Risk and Hazard Characterization Summary

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STI

Scientific Questions

- Which air toxics have the highest risk- and hazard-weighted concentrations nationally?
  - Which toxics are possibly problems but aren't measured well enough to be quantified?
  - Which toxics that aren't measured are identified as problems by models and emissions inventories?
- How do spatial variations of concentrations change relative to levels of concern?
  - Do concentrations vary across health benchmark values?
  - Which areas appear to have higher cumulative risk-weighted concentrations based on commonly measured pollutants?
  - Do concentrations vary substantially within cities relative to health benchmarks?
  - Do cumulative risk-weighted concentrations drop off in rural and remote areas? Is the drop-off large enough to reduce risk below levels of concern? Which pollutants contribute the most to risk in these areas?
- Are ozone, PM, and toxics cumulative risk-weighted concentrations high in the same areas?

Overview

- This summary provides an overview of results to date on analyses of the importance of species using risk- or hazard-weighting of air toxics data collected from 1990-2005, focusing on the most recent three years of data (2003-2005).
- 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. I will be happy to answer any method detail questions during or after the talk.

Data Preparation

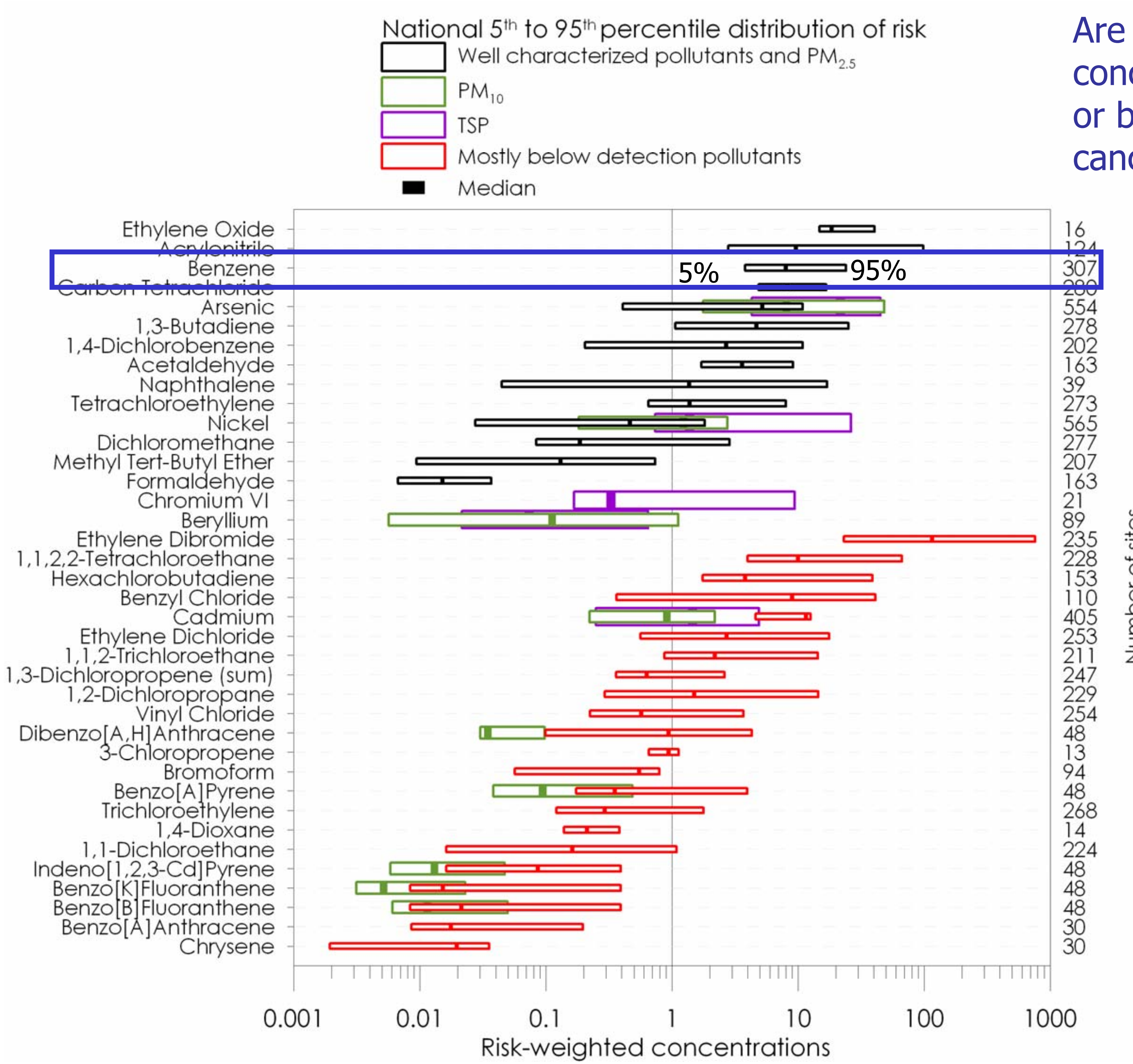
- For most of the analyses here, toxics concentrations were aggregated to include data from 2003-2005; these three years had the largest number of valid annual averages.
- Site averages are the mean of annual mean concentrations from 2003-2005 (1-3 years of data). These averages were used to minimize meteorological and data reporting artifacts in the data set.
- Sites and pollutants with fewer than 15% of records reported above MDL were treated as less certain. Annual mean concentrations for these sites and pollutants are likely below MDL, but quantification is not feasible. These sites are usually included in the analyses shown, but are colored or marked to indicate that the values shown are only known to be less than the MDL value.
- For all risk- and hazard-weighting, EPA OAQPS recommended chronic and acute health benchmarks were used. These health benchmarks are available on the internet at http://www.epa.gov/ttn/atw/toxsource/table1.pdf

What Is the National Picture of Ambient Risk-Weighted Concentrations?

- The following slides provide a summary of the range of risk-weighted concentrations for air toxics with cancer benchmarks organized by highest risk weighting to lowest – first for toxics with >15% of data above detection nationally and then for toxics with most data below detection (>85%).
- Risk weighted concentrations are computed by multiplying ambient concentrations by unit risk factors (URF). For example, a benzene ambient concentration of 2 $\mu g/m^3$ and a URF of 7.8×10^{-6} $(\mu g/m^3)^{-1}$ provides an estimate of risk of 1.6×10^{-5} or "16 in a million"
- These slides aim to answer the following questions:
  - Are concentrations above cancer health benchmarks?
  - Are concentrations characterized well enough to assess health risks?

EPA OAQPS-recommended health benchmarks were used (2005 version, not July 2007 version).

