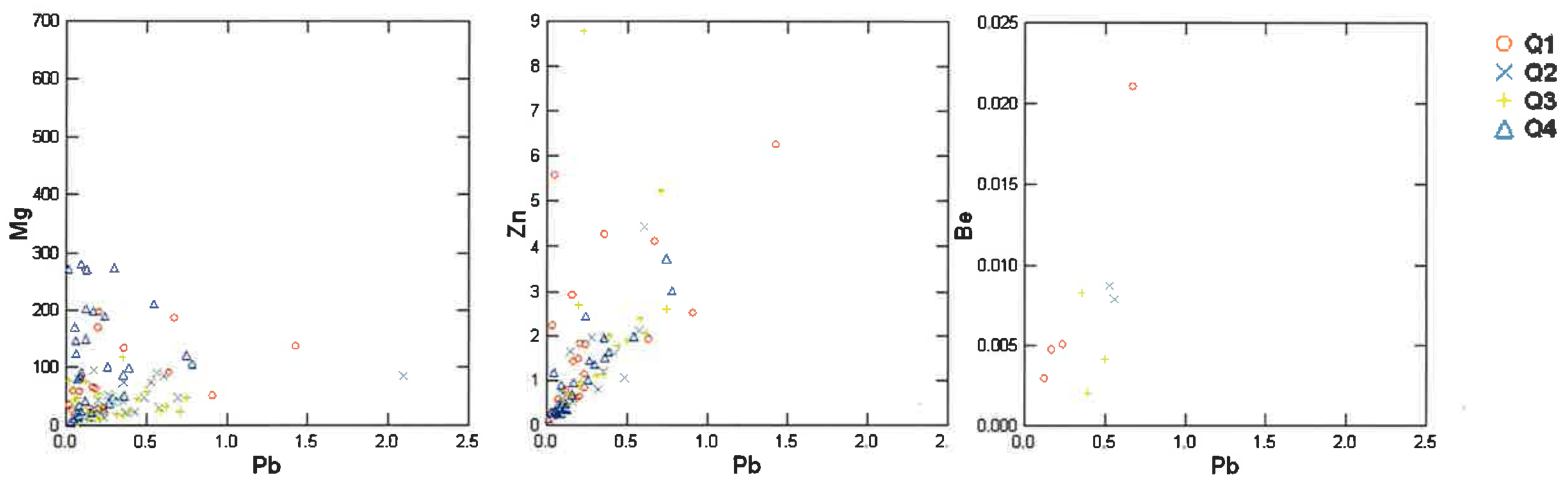
No strong correlations seen

Possible seasonal stratification



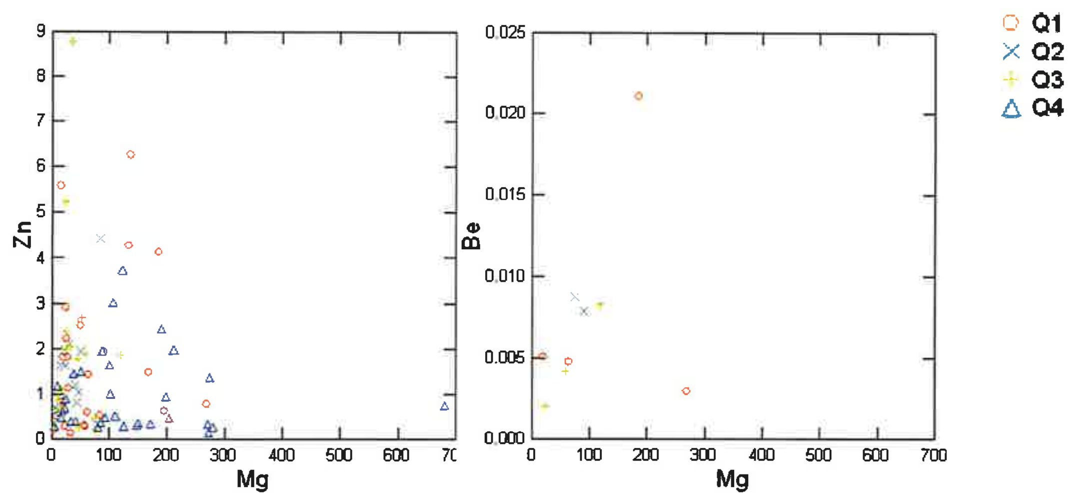
<u>Nickel</u>

Good correlation with Zn



<u>Lead</u>

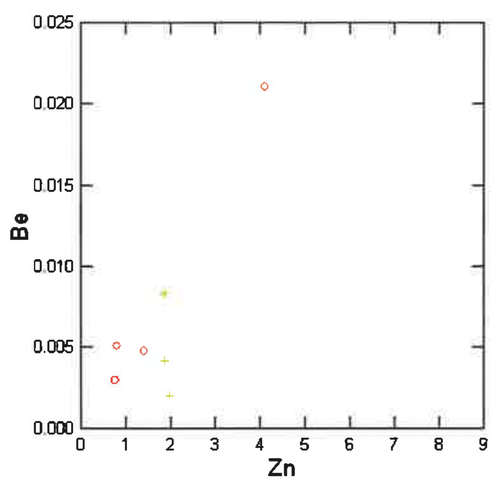
Possible seasonal stratification



<u>Magnesium</u>

No strong correlations

Seasonality with Zinc?

