Trends and Accountability

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The goal of this task is to identify and understand temporal variability in key air toxics, and relate changes in concentrations over time to control measures.

Scientific Questions

- Long-term variability characterization
 - What are the trends in air toxics?
 - Which pollutants can we estimate trends for?
 - Which pollutants are declining nationally?
 - Are any pollutants increasing nationally?
 - How much do trends vary spatially?
 - When do we estimate that trends of key risk-driving pollutants will reach the 10⁻⁶ level if trends continue at current rates?
- Accountability
 - Top-down
 - How can one systematically assess trends to identify effects of control measures?
 - What specific trends can be linked to control measures?
 - Bottom-up
 - What control measures went into affect (when, where)?
 - How big of an impact on ambient concentrations might these individual and aggregate control measures be expected to have?
 - Which specific control measures might be reflected in measurable changes in ambient concentrations of toxics?

Overview

- This summary provides an overview of results to date on exploratory analyses of air toxics data collected from 1990-2006.
- This work is part of Phase V of national level air toxics analyses.
- Data preparation and other method details are minimally described here in order to focus on the results and implications. These details are provided in other talks

Data Availability by Year



How Have Air Toxics Concentrations Changed Over Time?

Motivation – understanding changes in concentrations has implications for

- Human exposure
 - Nationally
 - Locally
- Accountability
 - Have control measures been effective in reducing concentrations of air toxics?
 - Can we show examples of declining concentrations at the national, state, and/or local levels?
 - Can we show that certain areas have not had concentrations decline when these control measures were not implemented?
 - Do trends indicate the most effective way to further reduce human exposure to air toxics?

Trends: Approach and Methods

- Create trends for (a) three trend periods: 1990-2006, 1995-2006, and 2000-2006;
 (b) longest trend possible at each site
 - 75% completeness for trend period required
 - Data from 1990 or 1991 required for 1990-2006 trend period
- Trends were created at the site level
 - Trends required consistent site, parameter, and method codes over time (POC can float between years)
 - Individual trends were plotted along with MDL values and standard deviation in annual average
 - Linear regressions were fitted to the trends
 - F-test was performed to identify if trend was statistically significant (i.e., non-zero) at 95% confidence level

Example Individual Site Trend



A tool was developed to produce site level trend statistics and graphics by pollutant. Visual inspection is key to properly classifying the trends.

Counts of Trend Sites by Pollutant



National Picture of Trends

- Data were aggregated at the national level.
- Sites with more than 85% of data below MDL were not included in aggregation (because trends at these sites are unlikely to be identified using simple methods).
- The distribution of trends nationally was plotted for each pollutant with at least 15 monitoring sites with trends in one of the three trend periods.



National distribution of the trends in VOCs for 2000-2006

The distribution of trends in VOCs and carbonyls is shown in this figure *(only one trend period is shown here for simplicity)*.

The x-axis is the percentage change in concentrations per year. Data to the left of the zero line indicate decreasing concentrations; data to the right of the zero line indicate increasing concentrations.

Each bar shows the 10th, 50th, and 90th percentile values for a given pollutant.

The total number of trend sites is shown on the right y-axis.

*90th percentile percentage change per year was cutoff at 30



National distribution of the trends in VOCs for 2000-2006

Hydrocarbon trends for the 2000-2006 trend period show a distinct pattern of decreasing concentrations at most sites.

In contrast, the carbonyl compounds did not have distributions that were clearly decreasing – they are centered close to the zero line.

*90th percentile percentage change per year was cutoff at 30



National distribution of the trends in VOCs for 1995-2006

Note that there are far fewer sites with data records of 10+ years for the 1995-2006 trend period, but the general pattern is the same as the previous slide.

Hydrocarbon trends for the 1995-2006 trend period show the same distinct pattern of decreasing concentrations at most sites.

Similarly, the carbonyl compounds did not have distributions that were clearly decreasing – they are centered close to the zero line.

*90th percentile percentage change per year was cutoff at 30



National distribution of the trends in VOCs for 1990-2006

Very few sites have the longterm records required for the 1990-2006 trend period when we require method codes to remain constant.