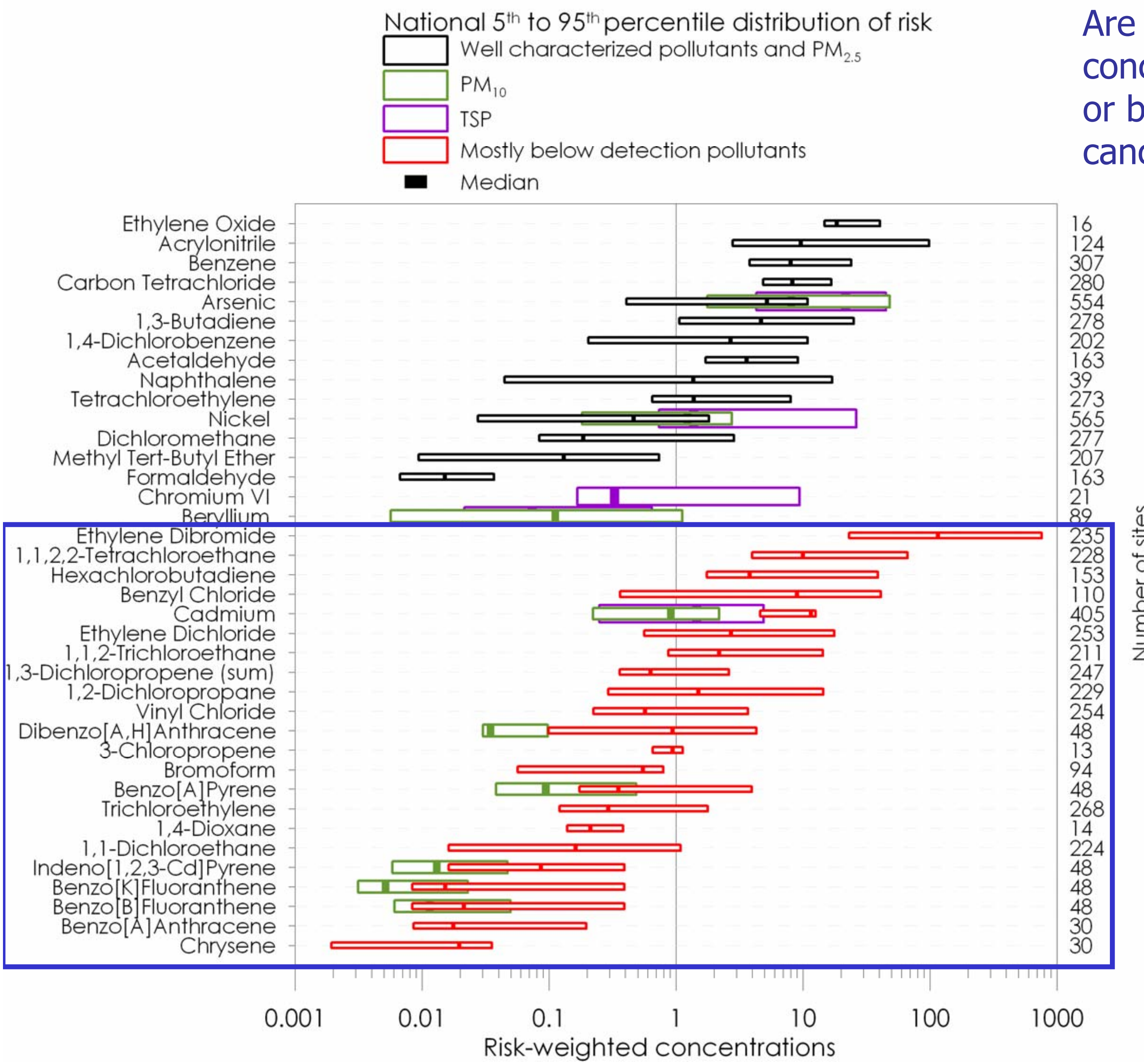
Are national concentrations above or below the 1x10^{-6} cancer benchmark?



National concentration ranges are normalized by their 10^{-6} cancer benchmarks to display risk-weighted concentrations.

Using benzene as an example, the 5th to 95th percentile risk range runs from about 4 to 24-in-a-million at national monitoring sites, with a median value of 8.

Are national concentrations above or below the 1x10^{-6} cancer benchmark?