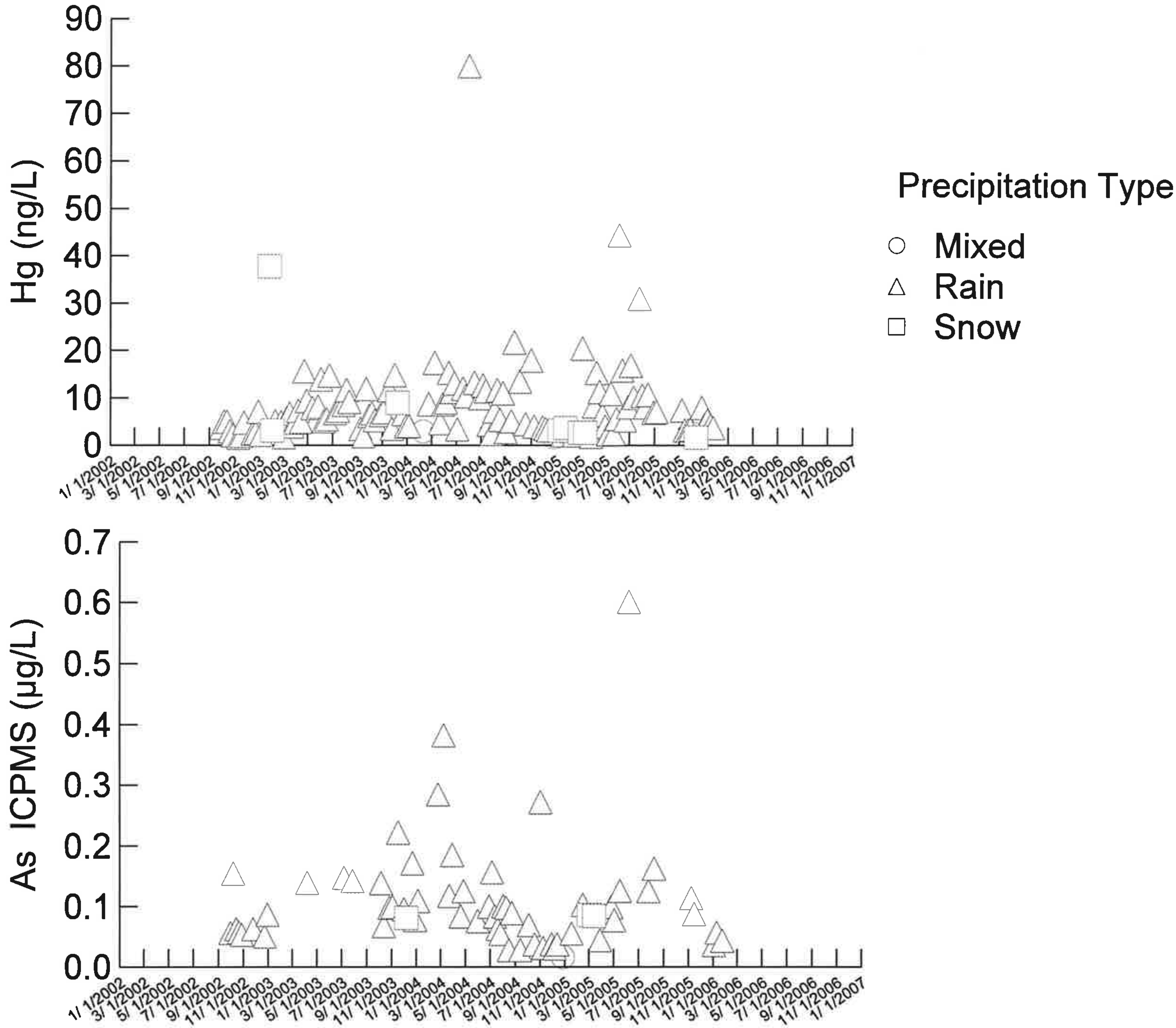


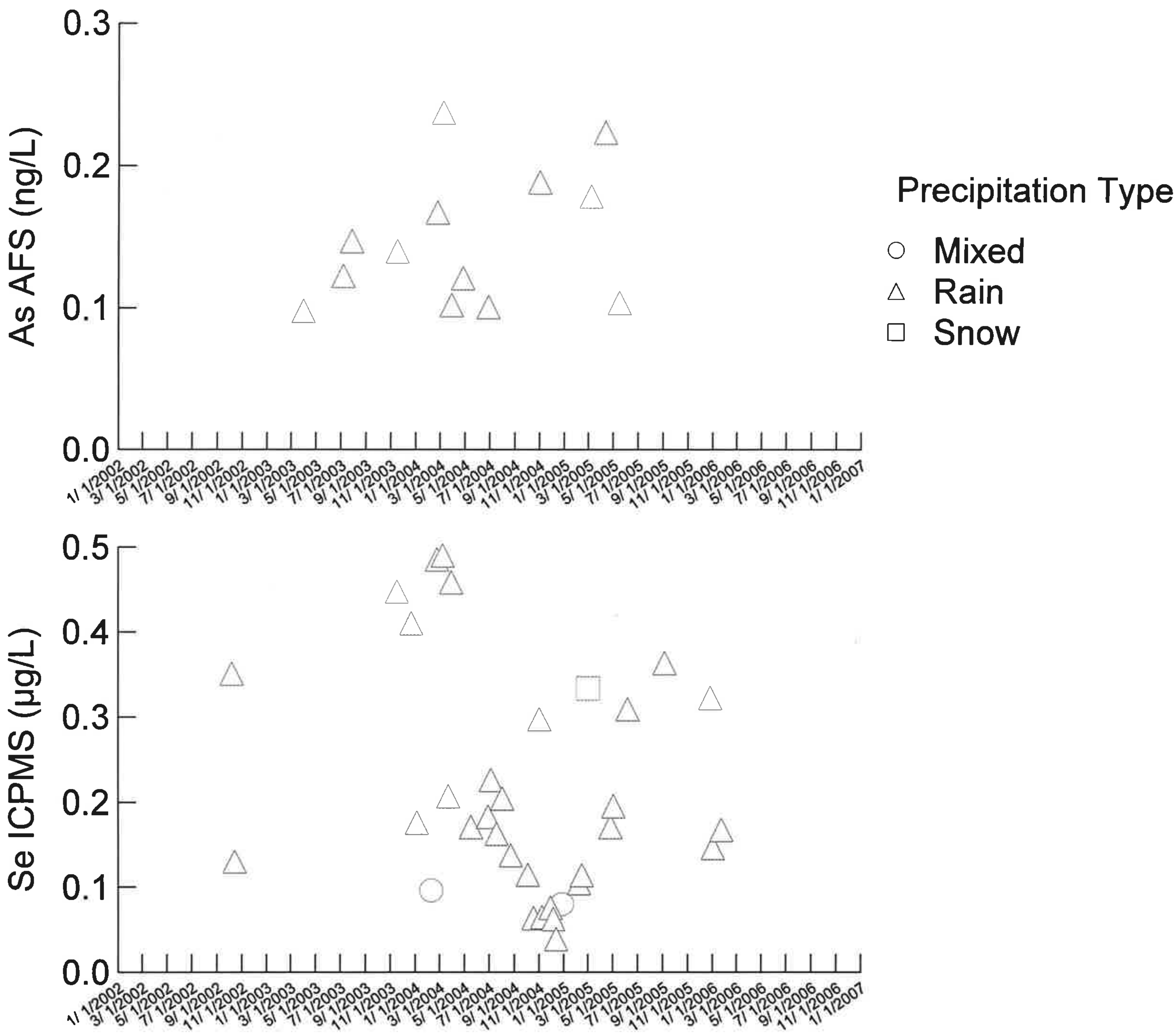
<u>Beryllium</u>

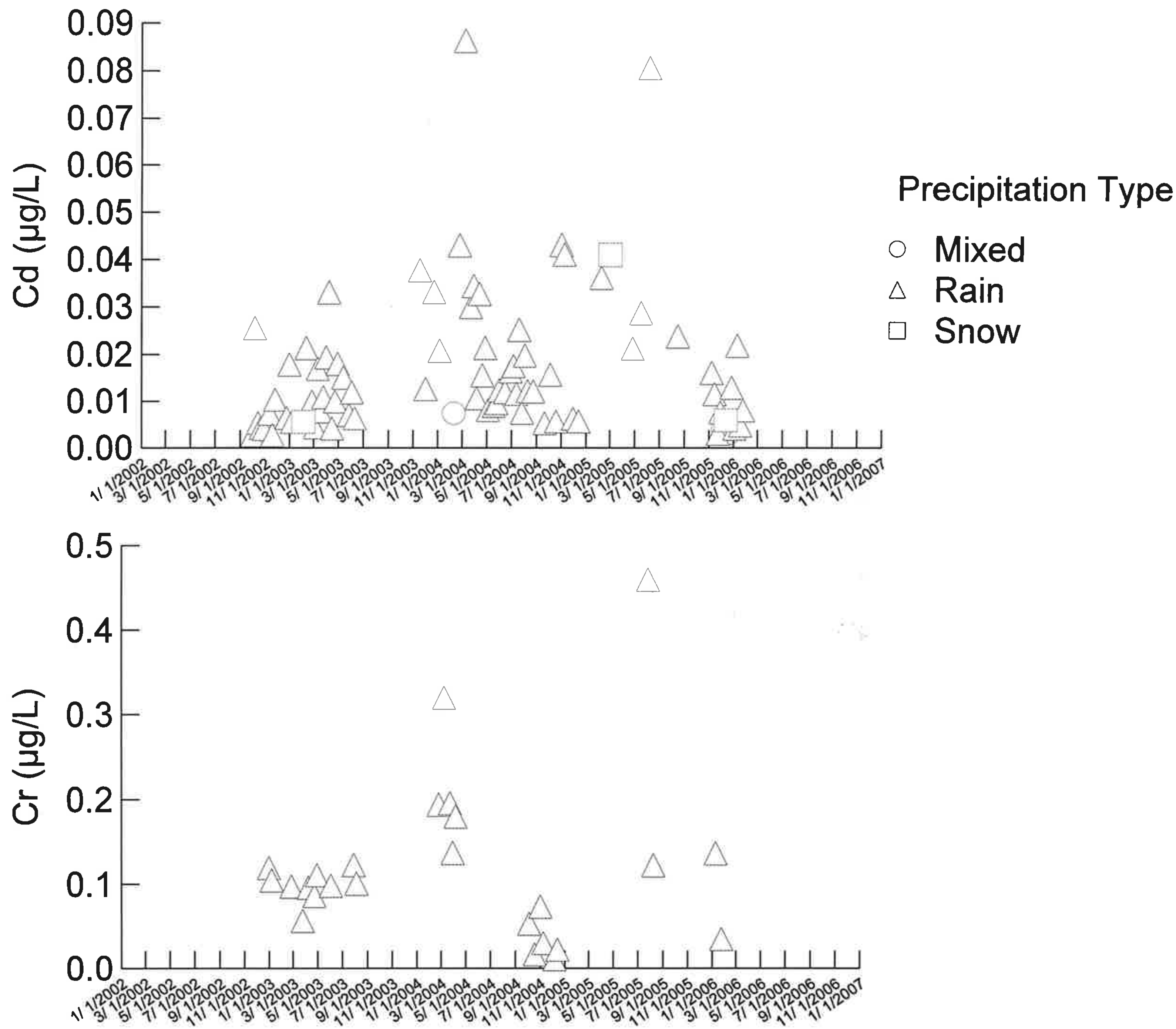
Limited data above detection limit

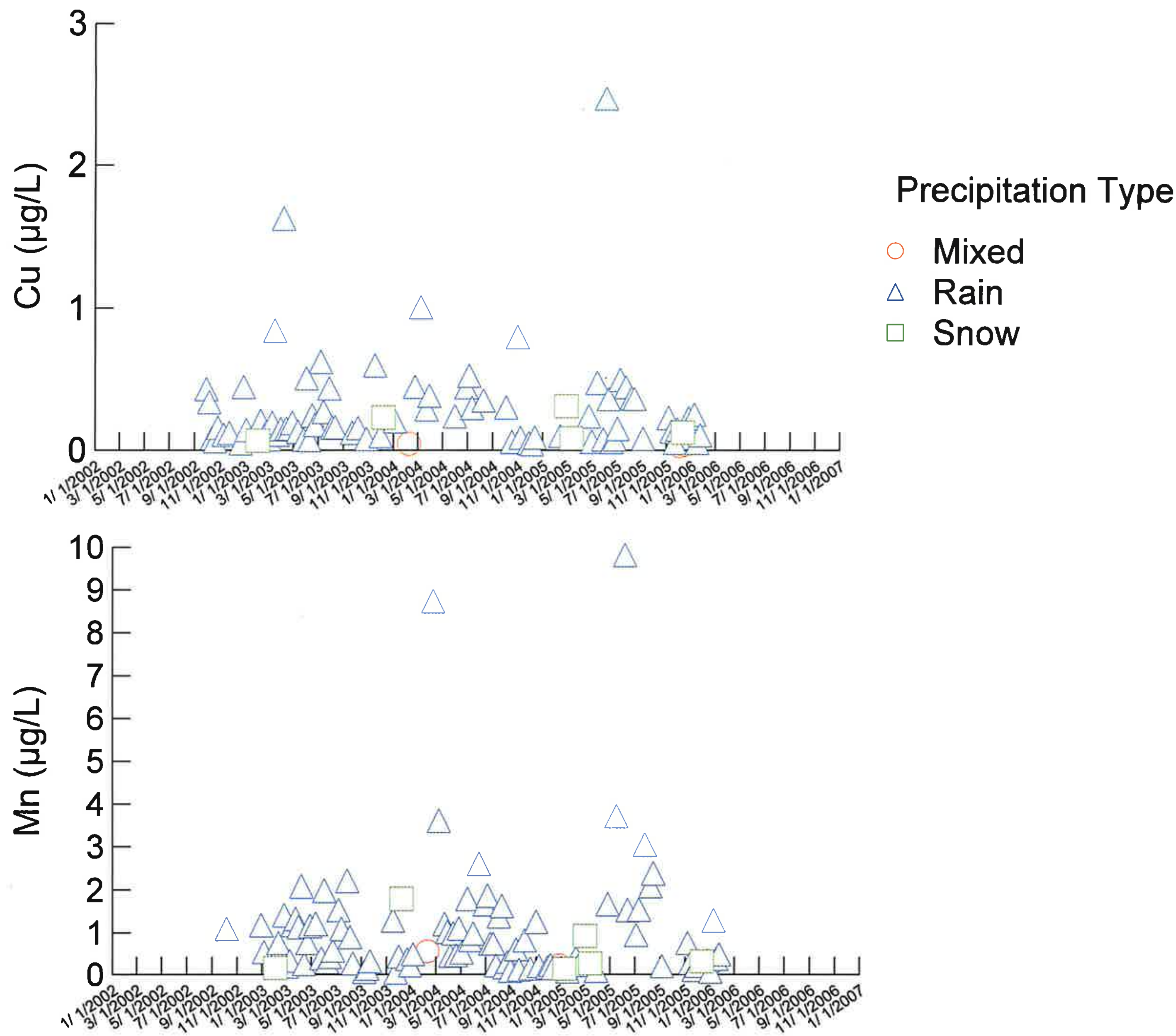
Time Series Analysis Graphs

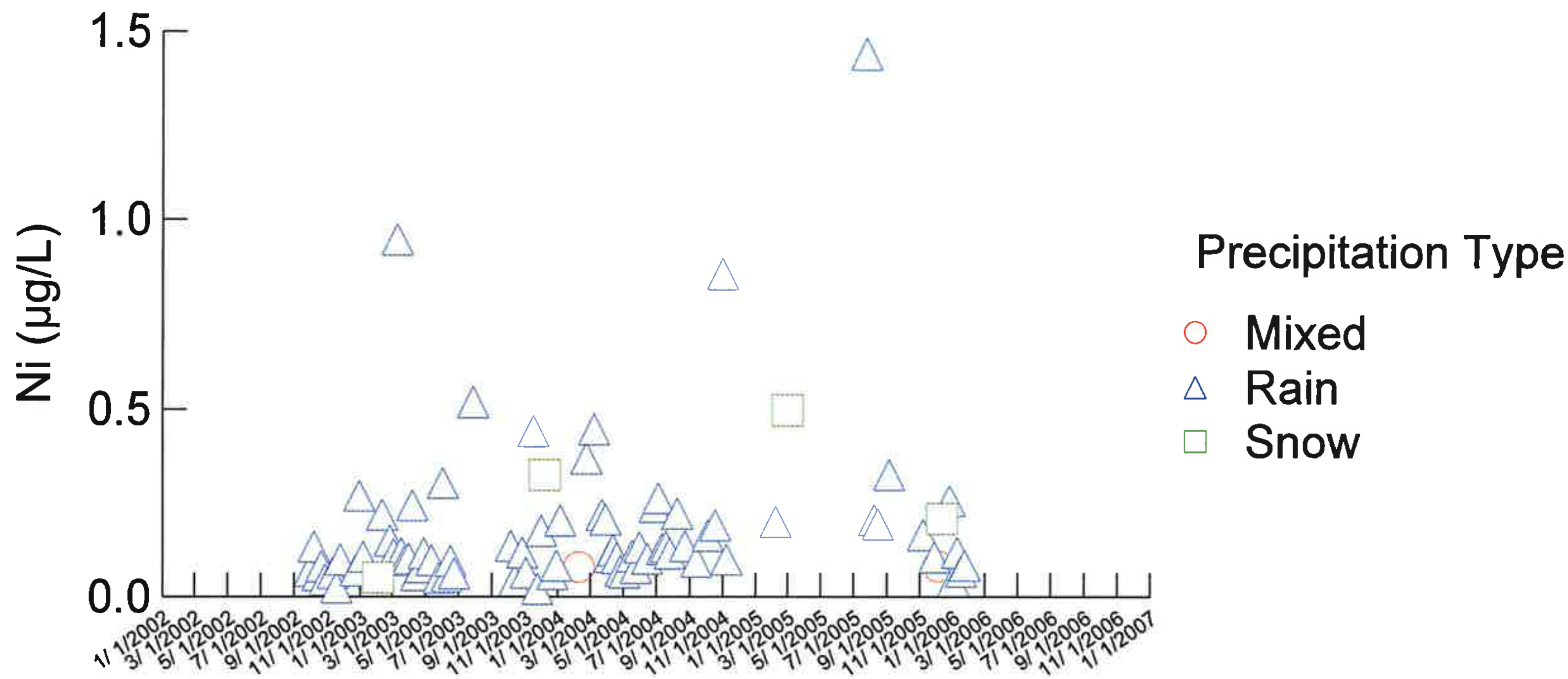
- The following graphs show all sample concentrations (weekly) over the sampling period. Samples are further identified by precipitation type.
- Most "high" concentrations were observed during rain events.
- Hg and Zn had some high concentrations during snow events.
- Several pollutants were high on July 19, 2005; this date was flagged as a low-volume event.