Note that pollutants with fewer than 10 sites are no longer represented with a 10th-90th percentile bar; only the median trend is shown.

Hydrocarbon trends for the 1990-2006 trend period are still of the same magnitude as other periods shown previously, but are very sparse.

Carbonyl compound data are sparse.

*90th percentile percentage change per year was cutoff at 30



National distribution of the trends across three trend periods

Trend distributions are remarkably consistent across trend periods.

Hydrocarbon trends for the three trend periods show a distinct pattern of decreasing concentrations at most sites.

In contrast, the carbonyl compounds appear to be evenly split between increasing and decreasing concentrations – they are centered close to the zero line.

^{*90}th percentile percentage change per year was cutoff at 30



National distribution of the trends in VOCs for any site with 5+ years of monitoring data

It is also possible to plot the distribution in trends for the longest 5+ year trend period at all sites in the United States.

While the trend periods are not consistent across sites, this way of inspecting the data captures a larger number of sites where data were collected that did not meet the criteria for the other trend periods.

This data set is entirely consistent with the results from the other time periods.

*90th percentile percentage change per year was cutoff at 30



National distribution of the trends in chlorinated VOCs for three trend periods

At the sites where chlorinated VOCs are measured reliably, the median sites show decreasing concentrations.

However, it is important to recognize the sparseness of the data set as a result of sites being excluded from the analysis. Most of these pollutants had a large fraction of their sites excluded because more than 85% of data were below MDL.

*90th percentile percentage change per year was cutoff at 30



National distribution of the trends in total suspended particulate (TSP) metals for three trend periods

The two early trend periods show a distribution of decreasing concentrations for lead TSP at most sites. In contrast, the 2000-2006 trend period is balanced between increasing and decreasing trend sites.

The small number of sites with data records that meet trend criteria for the rest of the TSP metals makes it difficult to assess national trends with confidence. Concentrations may be decreasing for some of the pollutants, but the median decrease is rarely very different from zero or consistent across time periods.



National distribution of the trends in TSP metals for any 5+ year trend period

Adding the 5+ year trend period greatly enhances the number of monitoring sites available for assessment.

If we weight the data towards the 5+ year trend period, the Nickel and Cadmium decreasing trends are relatively convincing.

Manganese and chromium trends remain balanced between increasing and decreasing trends, with a slight bias towards increasing values.



National distribution of the trends in PM_{2.5} metals for any 2000-2006 and any 5+ year trend period

Additional investigation of trends of these pollutants shows they track MDL even when >15% of data is above MDL.

Therefore, these trends are not reliable.



Other PM_{2.5} Metal Examples





All have concentrations that track MDLs in suspicious ways. While these trends may not necessarily result from MDLs, we are skeptical of using $PM_{2.5}$ metals data for trends without additional assessment.

2006

2007

Summary of National Trends

- Hydrocarbon concentrations are decreasing at consistent rates of 4 to 6% declines per year nationally over multiple trend periods.
- The distribution of trends for carbonyl compounds is centered at zero; approximately equal numbers of sites have increasing or decreasing trends
- Chlorinated VOCs are declining where measured reliably; many of these compounds are not measured reliably (i.e., data are usually below MDL).
- Lead TSP concentrations are declining nationally over the earlier trend periods. Other metal TSP concentrations have too few trend sites to draw national conclusions.
- PM_{2.5} metal concentration trends are suspect.

Spatial Patterns in Concentration Trends

- Trends in concentrations were plotted as proportional symbols to indicate the direction, magnitude, and statistical significance of trends at sites in the United States.
- These maps help to identify areas where trends are consistent and significant and assist us in assessing possible spatial differences in trends and spatial coverage of trend sites.



Summary of Spatial Patterns

- Some pollutants are nationally representative with only a few areas or sites not conforming. These include benzene, ethylbenzene, xylenes, toluene, methyl chloroform, and MTBE.
- Chlorinated VOCs had less consistent national trends than the hydrocarbons. These pollutants had more heterogeneity within and across regions.
- TSP metals are not measured consistently across the United States.
- Some areas had consistent trend patterns across a set of pollutants:
 - Minnesota had increasing concentrations for multiple chlorinated VOCs and 1,3-butadiene (monitoring issue?).
 - South Carolina had increasing concentrations of styrene and ethylbenzene (possibly fiberglass production?).
 - Houston and Beaumont, Texas, often had heterogeneous trends. This may be due to local point source emissions.
 - Indiana/Illinois often had heterogeneous trend patterns. This may be due to local point source emissions.