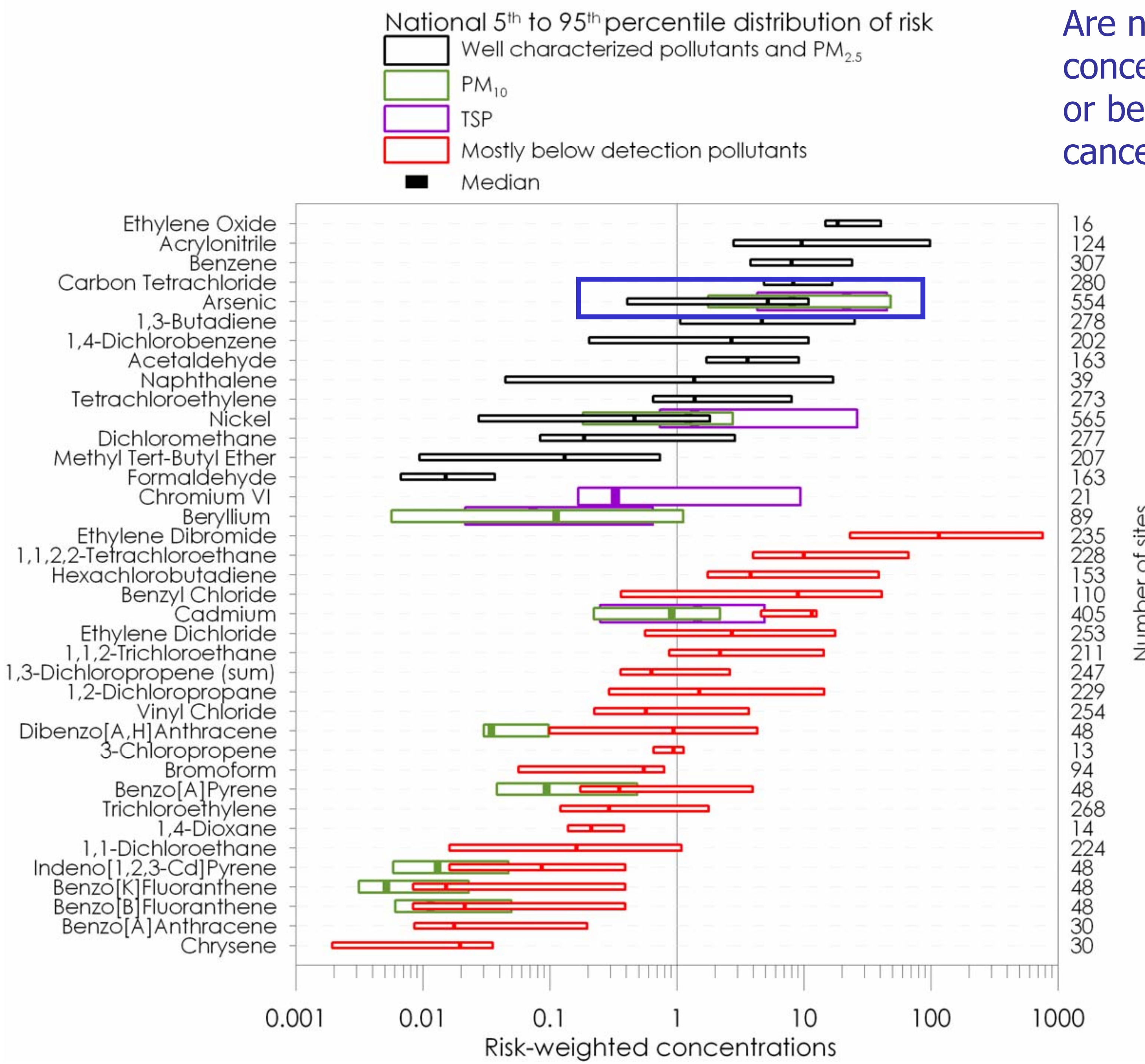


Pollutants colored red had >85% of daily samples below detection nationally at sites used in this analysis.

Risk-weighted concentration ranges are ***conservative upper limits*** based on MDL/2 substitution.

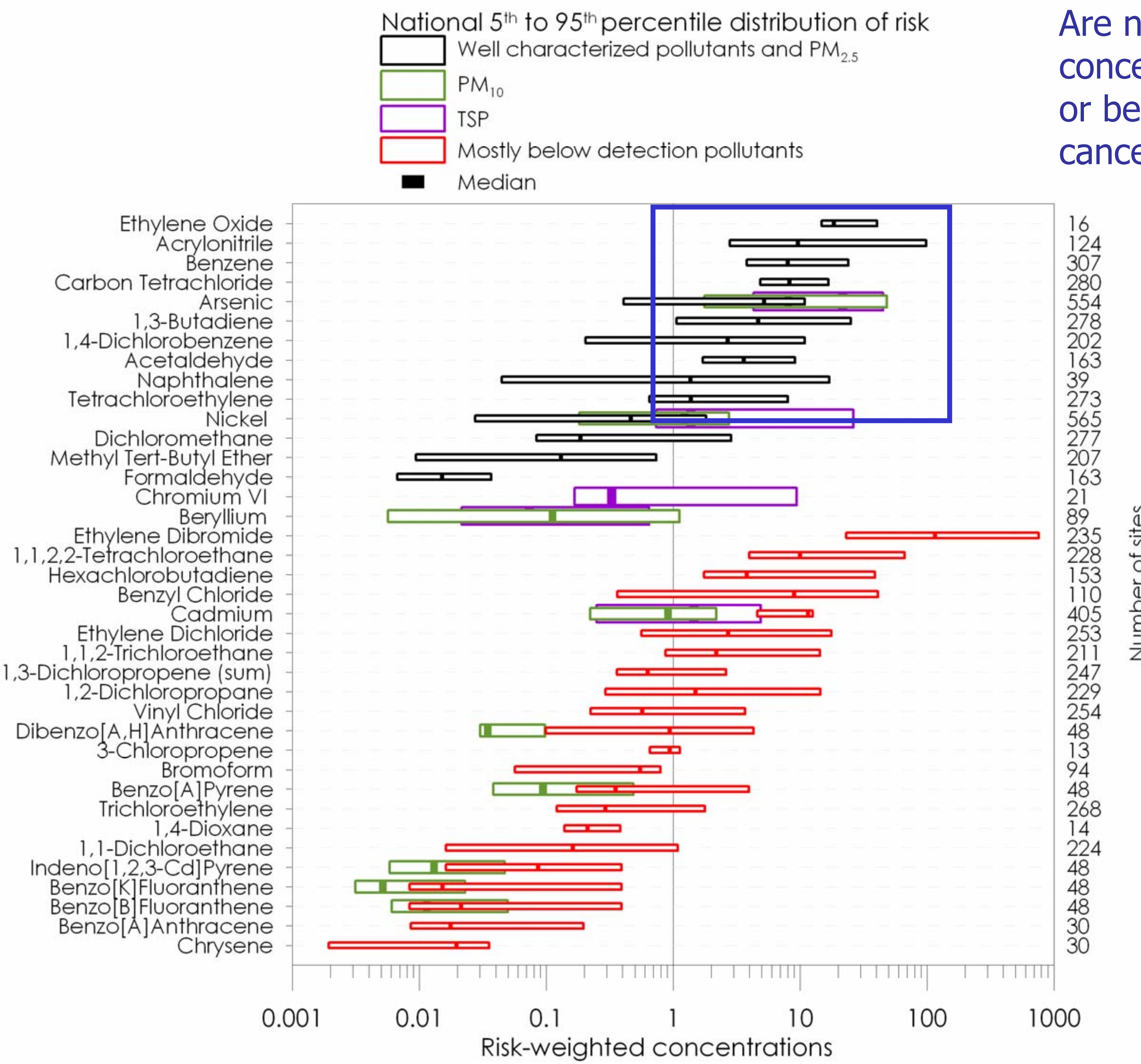
Actual ambient risk-weighted concentrations for these pollutants are likely lower than the ranges shown.

Are national concentrations above or below the 1x10^{-6} cancer benchmark?



Pollutants such as particulate metals that are measured in multiple size fractions are all shown on one line.

Larger size fractions have taller bars and are colored green or purple, while $PM_{2.5}$ is shown as either black or red.