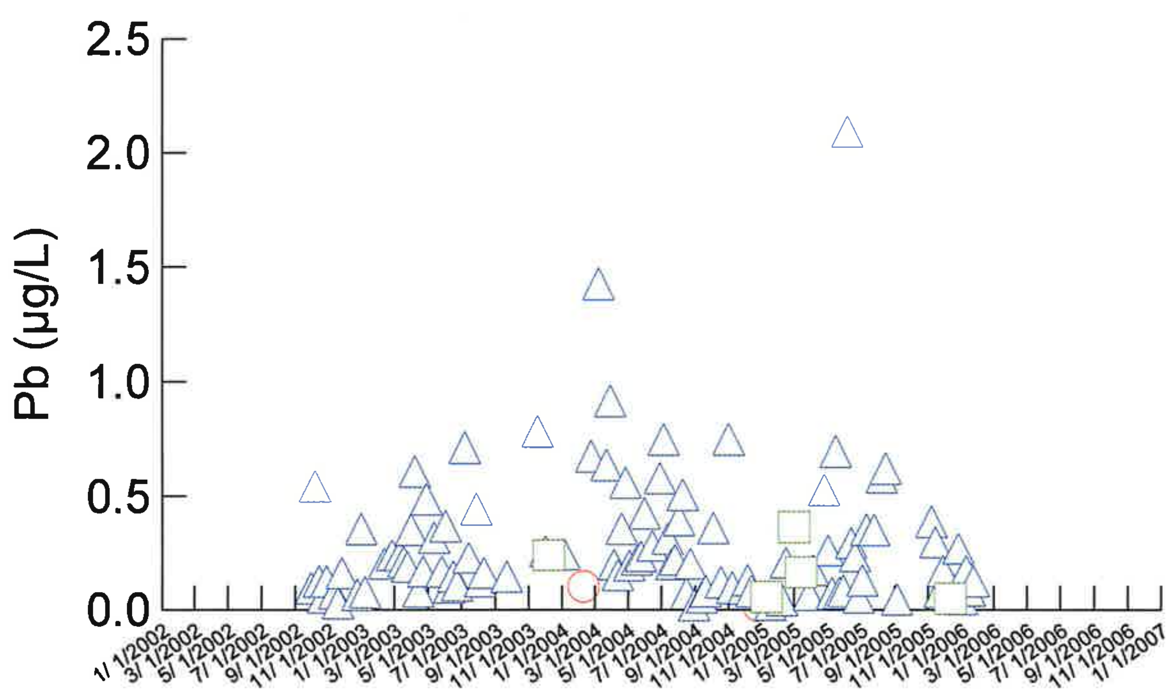

Hg (ng/L)
As ICPMS (µg/L)
Precipitation Type
Mixed
Rain
Snow


As AFS (ng/L)
0.3
0.2
0.1
0.0
Se ICPMS (µg/L)
0.5
0.4
0.3
0.2
0.1
0.0
1/ 1/2002
3/ 1/2002
5/ 1/2002
7/ 1/2002
9/ 1/2002
11/ 1/2002
1/ 1/2003
3/ 1/2003
5/ 1/2003
7/ 1/2003
9/ 1/2003
11/ 1/2003
1/ 1/2004
3/ 1/2004
5/ 1/2004
7/ 1/2004
9/ 1/2004
11/ 1/2004
1/ 1/2005
3/ 1/2005
5/ 1/2005
7/ 1/2005
9/ 1/2005
11/ 1/2005
1/ 1/2006
3/ 1/2006
5/ 1/2006
7/ 1/2006
9/ 1/2006
11/ 1/2006
1/ 1/2007
Precipitation Type
Mixed
Rain
Snow


Cd (µg/L)
Cr (µg/L)
Precipitation Type
Mixed
Rain
Snow


Cu (µg/L)
0
1
2
3
Mn (µg/L)
0
1
2
3
4
5
6
7
8
9
10
1/ 1/2002
3/ 1/2002
5/ 1/2002
7/ 1/2002
9/ 1/2002
11/ 1/2002
1/ 1/2003
3/ 1/2003
5/ 1/2003
7/ 1/2003
9/ 1/2003
11/ 1/2003
1/ 1/2004
3/ 1/2004
5/ 1/2004
7/ 1/2004
9/ 1/2004
11/ 1/2004
1/ 1/2005
3/ 1/2005
5/ 1/2005
7/ 1/2005
9/ 1/2005
11/ 1/2005
1/ 1/2006
3/ 1/2006
5/ 1/2006
7/ 1/2006
9/ 1/2006
11/ 1/2006
1/ 1/2007
Precipitation Type
Mixed
Rain
Snow


Ni (µg/L)
0.0
0.5
1.0
1.5
1/ 1/2002
3/ 1/2002
5/ 1/2002
7/ 1/2002
9/ 1/2002
11/ 1/2002
1/ 1/2003
3/ 1/2003
5/ 1/2003
7/ 1/2003
9/ 1/2003
11/ 1/2003
1/ 1/2004
3/ 1/2004
5/ 1/2004
7/ 1/2004
9/ 1/2004
11/ 1/2004
1/ 1/2005
3/ 1/2005
5/ 1/2005
7/ 1/2005
9/ 1/2005
11/ 1/2005
1/ 1/2006
3/ 1/2006
5/ 1/2006
7/ 1/2006
9/ 1/2006
11/ 1/2006
1/ 1/2007
Precipitation Type
Mixed
Rain
Snow


Pb (µg/L)
0.0
0.5
1.0
1.5
2.0
2.5
1/ 1/2002
3/ 1/2002
5/ 1/2002
7/ 1/2002
9/ 1/2002
11/ 1/2002
1/ 1/2003
3/ 1/2003
5/ 1/2003
7/ 1/2003
9/ 1/2003
11/ 1/2003
1/ 1/2004
3/ 1/2004
5/ 1/2004
7/ 1/2004
9/ 1/2004
11/ 1/2004
1/ 1/2005
3/ 1/2005
5/ 1/2005
7/ 1/2005
9/ 1/2005
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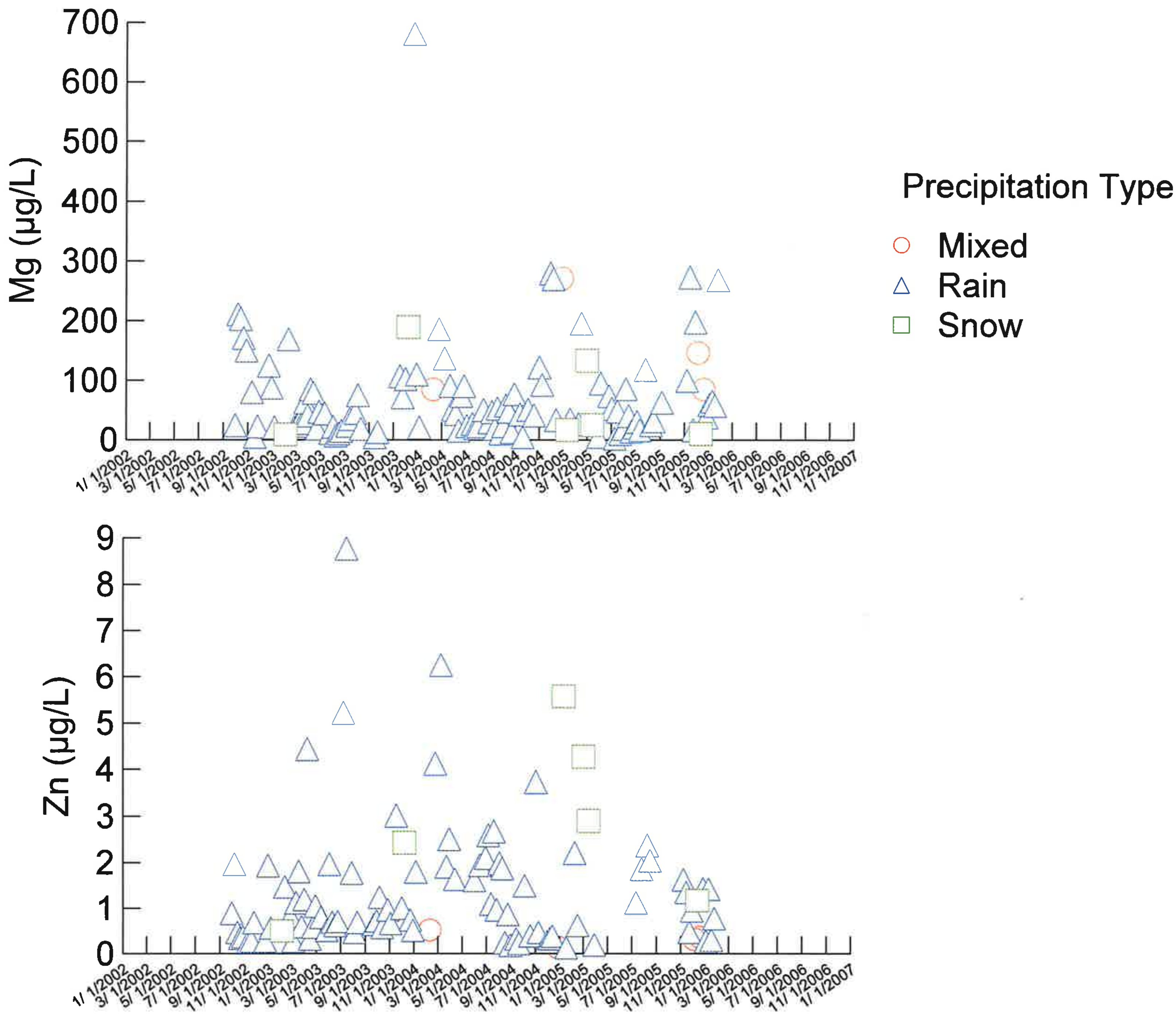
11/ 1/2006
1/ 1/2007



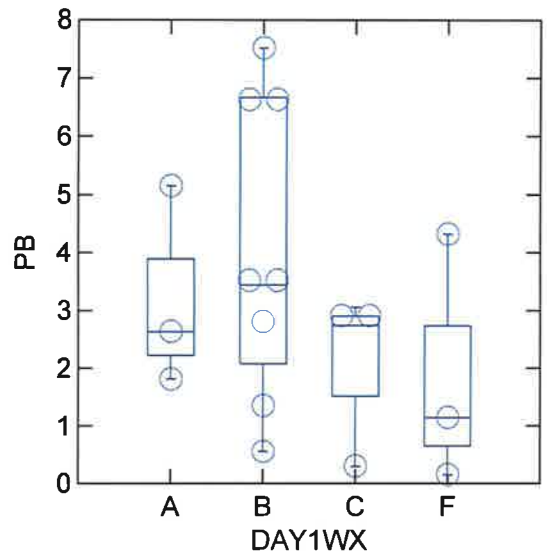
Mg (µg/L)
Zn (µg/L)
Precipitation Type
Mixed
Rain
Snow

Deposition μg/m²

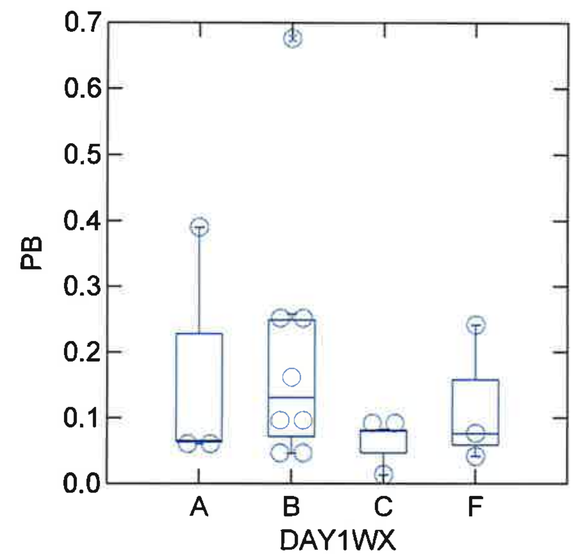
Concentration μg/L

Winter

Single-event weeks with valid PB deposition data (N=17)

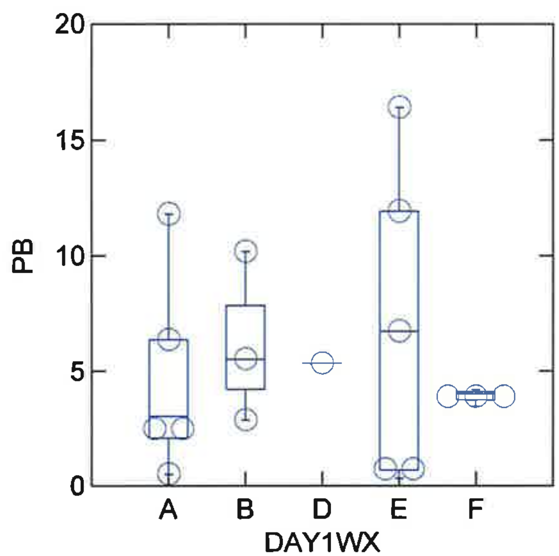


Single-event weeks with valid PB data (N=17)