Accountability Analysis

- Identifying and characterizing trends in air toxics does not specifically explain which, if any, control measures are contributing to those changes.
- We have developed methods to identify specific control measures using data at either the national or local scale.
 - Top-down approach: Use existing trends to identify control measures.
 - Bottom-up approach: Identify known control measures and determine if trends in pollutants meet expectations.

Top-down Accountability Approach

- Hypothesis: If pollutants are emitted by the same source, emissions should covary over long-time scales. In other words, trends should be parallel if normalized.
 - Identify covariant trends in Mobile Source Air Toxics (MSATs) as an indicator of sites dominated by mobile source emissions.
 - Characterize MSAT trend "signature".
 - Screen sites with trends >5 years to identify:
 - Mobile source emission-dominated sites and signature
 - Sites where other emissions sources may be important
 - Identify spatial differences in trends, if any.
 - Provide evidence that mobile source controls are indeed reducing concentrations of air toxics.

Top-down Accountability Method

- Identify sites with long-term (6+ years) records of measurements of selected MSATs (primary emissions only):
 - Benzene, toluene, 1,3-butadiene, xylenes, and ethylbenzene
 - Carbon tetrachloride as internal tracer (non-MSAT)
- Only require the site and parameter to be consistent over the trend period (method and POC can float between years).
- Normalize annual average concentrations at each site using maximum concentration over the trend period for each pollutant (i.e., divide each year by highest value measured).
- Plot trends and visually screen them for covarying linear trends.



Top-down Approach Example: Site 060371002, Burbank, CA (2 of 3)



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Top-down Approach Example: Site 060371002, Burbank, CA (3 of 3)



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Other Types of Emissions Signatures

Four major categories of trend signatures were observed:

- Mobile source signature (shown in previous slides, yellow on following maps)
- Mobile source signature with shallow or increasing 1,3-butadiene
- Mobile source signature with shallow or increasing benzene and/or 1,3-butadiene
- Other noncovariant signatures (usually have at least one increasing trend)



Benzene Signature Sites: Examples



Spatial Characterization of Trend Profile "Signatures"

- Visual inspection of the slopes of trends provides useful information on the covariance of pollutant concentrations over time.
- The percentage change in concentrations per year was plotted on maps for each of the pollutants shown in the scatter plots to spatially investigate the trends profiles.
- Mobile source signatures have MSAT profiles of similar magnitudes; other signatures have increasing or varying magnitudes among the pollutants.



Identifying Spatial Patterns in Trend Signatures





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California: Mobile Source Signatures

Most California profiles are flat (i.e., similar magnitude trend for each MSAT), indicating the relative dominance of mobile source emissions on these sites.

Also note that carbon tetrachloride is not an MSAT and should not covary with the others (which it does not).

Minnesota: Increasing 1,3-butadiene?



Trends of 1,3butadiene appear to have increased at all sites in Minnesota. The sites with yellow circles had obvious MDL changes that may affect the trend.

Other sites did not have obvious MDL issues, perhaps they were changed but a method MDL was reported?

Northeast: Mostly Mobile Source Dominated



Most of the northeastern sites were characterized as mobile source signatures.

Notable exceptions include the two most northern sites and some 1,3butadiene sites in the Buffalo area.

Note that lavender-filled areas are counties with monitors.

Southeast Texas: Industrial Influence?



The Houston and Beaumont areas had a large fraction of benzene sites and increasing M trend sites.

Note that lavender-filled areas are counties with monitors.

MSOffice2 how are these designated in the plot - noncovariant? HRH, 9/13/2007

Indiana and Chicago: Industrial Influence?

Mobile Source Signature

Non-covariant Other

> 1,3-Butadrene Ethylbenzene MP_Xylene O_Xylene Toluene Benzene C Tet

Mobile Source Signature (MDL issues for 1) Mobile Source with Slower 1,3-Butadiene Decline Mobile Source with Slower Benzene Decline Indiana sites had slower rates of decline for benzene (orange bar) and increasing or flat 1,3-butadiene rates (dark green bar).