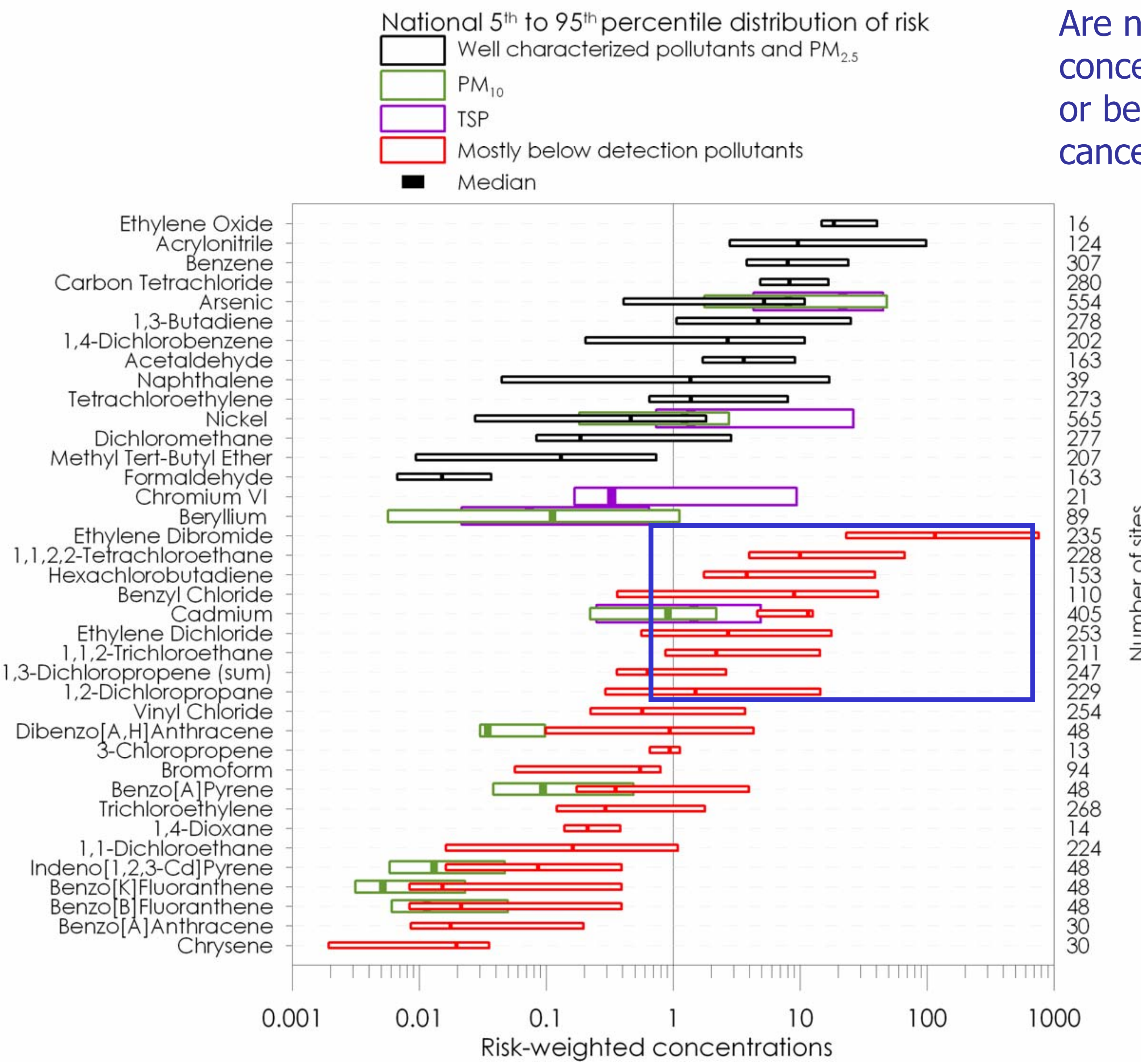


Are national concentrations above or below the $1x10^{-6}$ cancer benchmark?

The pollutants in the blue box are usually significant contributors to risk where measured.

The combined risk burden from these pollutants will be a substantial fraction of total risk.

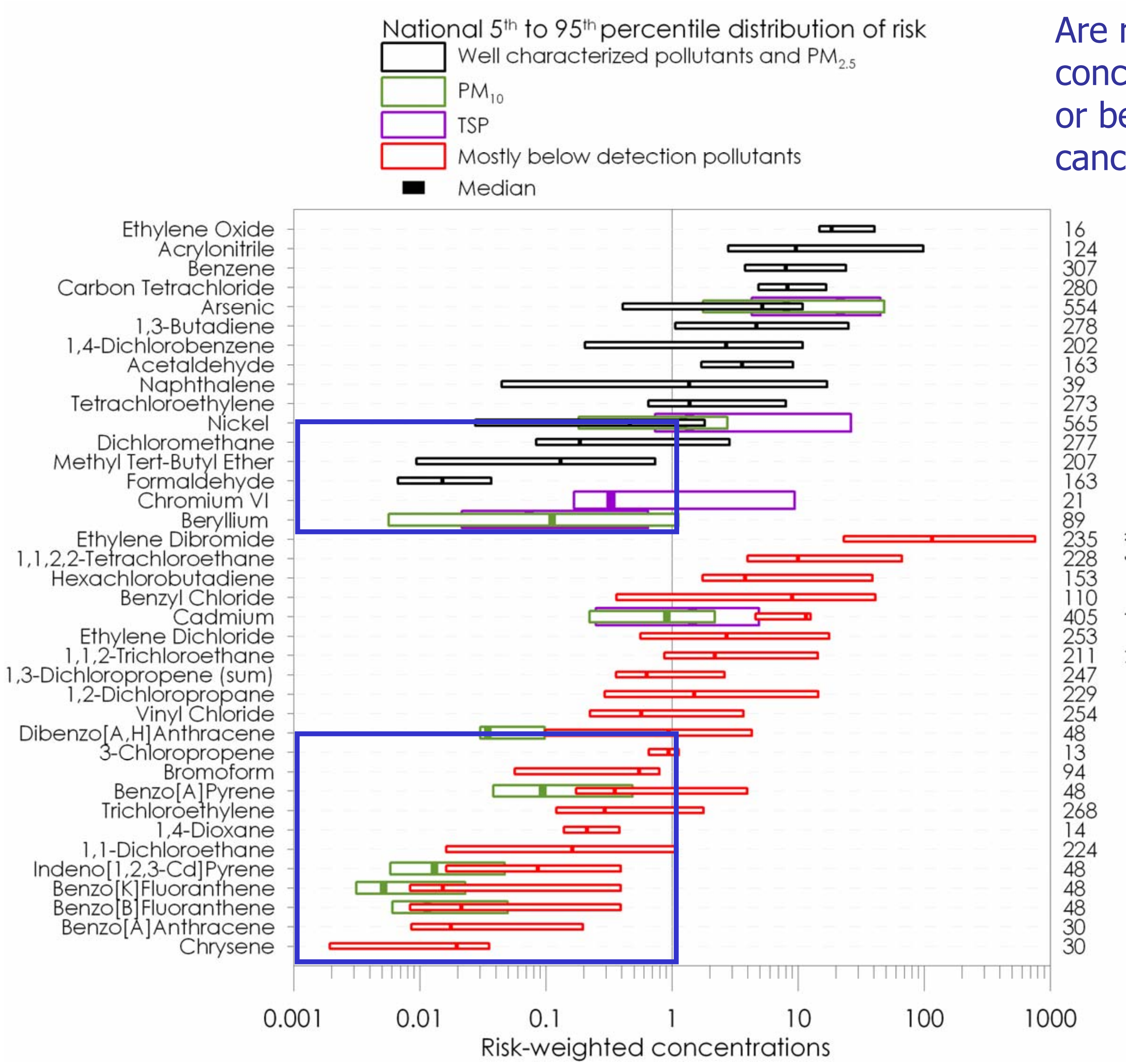
Note ethylene oxide and naphthalene concentrations have few sites in the United States and ranges may not be nationally representative.