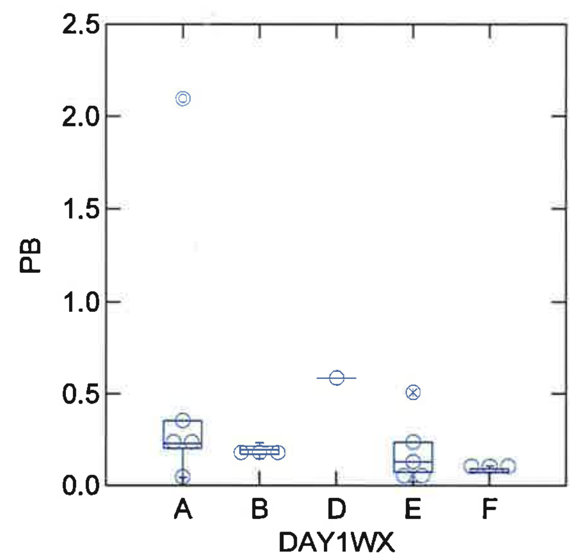


Summer

Single-week events with valid PB deposition data (N=16)



Single-week events with valid PB data (N=16)



ATTACHMENT 2

CASCO BAY METEOROLOGICAL TYPING AND SELECTED CASE STUDY ANALYSES

TECHNICAL MEMORANDUM

Sonoma Technology, Inc.
1360 Redwood Way, Suite C
Petaluma, CA 94954-1104
707/665-9900
FAX 707/665-9800
www.sonomatech.com

March 12, 2008

To: Dr. Diane Gould STI-906058.02-3286

From: Steven G. Brown, Dianne S. Miller, Hilary R. Hafner

Re: Casco Bay meteorological typing and selected case study analyses

OVERVIEW

The goal of these analyses was to determine whether weather system type impacts trace metal deposition or concentration. The analyses focused on samples for which a single precipitation event occurred. Then, to understand whether regional trace metal aerosol concentrations are related to trace metal deposition or concentration, we examined the Interagency Monitoring of Protected Visual Environments (IMPROVE) aerosol trace metal concentrations for the day before the precipitation event at Casco Bay along with the air mass trajectories associated with that event.

DATA AND METHODOLOGY

To complete the analyses, the number of rain-making weather systems that moved through the region during each sampling period had to be determined. We used the daily precipitation observations from the Portland, Maine, National Weather Service (NWS) monitoring site (72606) to identify single days with observed rainfall during each weekly sample. Next, we looked at the NWS's Daily Weather Maps archive to determine which weather patterns led to the rain and if all rainy days in the period were caused by one system or by multiple systems. Six unique weather patterns were identified: cold frontal passage (pattern A), low pressure system moving through from west to east (pattern B), low pressure system moving up the coast (pattern C), warm frontal passage or approach (pattern D), stationary front nearby (pattern E), and low pressure system offshore (pattern F). Examples of these weather patterns are shown in **Figures 1 through 6**.

In the winter months, the daily observations from Portland were used to identify the precipitation as rain, snow, or mixed. If no accumulated snow, or less snow than liquid accumulation, was observed, the day was classified as rain. To differentiate snow days from mixed days, the snow-to-liquid ratio was used. On average, the snow-to-liquid ratio is around

10:1, meaning 10 inches of snow will melt down to 1 inch of liquid. With very wet snow, this ratio can fall to as low as 5:1. Therefore, if the snow-to-liquid ratio was high, the day was classified as snow. If there was some accumulated snow and the snow-to-liquid ratio was significantly smaller than 5:1, the day was classified as mixed. For mixed precipitation days, temperature data were subjectively used to assist with and/or confirm the classification. February 2, 2003, is an example of a mixed precipitation day. The high temperature in Portland was 38ºF, the liquid precipitation total was 0.86 inches, and the accumulated snowfall total was 1.5 inches. The snow-to-liquid ratio was less than 2:1 and the temperature was well above freezing for part of the day. Therefore, the precipitation was likely mixed.

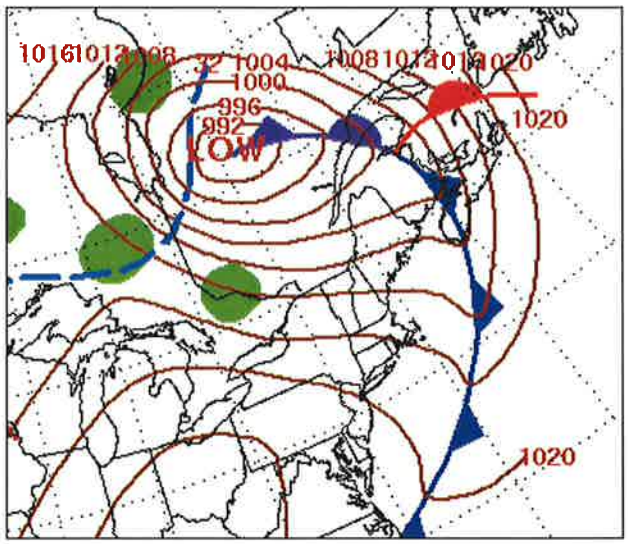
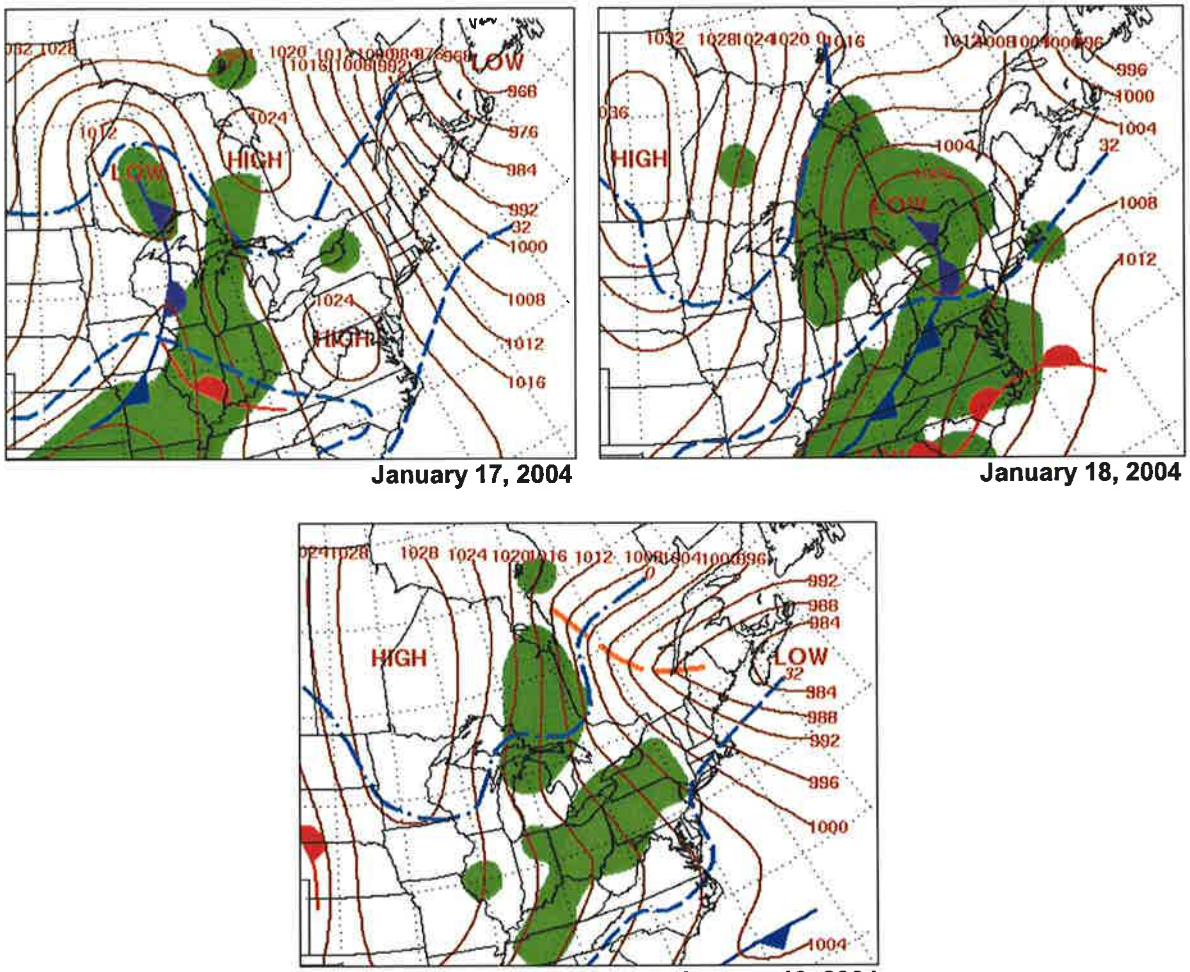


Figure 1. Pattern A example: a cold frontal passage on November 7, 2005.



January 17, 2004

January 18, 2004

January 19, 2004

Figure 2. Pattern B example: a low pressure system moving through from west to east, January 17-19, 2004.

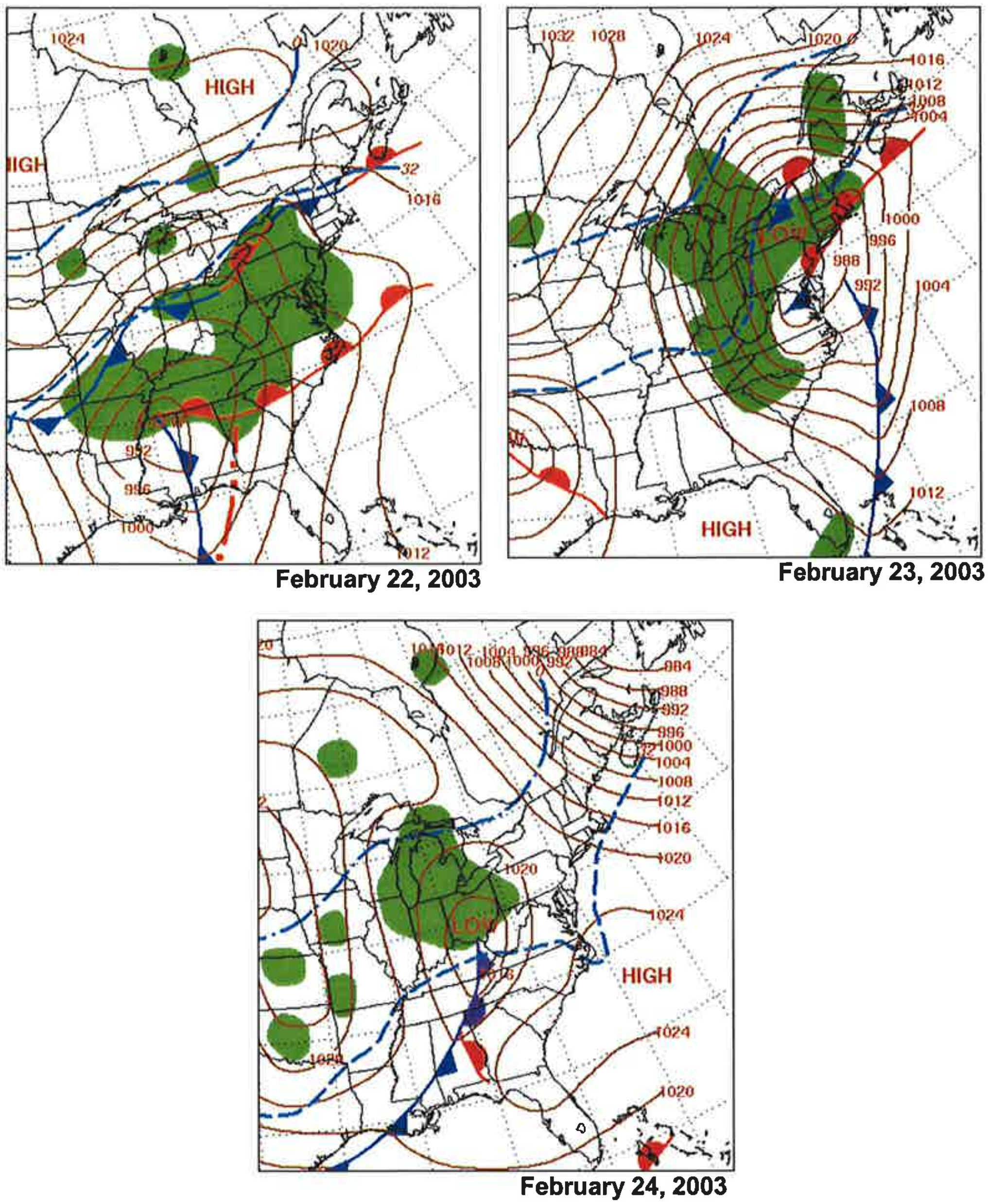


Figure 3. Pattern C example: a low pressure system moving up the coast, February 22-24, 2003.