Accountability Summary

- Most sites in the United States conform to our expected mobile source trend profile signature.
 - California and the Northeast had the largest number of these sites
- Two mobile source-like signatures accounted for most of the rest of the sites
 - 1,3-butadiene signature sites had shallow or increasing 1,3-butadiene (possible measurement issues?). These were concentrated in Minnesota and New York.
 - Benzene signature sites had shallow or increasing benzene (likely explained by nearby point-source emissions for some sites; others are not clear). These were concentrated in Texas and Indiana.
- Some sites had increasing trends or noncovariant trends in multiple MSATs.
 These sites may have nearby emissions sources that are influencing trends.
 - These sites may be good candidates for case-study analyses of other emissions sources. These sites were concentrated in Texas.
- The top-down approach may be applicable to other pollutants from mobile sources (CO, NO_x, black carbon) or other emissions sources with multiple coemitted pollutants.

Accountability Summary

- In general, MSATs showed a 4 to 6% decrease per year in spite of increases in vehicle miles traveled (VMT) of 3 to 4% per year.
- Harley et al., (2006) has shown that a 4% per year decline in benzene, for example, was attributable to fleet turnover.

NATTS Top-down Accountability Analysis

The top-down accountability analysis was extended to NATTS sites in order to classify whether each site was mobile source dominated or influenced by multiple sources.

- NATTS sites have typically been in operation for less than six years, so most did not meet our trend length criterion
- In addition, short trend periods (3-4 years) do not provide enough annual averages to robustly assess changes due to the inherent variability and uncertainty in annual averages
- Therefore, an additional analysis was performed to assess scatter plots of the daily average primary MSATs at all NATTS sites. Sites with highly correlated concentrations are most likely dominated by mobile source emissions.

Example Scatter Plot Analysis



Tight correlation

Bifurcation: either multiple sources or possible pollutant misidentification

If mobile source pollutants display tight correlations at the daily level over several years, we can still classify a monitoring site as mobile source emission dominated. Of the NATTS sites we analyzed, two-thirds could be classified.

NATTS Accountability Site Classifications

Classification	NATTS site				
MSAT	Phoenix AZ AZ Department of Environmental Quality 04-013-9997				
MSAT	Providence RI RI Department of Environmental Management 44-007-0022				
MSAT	San Jose CA Bay Area Air Quality Management District 06-085-0005				
MSAT	Tampa FL (1) Hillsborough County Environmental Protection Commission 12-057-3002				
MSAT	Tampa FL (2) Pinellas County Department of Environmental Management 12-103-0026				
MSAT	Washington DC DC Department of Health 11-001-0043				
MSAT	Grand Junction CO CO Department of Health and Environment 08-077-0017/0018				
MSAT	New York (Bronx) NY NY Department of Environmental Conservation 36-005-0110				
MSAT	Rochester NY NY Department of Environmental Conservation 36-055-1007				
MSAT	Seattle WA WA Department of Ecology 53-033-0080				
QC, MDL issues	Atlanta (Decatur) GA GA Department of Natural Resources 13-089-0002				
MSAT, needs QC	Bountiful UT UT Department of Environmental Quality 49-011-0004				
Other sources?	Chicago (Northbrook) IL IL Environmental Protection Agency 17-031-4201				
MDL, reporting	Hazard KY KY Department of Environmental Protection 21-193-0003				
MSAT, needs QC	Roxbury MA MA Department of Environmental Protection 25-025-0042				
MDL, little data	Chesterfield SC SC Department of Health and Environmental Conservation 45-025-0001				
Other sources?	Detroit (Dearborn) MI MI Department of Environmental Quality 26-163-0033				
MDL, little data	Harrison County TX TX Commission on Environmental Quality 48-203-0002				
Other sources?	Houston (Deer Park) TX TX Commission on Environmental Quality 48-201-1039				
MDL influences	La Grande OR OR Department of Environmental Quality 41-061-0119				
no data	Mayville WI WI Department of Natural Resources 55-027-0007				
Needs QC	St. Louis MO MO Department of Natural Resources 29-510-0085				
MDL influences	Underhill VT VT Department of Environmental Conservation 50-007-0007	47			