Are national concentrations above or below the $1x10^{-6}$ cancer benchmark?

The pollutants in the blue box are possibly significant contributors to risk, but the risk cannot be quantified at this time due to high MDLs relative to the cancer benchmarks (only an upper limit can be shown).

The combined risk burden from these pollutants could be a substantial fraction of total risk.



Are national concentrations above or below the $1x10^{-6}$ cancer benchmark?

Pollutants with risk that are typically below a value of 1 are not identified as problems using this analysis. This is true both for pollutants measured well and not well.

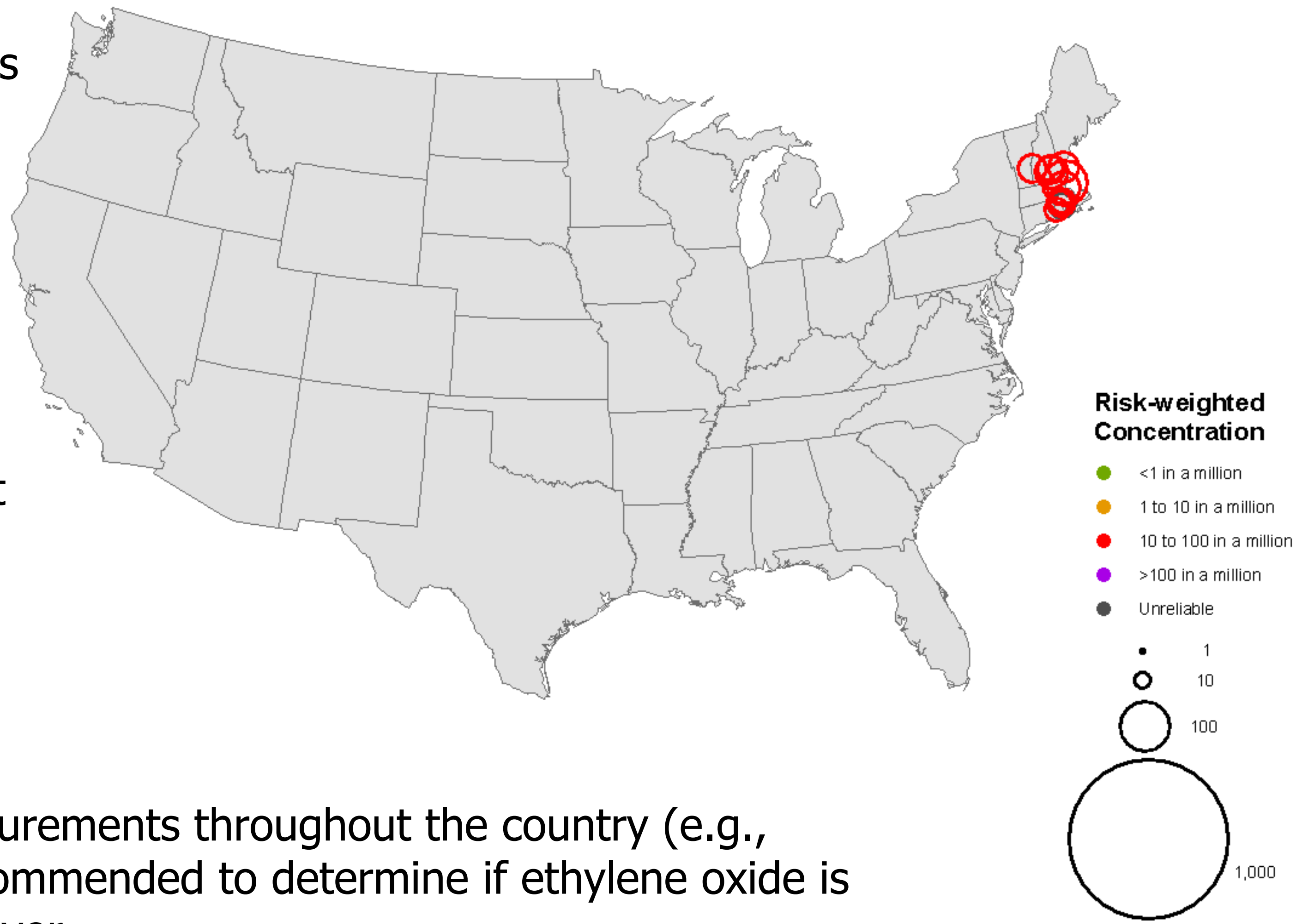
These pollutants do not contribute substantially to cancer risk where measured.

Risk-weighted Concentrations: Spatial Distribution

- The following slides show maps of the site level data included in the previous summaries of national concentration and risk-weighted concentration ranges.
- These maps help us assess the spatial representativeness of the toxics, show where concentrations or risk-weighted concentrations are highest and lowest, and show where concentrations are typically below detection.