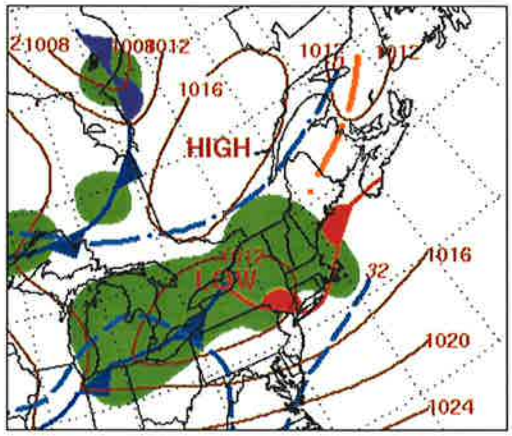


Figure 4. Pattern D example: a warm front approaching or moving through on January 12, 2004.

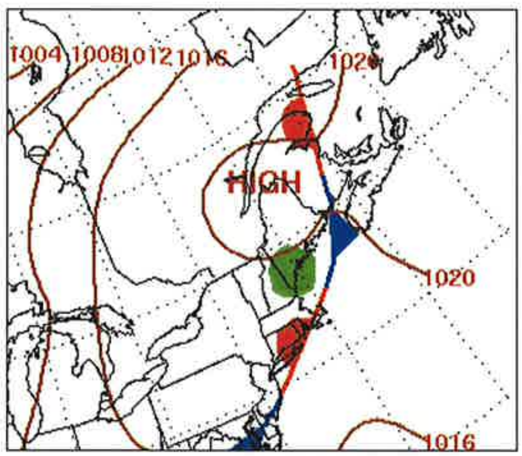


Figure 5. Pattern E example: a stationary front near the region on September 26, 2003.

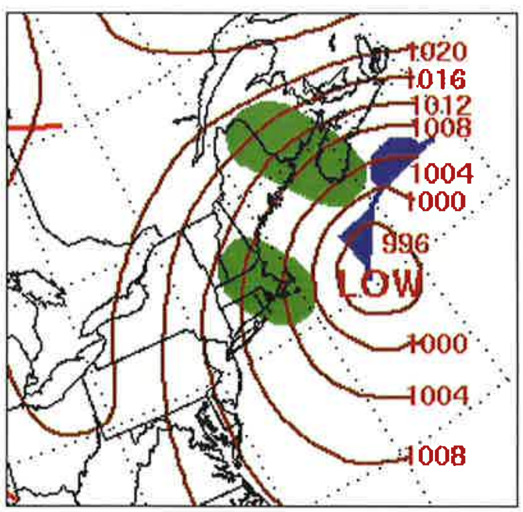


Figure 6. Pattern F example: a low pressure system offshore on May 8, 2005.

After the samples were categorized by weather pattern and precipitation type, we created box plots of all species typically well above detection limits (manganese, nickel, lead, and zinc) for concentration and deposition to look for trends. This portion of the analysis was limited to the summer season, defined as May through September, and the winter season, defined as November through February. Spring and fall were omitted from this analysis because the weather patterns are variable and can be similar to either summer or winter. Plots were made for each season with the sample data grouped by weather pattern. For the winter months, additional plots were created with the sample data grouped by precipitation type.

Five samples were selected for case study analysis. These samples were chosen because the concentration and/or deposition of at least one of the metal species was above average and only one rain-producing weather pattern occurred during the sampling period. For each case study, backward HYSPLIT trajectories were run at 500 m during the day on which precipitation first occurred to look at the potential source region of the metals. In addition, we compared the sample concentration data with the IMPROVE data at other sites in the Northeast on the day(s) prior to the precipitation event, where available.

RESULTS

Examination of Deposition and Concentration by Synoptic Pattern

Box plots were created to show the distribution of concentration and deposition data by weather pattern for each species of interest by season. Of the 124 original samples, the number of valid summer samples with only one rain-producing weather event ranged from 8 to 16, depending on the species, and the number of valid winter samples with only one rain-producing weather event ranged from 17 to 19. The individual data points are overlaid on each box plot to show how many samples fell into each weather pattern. Given the small number of samples available, all results and conclusions from these plots should be considered preliminary.

Figures 7 through 10 show results of deposition and concentration by season and weather pattern. The number of samples by season is limited. In general, no consistent trend was seen by species, weather pattern, or season. While some weather patterns had events with higher concentration or deposition, these weather patterns did not always produce high values. Weather pattern C, a low pressure system moving up the coast, typically had the lowest concentration and deposition values for all species.

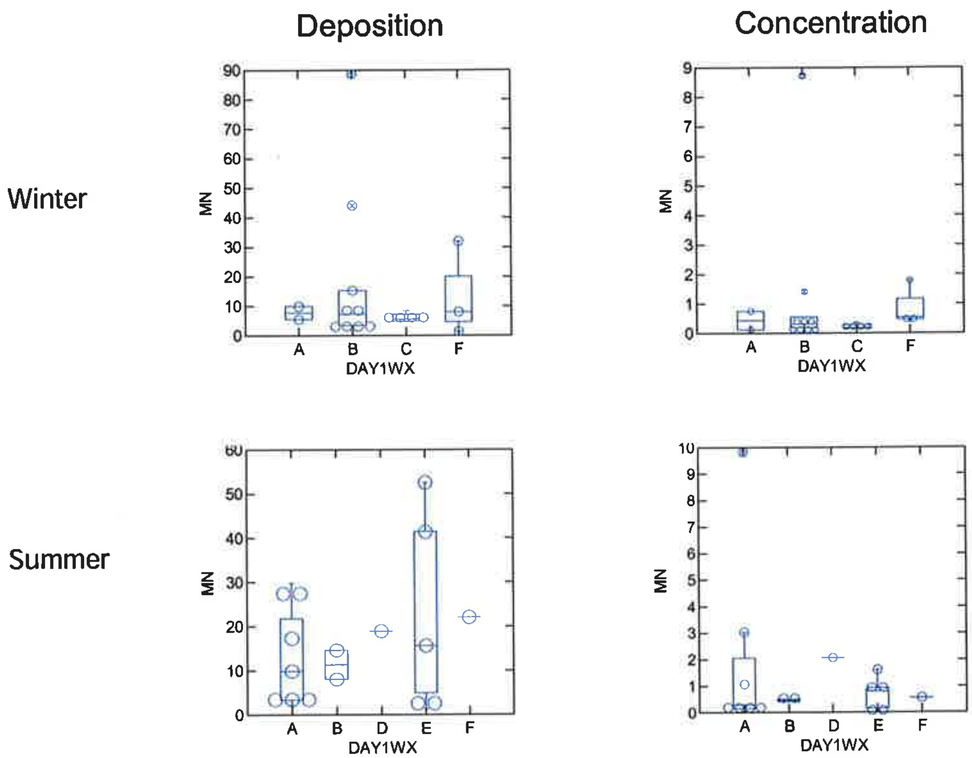


Figure 7. Box plots of manganese deposition (μg/m^2) and concentration (μg/L) by weather pattern (A through F) for single-week events in winter (N=18) and summer (N=15).

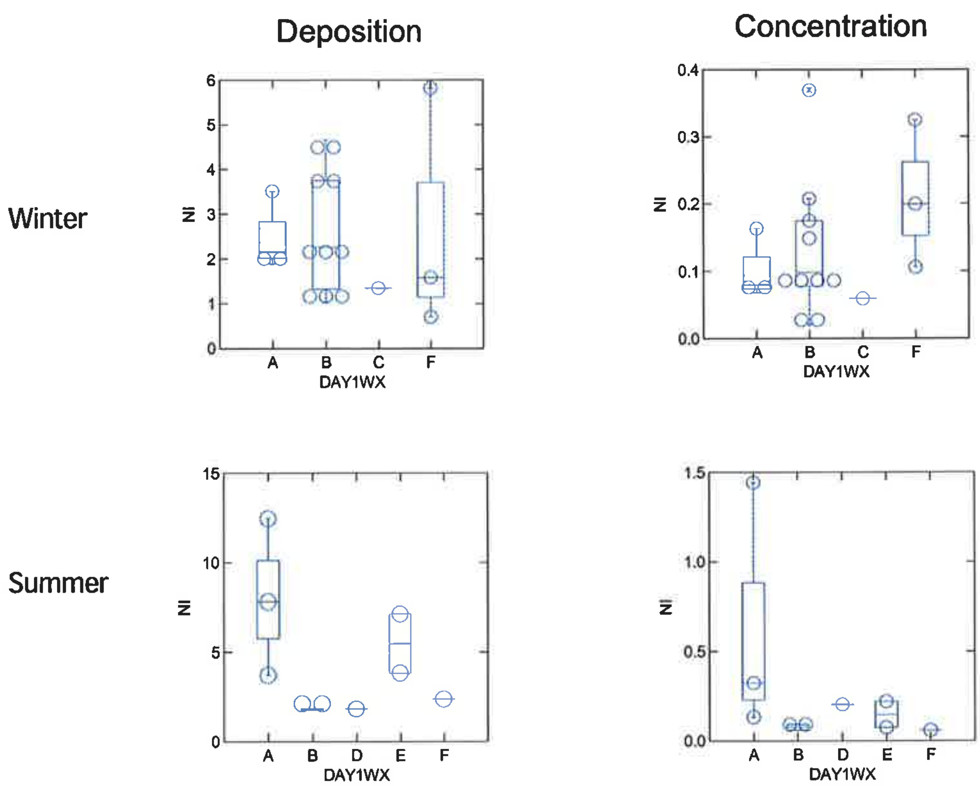


Figure 8. Box plots of nickel deposition (μg/m^2) and concentration (μg/L) by weather pattern (A through F) for single-week events for winter (N=17) and summer (N=9).

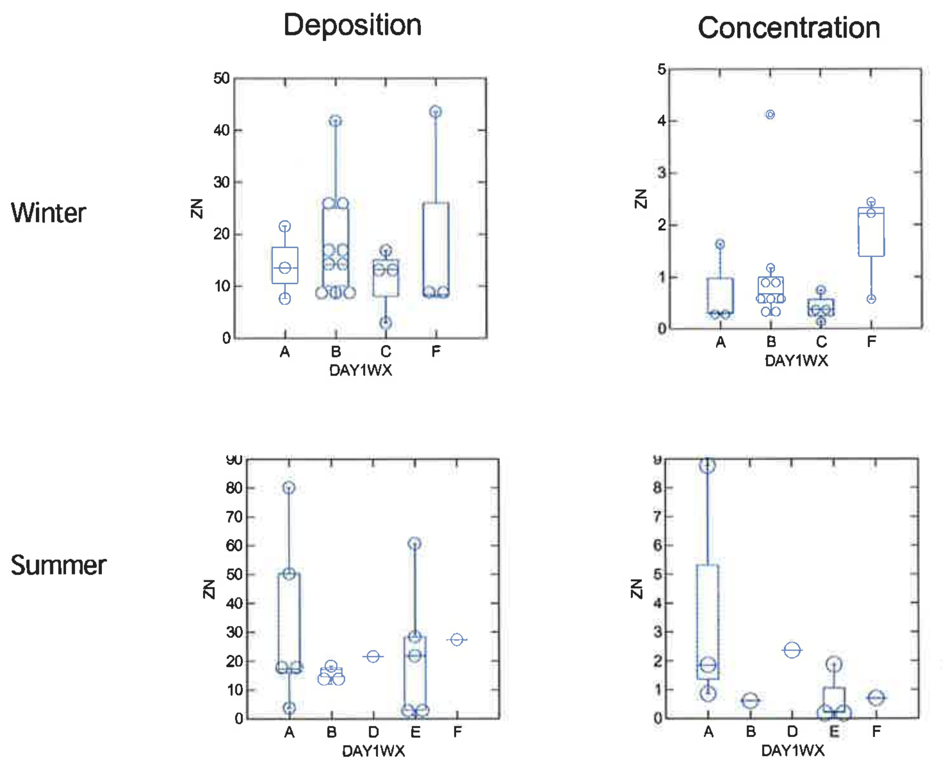


Figure 9. Box plots of zinc deposition (µg/m^2) and concentration (µg/L) by weather pattern (A through F) for single-week events for winter (N=19) and summer (N=8).