Bottom-up Approach

- Hypothesis: If control measures have been implemented on emissions sources that contribute a large fraction to total concentrations in an area, these emissions changes should be reflected in concentrations at nearby monitoring sites. Areas that are not near these emissions sources should be unaffected or have smaller changes over time.
- Identify control measures expected to have measurable effects on ambient concentrations.
 - Identify emissions sources contributing at least 20% of ambient concentrations.
 - Identify control measures that would be expected to reduce concentrations by at least 15% (measurable decline with some confidence). For an emissions source with 20% of total emissions, this would require a 75% reduction; if it was 60% of total emissions, this would only require a 25% reduction.
 - Identify monitoring sites near (<5 km) the emissions source and away from the emissions source (>10 km).
 - Analyze trends to identify:
 - If there was a large drop in concentrations when a control measure was implemented.
 - If trends follow expected patterns.
 - If trends at sites not near the emissions source also show the same or similar trends.
 - This type of analysis is most convincing if sites that would not be expected to show trends have shallower or unaffected trends while those near the site have decreases of the magnitude expected. Method changes or differences make this analysis much more difficult.

Bottom-up Accountability Method

- Hazardous waste incinerators and cement kilns had a recent 2003-2004 MACT rule designed to reduce emissions of multiple toxic metals.
- Hypothesis: Monitoring sites near these facilities (<3 miles) should exhibit greater declines in the 2002-2005 time period than sites further away from these sites
 - Manganese, Selenium, Nickel, Cobalt, Antimony, Lead, Cadmium, and Chromium were all targeted for reductions
 - Estimated magnitudes of these reductions are not well described in the MACT database (e.g., reduction magnitudes are larger than the sum of emissions from all sources in NEI 1999).
- Complications: PM_{2.5} metals concentrations track MDLs at many sites.
- Identify monitoring sites with trends that appear to not track MDL changes that are available from 2001 to 2005
 - Identify monitoring sites within 3 miles of kilns and incinerators
 - Determine differences, if any, in trends of interest at sites near sources compared to those far from sources
 - Assess if these trends also occur in pollutants not targeted by MACT (e.g., potassium or silicon)

Bottom-up Accountability Results

- The initial investigation of monitoring sites revealed that few sites were within 3 miles of incinerators or kilns
- Investigation of concentrations and trends at these sites from 2000 to 2006 showed that
 - Concentrations were not elevated at the sites in closest proximity to these sources
 - Trends showed no obvious or substantial declines in the 2004-2006 time period when regulations were implemented
- These preliminary results were discouraging, so this line of investigation was discontinued. This approach may be more effective for other control measures.

Extrapolating Trends in Risk-weighted Concentrations: Approach

- Given current trends in air toxics, can we estimate when pollutant concentrations will decline to levels below concern for some key risk drivers?
- Use median percentage change per year in concentrations, median concentration from national distribution, and extrapolate current rates of change to identify when trends will be below the 10⁻⁶ cancer benchmark level.

Analysis

Pollutant	Risk-weighted concentration 2004	Percentage change per year	Year below 10 ⁻⁶ asymptotic (linear)
Benzene	8.0	-5.1	2044 (2021)
Carbon tetrachloride	8.3	-0.9	2236 (2101)
1,3-Butadiene	4.7	-3.3	2050 (2028)
Acetaldehyde	3.6	-1.3	2103 (2060)
Tetrachloroethylene	1.4	-5.7	2009 (2009)
Arsenic PM _{2.5}	5.2	-2.2	2078 (2041)
1,4-Dichlorobenzene	2.7	-3.6	2031 (2022)

Using the asymptotic or the linear extrapolation

$$Year_{X} = 2004 + \frac{\ln(\frac{1}{Risk})}{\ln(1 - \frac{\% \text{ Change}}{100})}$$

$$Year_{X} = 2004 + \frac{100*(1 - \frac{1}{Risk})}{\% \text{ Change per year}}$$

Extrapolating Risk-weighted Concentrations: Discussion

- At current percentage rates of change, most toxics will still be at levels of concern beyond 2020.
- Only tetrachloroethylene concentrations will likely be below 10⁻⁶ benchmarks by 2010.
- The asymptotic analysis assumes trends will remain consistent as a percentage decrease relative to the proceeding year. This results in flattening concentration changes over time, extending the expected duration of these pollutants being above 10⁻⁶ levels.
- A linear concentration extrapolation results in risk levels below 10⁻⁶ at significantly earlier years.