Maps of Key Risk-Weighted Toxics: Ethylene Oxide

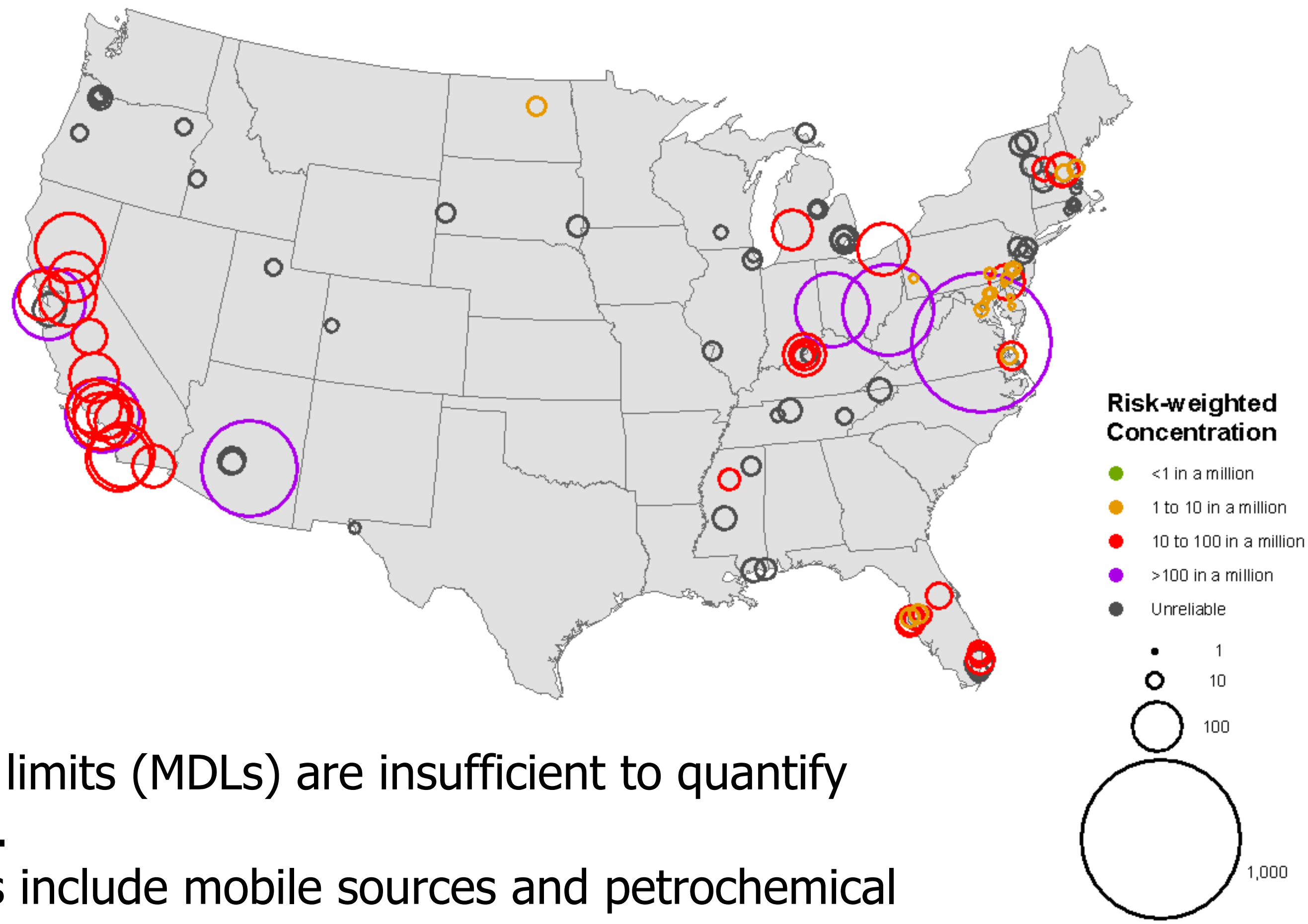
Ethylene oxide is only measured at a few sites in the Northeast United States, but it is above 10-in-a-million risk-weighted concentration at all these sites.



Additional measurements throughout the country (e.g., NATTS) are recommended to determine if ethylene oxide is always a risk driver.

Maps of Key Risk-Weighted Toxics: Acrylonitrile

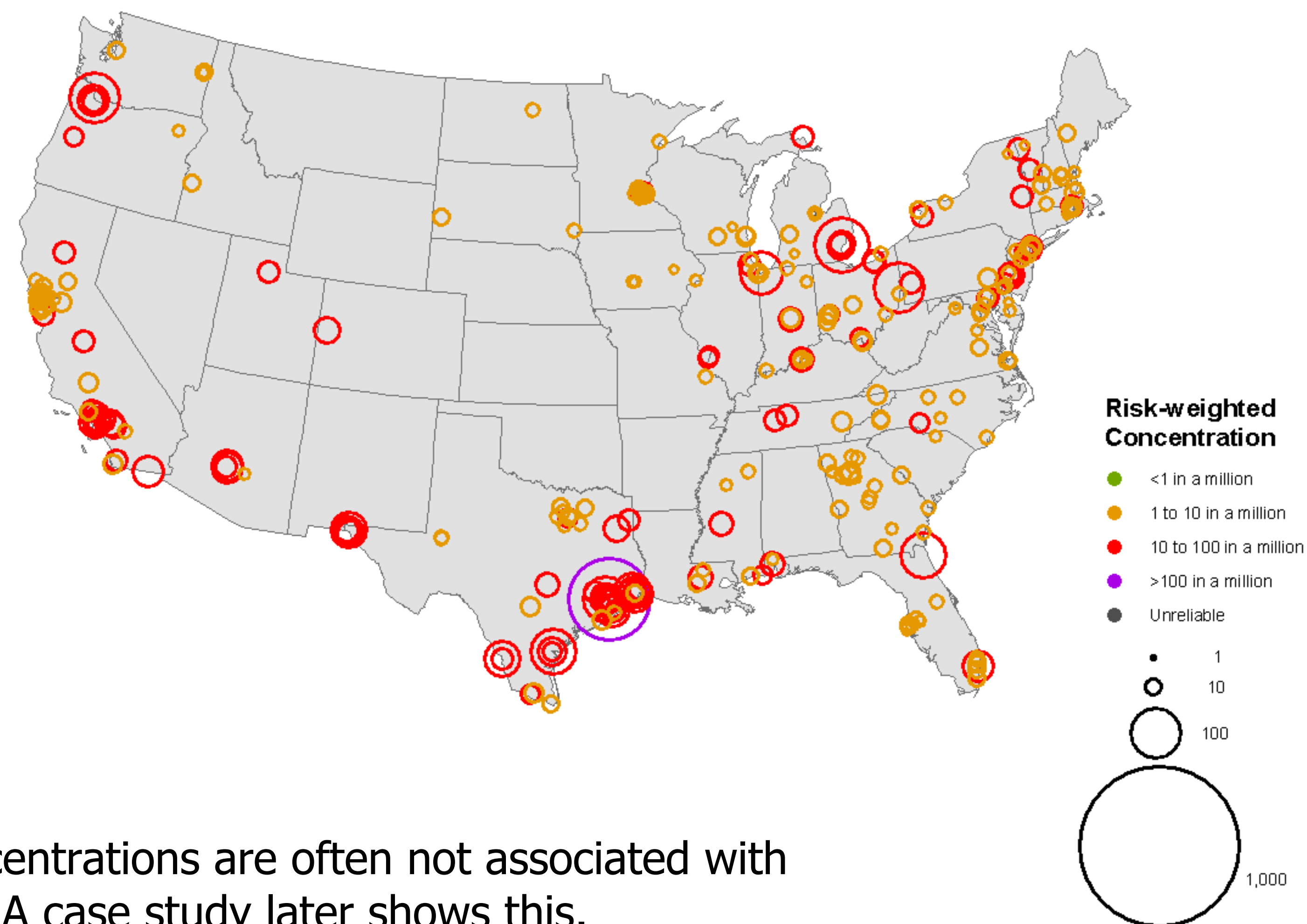
Acrylonitrile's reliable risk-weighted concentrations are above 1-in-a-million, and often above 10-in-a-million risk.