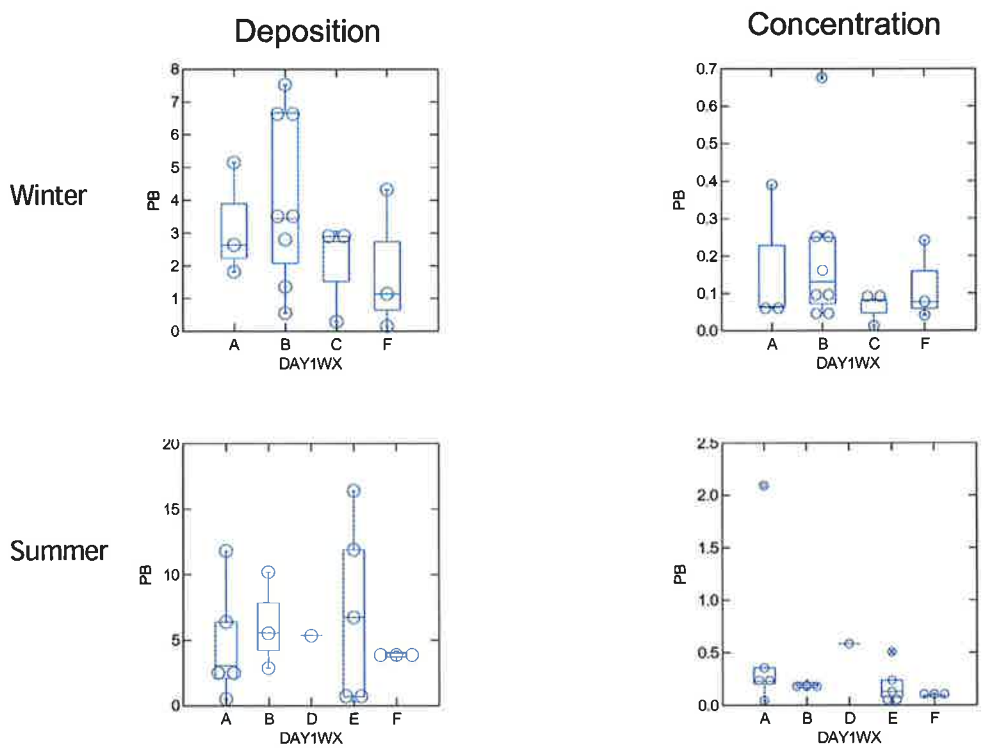


Figure 10. Box plots of lead deposition (µg/m^2) and concentration (µg/L) by weather pattern (A through F) for single-week events for winter (N=17) and summer (N=16).

Additional box plots were created for the winter season showing deposition and concentration by precipitation type for samples with a single rain-producing weather event. Examples are shown in **Figures 11 through 14**. No significant trends in the deposition data by precipitation type were seen. However, manganese, nickel, and zinc concentrations tended to be higher when the precipitation was snow.

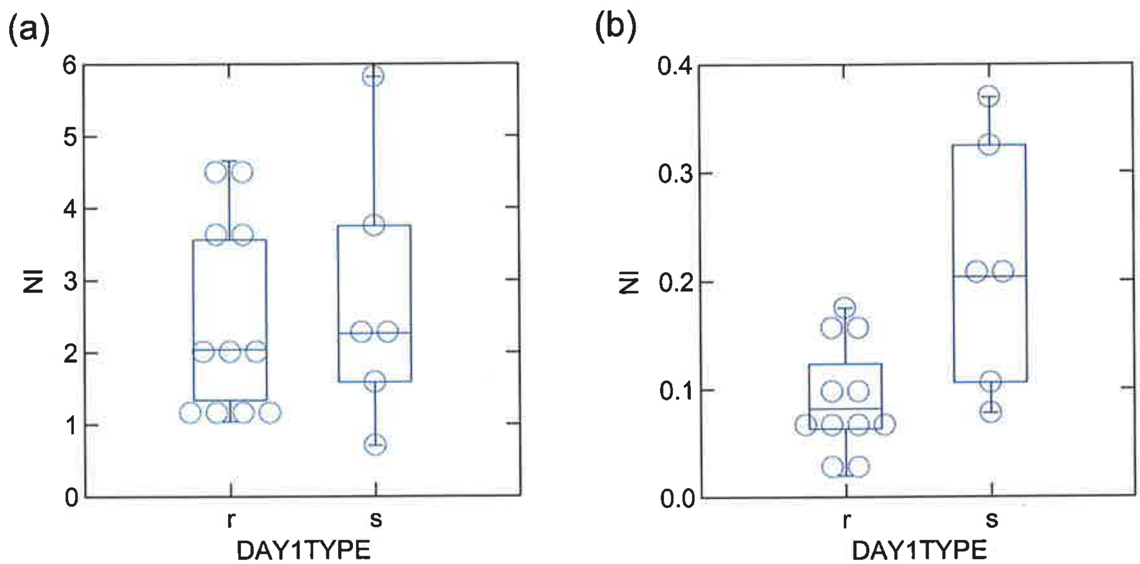


Figure 11. Box plots showing the distribution of nickel (a) deposition and (b) concentration by precipitation type for November through February single-event samples.

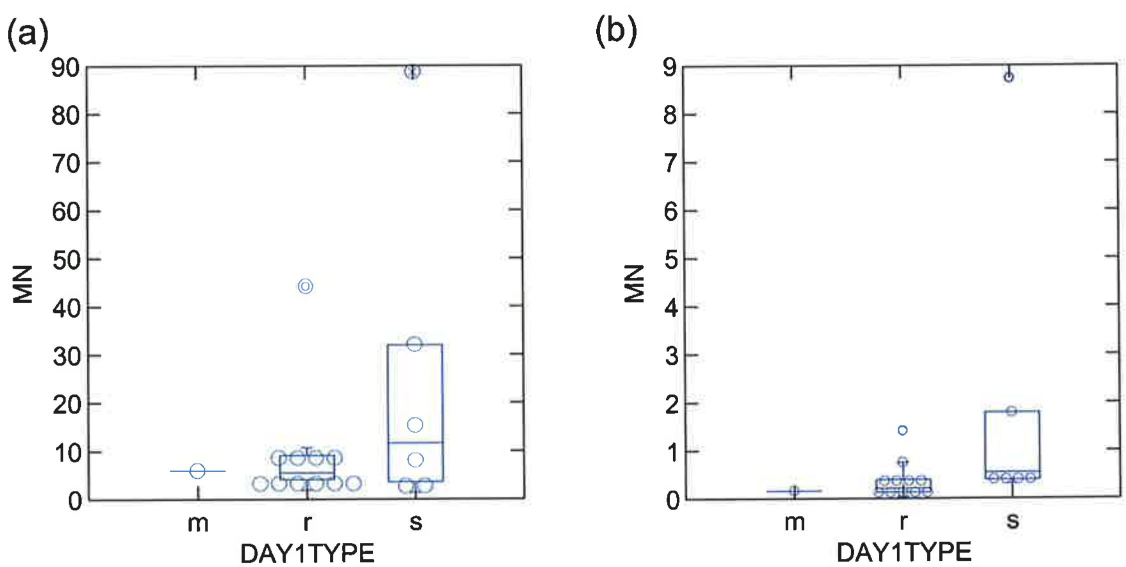


Figure 12. Box plots showing the distribution of manganese (a) deposition and (b) concentration by precipitation type for November through February single-event samples. N=18

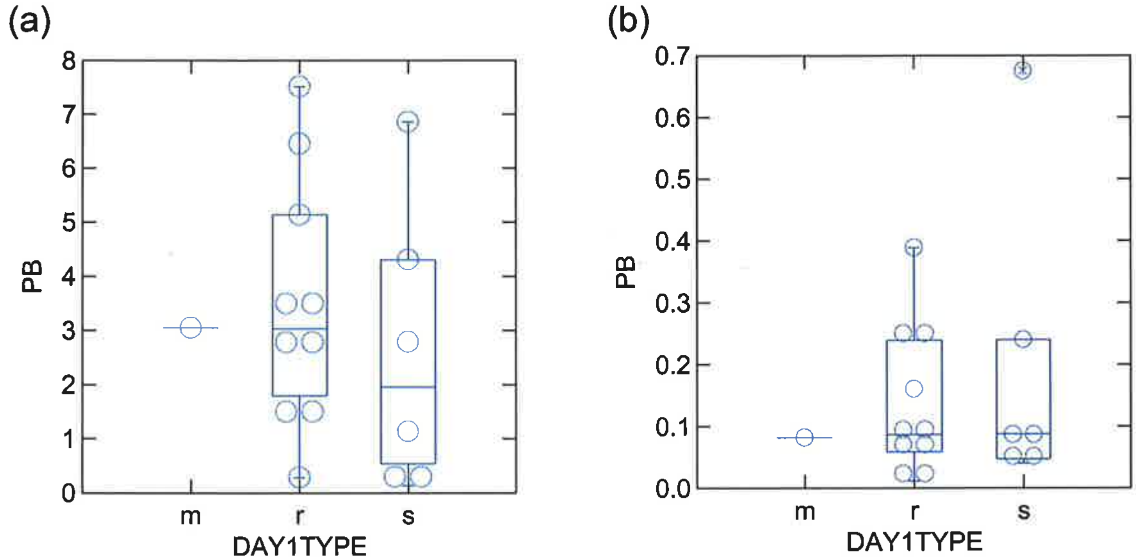


Figure 13. Box plots showing the distribution of lead (a) deposition (N=17) and (b) concentration by precipitation type for November through February single-event samples. N=17

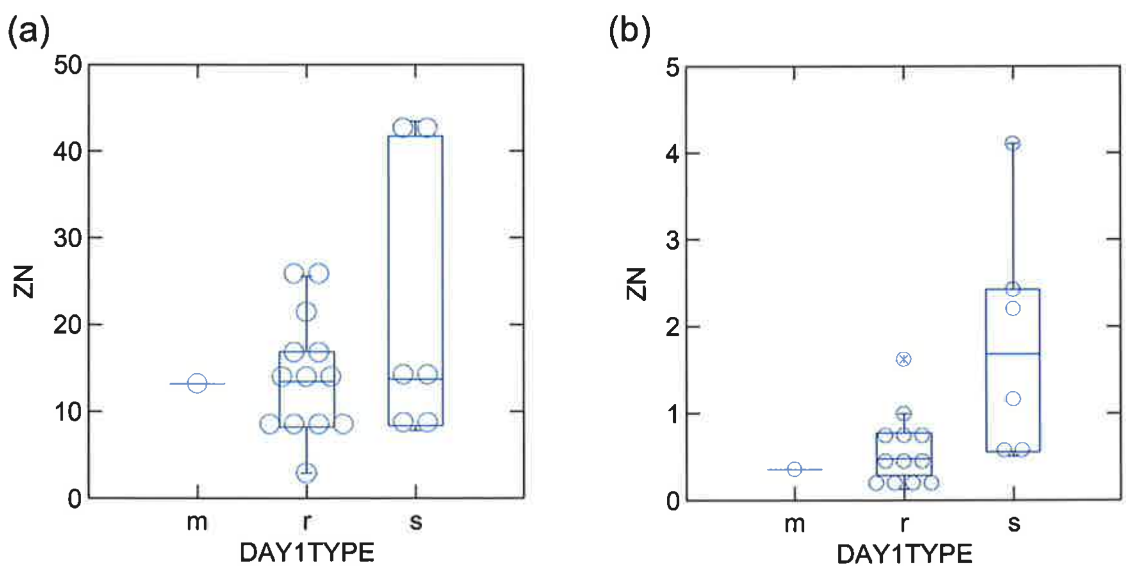


Figure 14. Box plots showing the distribution of zinc (a) deposition and (b) concentration by precipitation type for November through February single-event samples. N=19

Case Study Events

Case studies were conducted to understand the transport pattern and regional trace metal aerosol concentrations in the context of trace metal deposition at Casco Bay. Six samples with a single precipitation event were investigated; three in winter and three in summer:

- February 22, 2003 (much higher manganese than typical);
- February 21, 2004 (much higher manganese than typical, plus high zinc and lead);
- August 21, 2004 (higher values of all metals, including very high zinc);
- July 22, 2005 (much higher nickel than typical);
- August 9, 2005 (higher manganese and lower zinc than typical); and
- November 6, 2005 (higher lead than typical).