Conclusions (1 of 4)

• What are the trends in air toxics?

- Hydrocarbon concentrations are declining by approximately 4-6% per year
- Chlorinated VOCs are declining where measured reliably
- Carbonyl compounds are not changing at a national level
- Lead TSP is declining; other TSP and PM₁₀ metals have insufficient monitoring data to draw national conclusions
- PM_{2.5} metals have trends which track their MDLs.
- No pollutants are increasing at a national level
- What are the trends in risk driving toxics?
 - Benzene is declining by 5% per year
 - 1,3-butadiene is declining by 3% per year
 - Carbon tetrachloride is declining by 1% per year
 - Acetaldehyde is essentially unchanged
 - Arsenic has data issues which prevent national trends analysis
 - Tetrachloroethylene is decreasing at a median rate of 6% per year (among reliable sites)
 - 1,4-dichlorobenzene is declining at a median rate of 4% per year (among reliable sites)
 - Ethylene oxide, naphthalene, and acrylonitrile did not have sufficient reliable monitoring trend sites to consider their national trends

Conclusions (2 of 4)

What were the spatial differences, if any, in trends?

- We found that jurisdictional or network monitoring differences appear to be behind a significant portion of the variability within regions. Some of this may be due to actual differences, but others may be a result of reporting errors.
 - For example, Minnesota had increasing trends in almost all chlorinated VOCs and 1,3-butadiene. We believe this is more likely a result of a change in MDL that was not reported to AQS.
- Regions such as the Northeast and California had relatively homogeneous trends.
- Regions like Texas and the industrial Midwest had more heterogeneous trends, which may be a result of more major source emissions near monitoring sites.
- When will risk-weighted concentrations go below 10⁻⁶ levels for key risk contributing toxics?
 - Median tetrachloroethylene risk is expected to go below 10⁻⁶ levels nationally before 2010
 - Other risk contributors are expected to remain above 10⁻⁶ levels past 2020 at current rates of change

Conclusions (3 of 4)

- Can specific control measures be linked to changes in concentrations to demonstrate accountability?
 - The normalized top-down trend approach was used to demonstrate that mobile sources are indeed responsible for declining concentrations of many key hydrocarbons nationally
 - Most air toxics sites in the United States show a mobile source trend profile signature.
 - California and the Northeast had the largest number of these sites
 - Two mobile-source like signatures accounted for most of the rest of the sites
 - 1,3-butadiene signature sites had shallow or increasing 1,3-butadiene (possible measurement issues?). These were concentrated in Minnesota and New York.
 - Benzene signature sites had shallow or increasing benzene (likely explained by nearby point-source emissions for some sites; others are not clear). These were concentrated in Texas and Indiana.
 - Some sites had increasing trends or noncovariant trends in multiple MSATs. These
 sites may have nearby emissions sources that are influencing trends. These sites
 may be good candidates for case study analyses of other emissions sources.
 These sites were concentrated in Texas.
 - This method demonstrated that there were systematic differences in site classifications across regions. In particular, changes in concentrations in Texas, Indiana, and Minnesota were particularly different and may warrant further investigation for the effects of other source contributions.

Conclusions (4 of 4)

Can specific control measures be linked to changes in concentrations to demonstrate accountability?

- The bottom-up analysis approach was demonstrated, but was not successful for the hazardous waste incinerators and cement kilns investigated
 - MACT control measures are difficult to assess due to lack of information on the magnitude of changes and reconciliation with the NEI
 - Most monitoring sites are located away from major emissions sources, making direct analysis of concentrations from these sources problematic
 - Trends need to be large enough to differentiate from natural variability in the data



Hafner and McCarthy, 2004 Harley et al., (2006)