- Method detection limits (MDLs) are insufficient to quantify risk at many sites.
- Emissions sources include mobile sources and petrochemical industry (emitted as an intermediate product). In the inventory, cigarette smoke is also listed as a source.

Maps of Key Risk-Weighted Toxics: Benzene

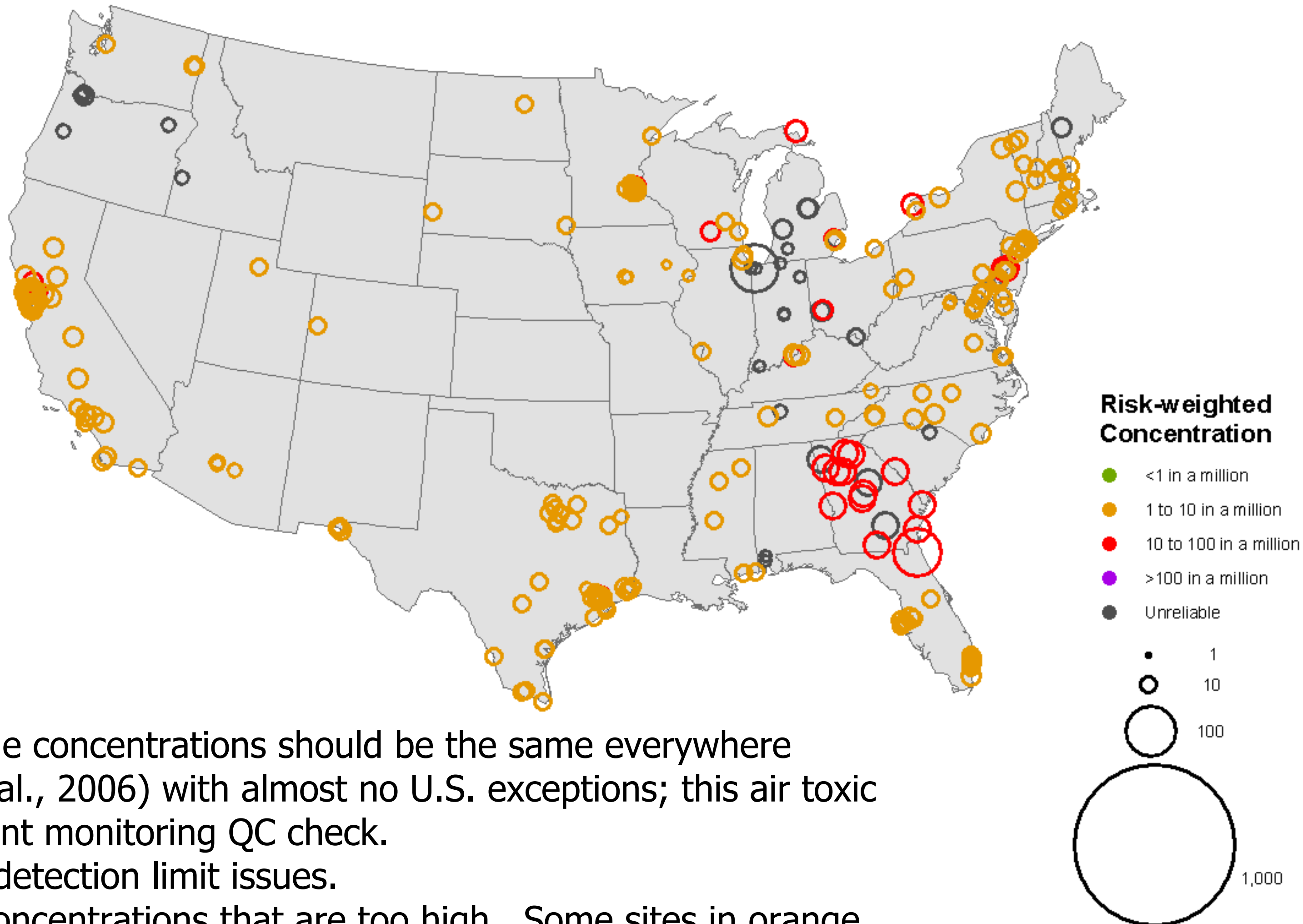
Benzene is above 1-in-a-million risk everywhere, and often above 10-in-a-million risk.



The highest concentrations are often not associated with mobile sources. A case study later shows this.