Results are shown in **Figures 15 through 20**. Each plot displays

- the trace metal deposition "fingerprint" at Casco Bay of species above detection (manganese, nickel, lead, and zinc) plus a corresponding table of concentration for the case study sample;
- the IMPROVE site trace metal $PM_{2.5}$ concentration fingerprint at each site;
- the average trace metal deposition and concentration at Casco Bay for the season in a table;
- the type of weather pattern and precipitation, plus the date of precipitation that impacted the weekly sample; and
- the HYSPLIT back trajectories at 500 m for the day on which precipitation occurred, run three times during the day.

No consistent pattern was seen in these case studies. The trace metal deposition fingerprint does not appear to vary in a similar manner to the $PM_{2.5}$ trace metals at the IMPROVE sites. No consistent association of trajectory pattern with deposition was seen, either in terms of proportional deposition among species or absolute concentration. However, this type of analysis over all single-precipitation event samples may elucidate a pattern for which the six case studies did not.

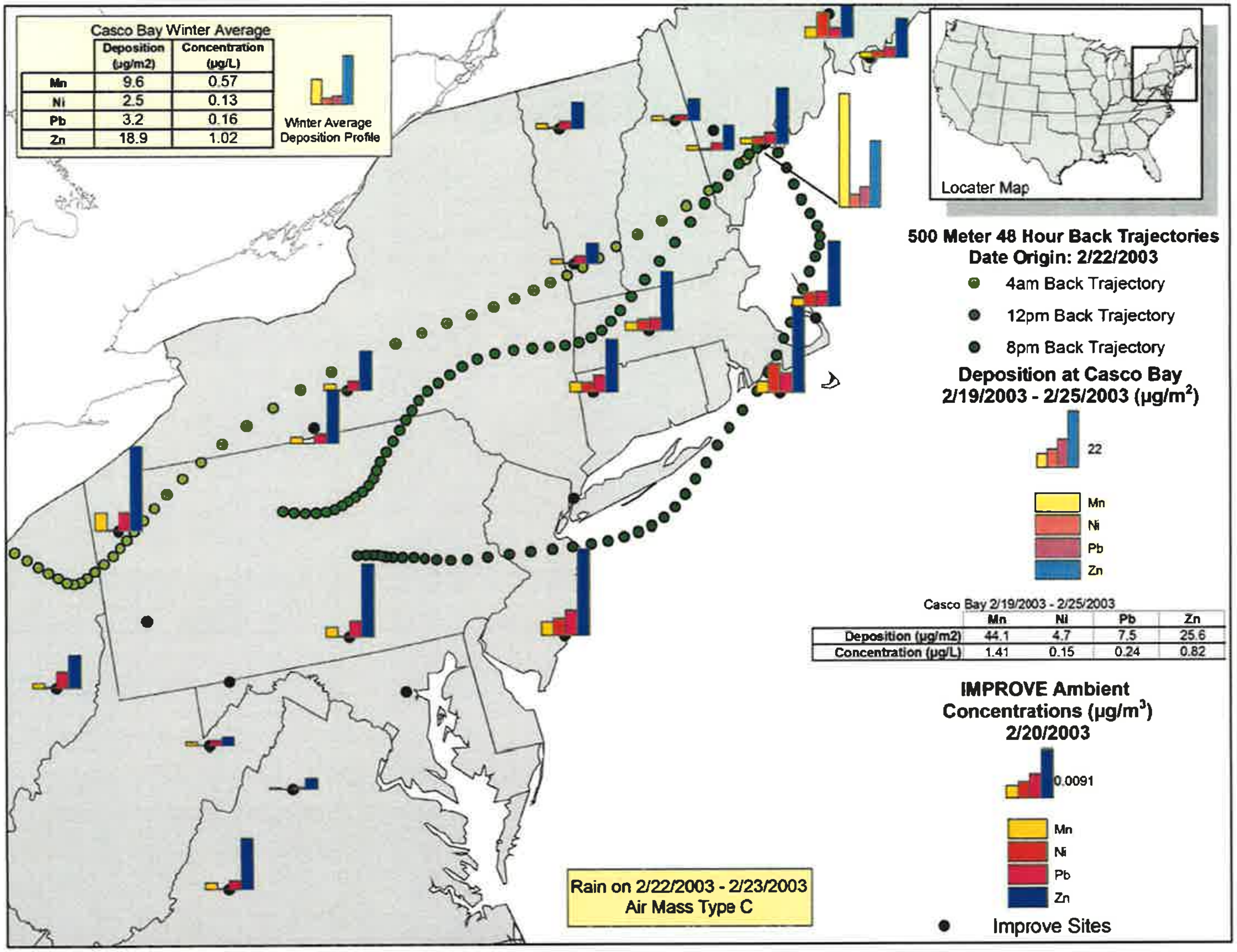


Figure 15. Case study analysis of February 22, 2003.

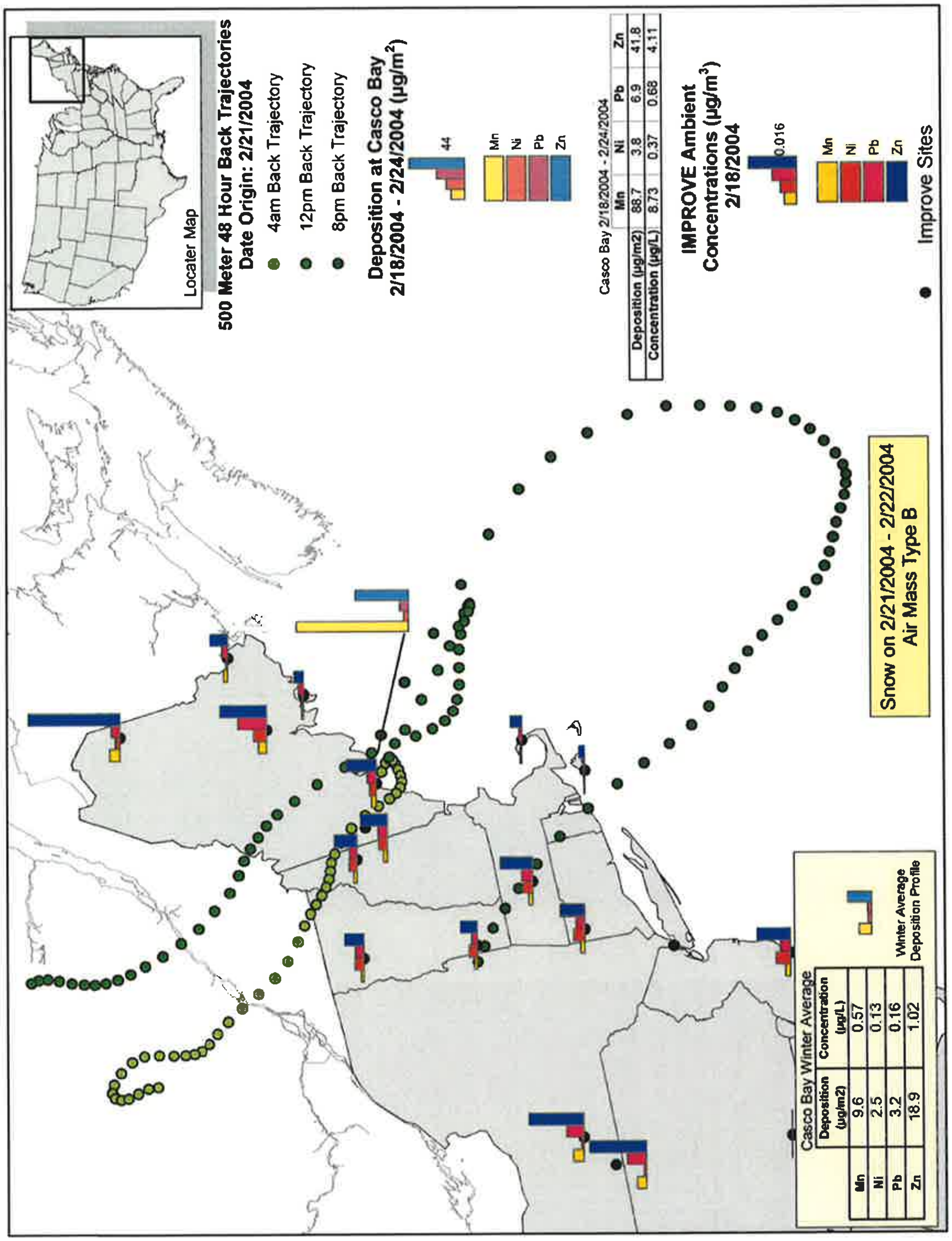


Figure 16. Case study analysis of February 21, 2004.

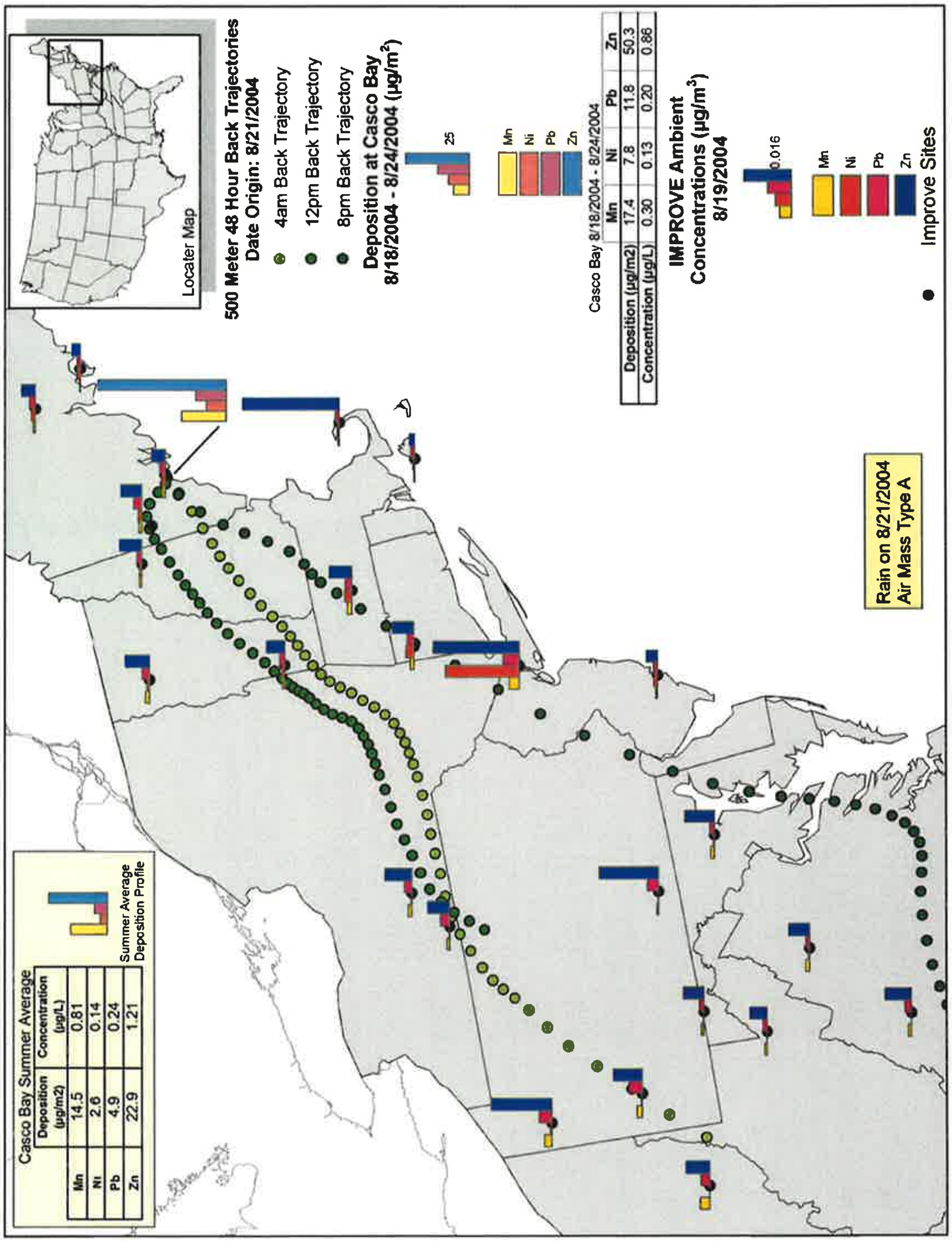


Figure 17. Case study analysis of August 21, 2004.

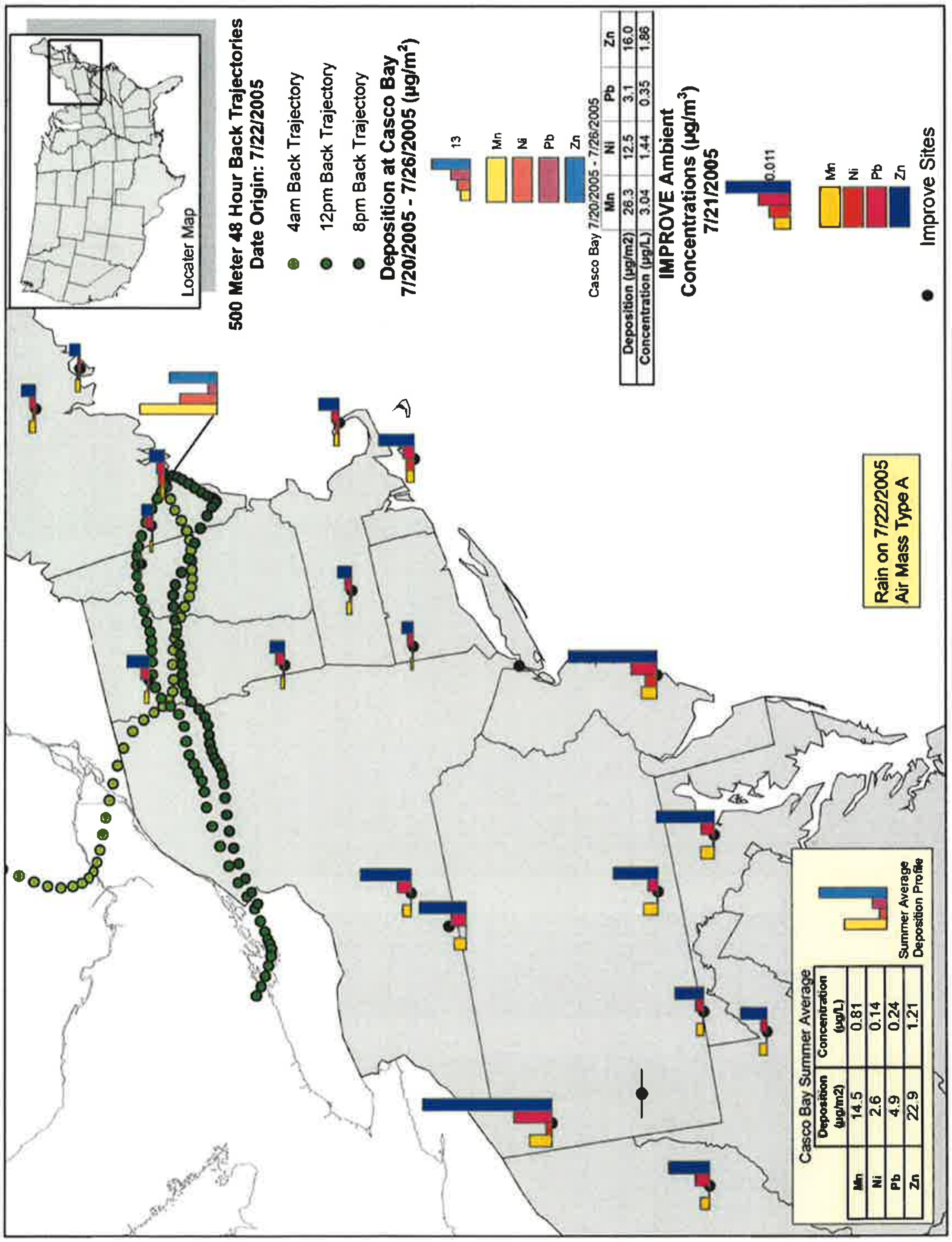


Figure 18. Case study analysis of July 22, 2005.

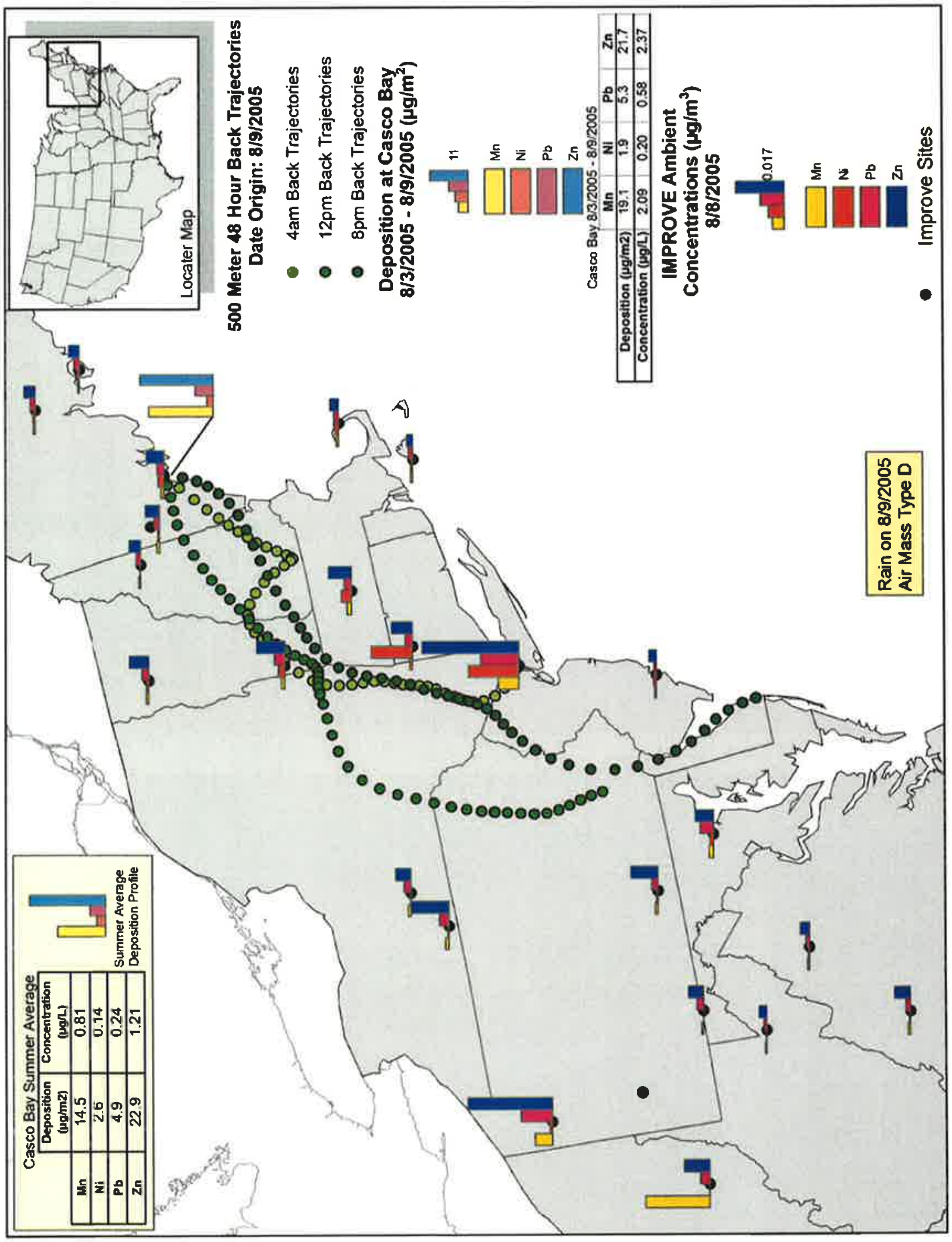


Figure 19. Case study analysis of August 9, 2005.

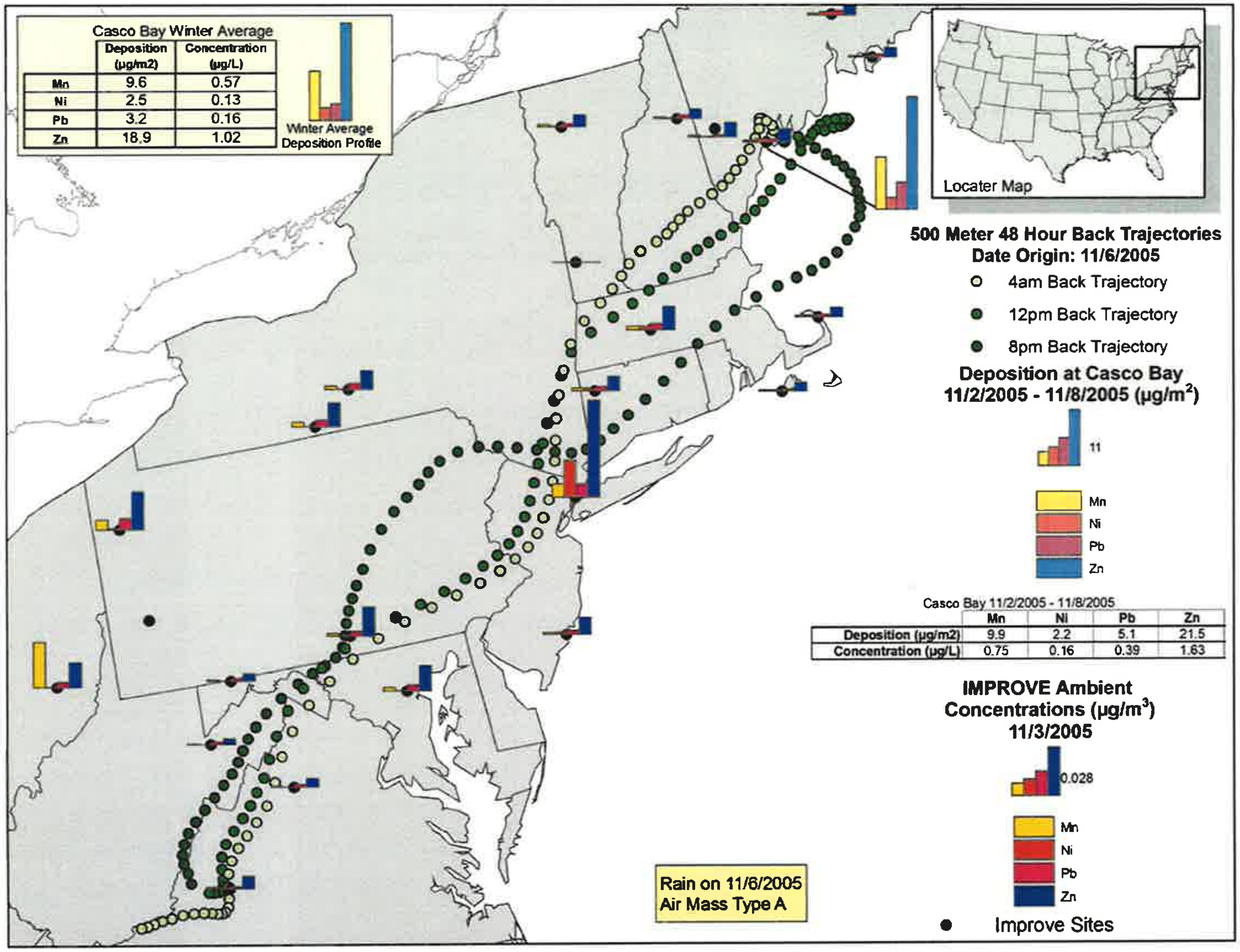


Figure 20. Case study analysis of November 6, 2005.