Maps of Key Risk-Weighted Toxics: Carbon Tetrachloride

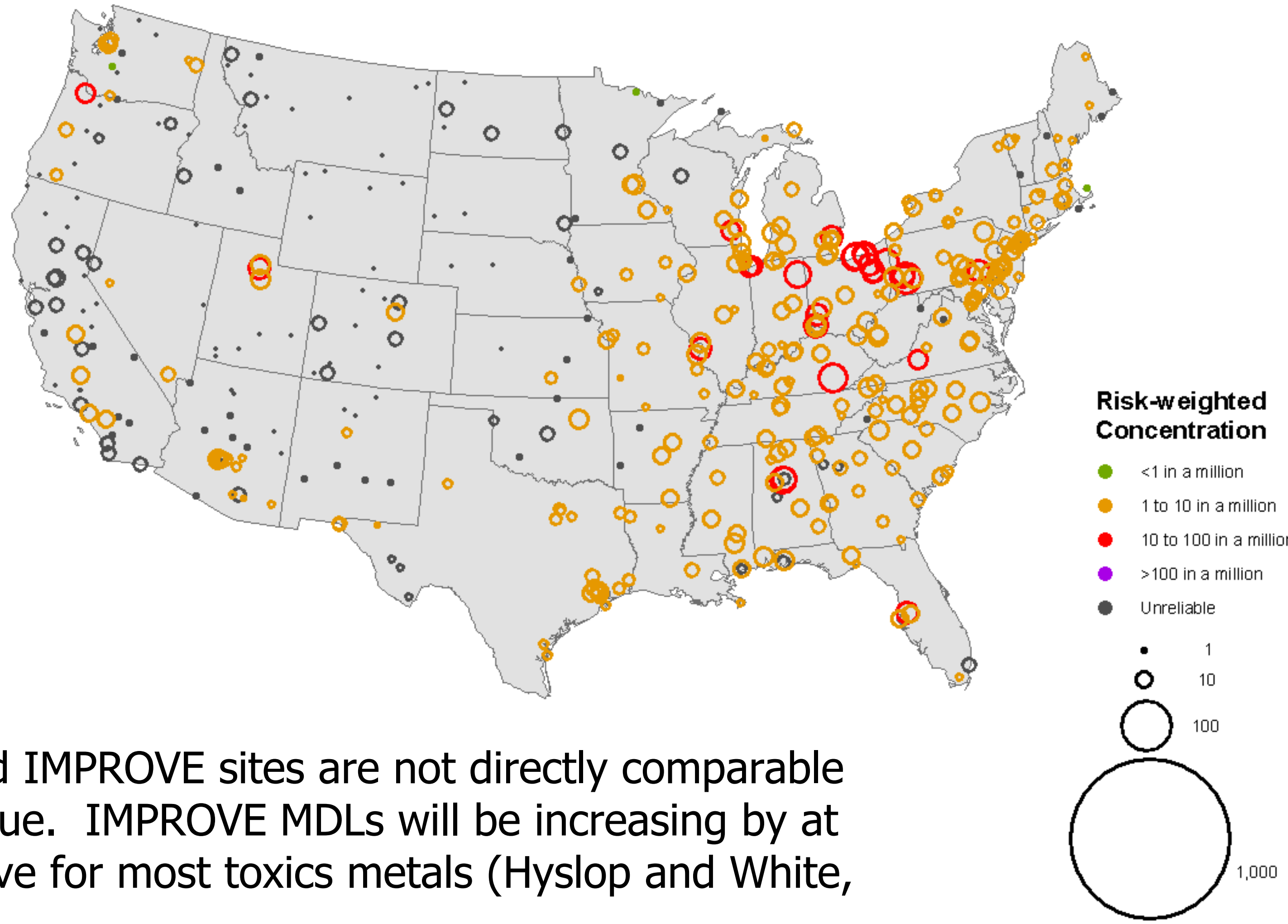
Carbon tetrachloride's risk-weighted concentrations should be 9-in-a-million.



- Carbon tetrachloride concentrations should be the same everywhere (e.g., McCarthy et al., 2006) with almost no U.S. exceptions; this air toxic provides an excellent monitoring QC check.
- Sites in gray have detection limit issues.
- Sites in red have concentrations that are too high. Some sites in orange have concentrations that are too low.

Maps of Key Risk-Weighted Toxics: Arsenic $PM_{2.5}$

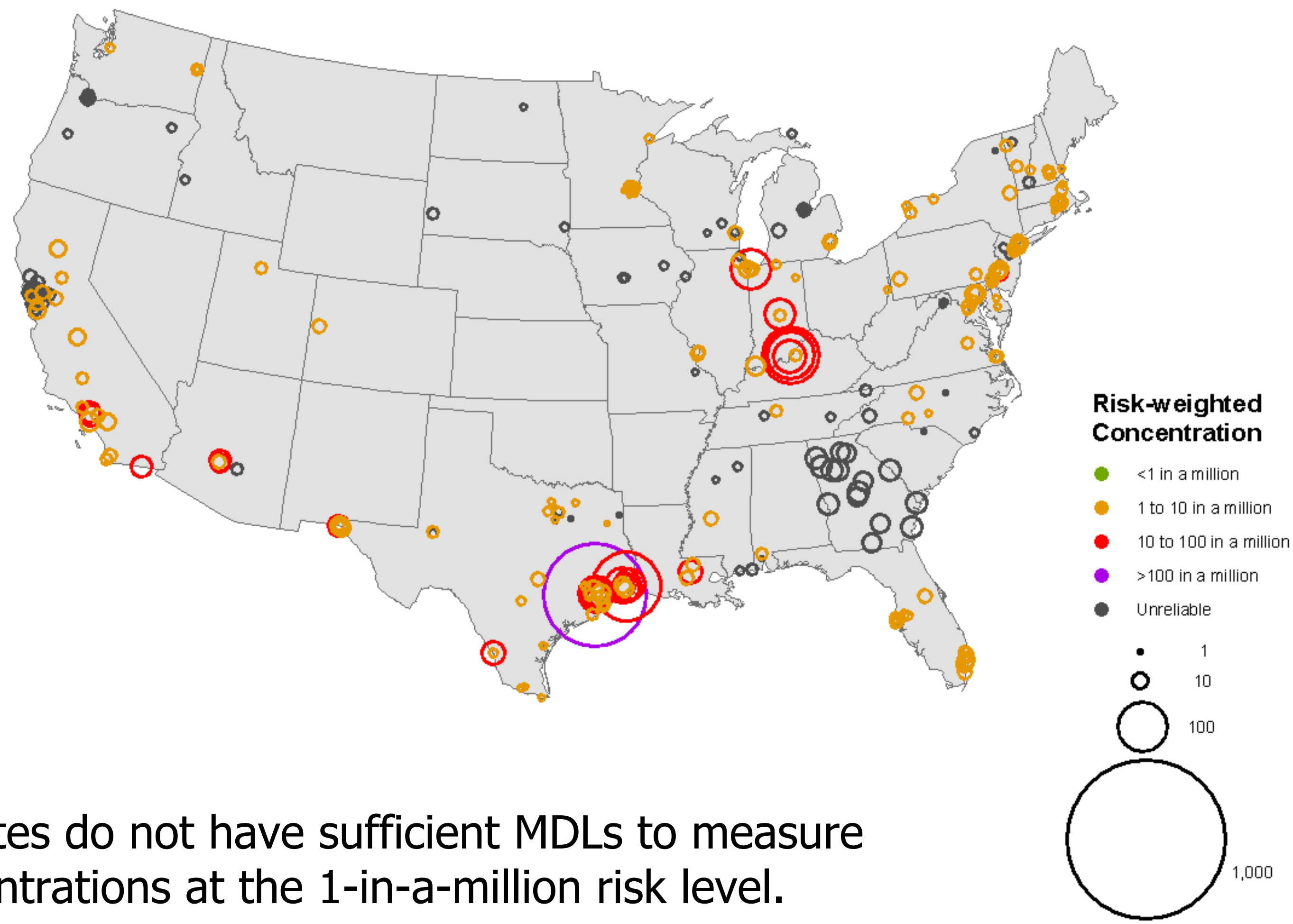
Arsenic $PM_{2.5}$ is typically above the 1-in-a-million risk level throughout the eastern United States.



Note that STN and IMPROVE sites are not directly comparable due to an MDL issue. IMPROVE MDLs will be increasing by at least a factor of five for most toxics metals (Hyslop and White, 2007).

Maps of Key Risk-Weighted Toxics: 1,3-Butadiene

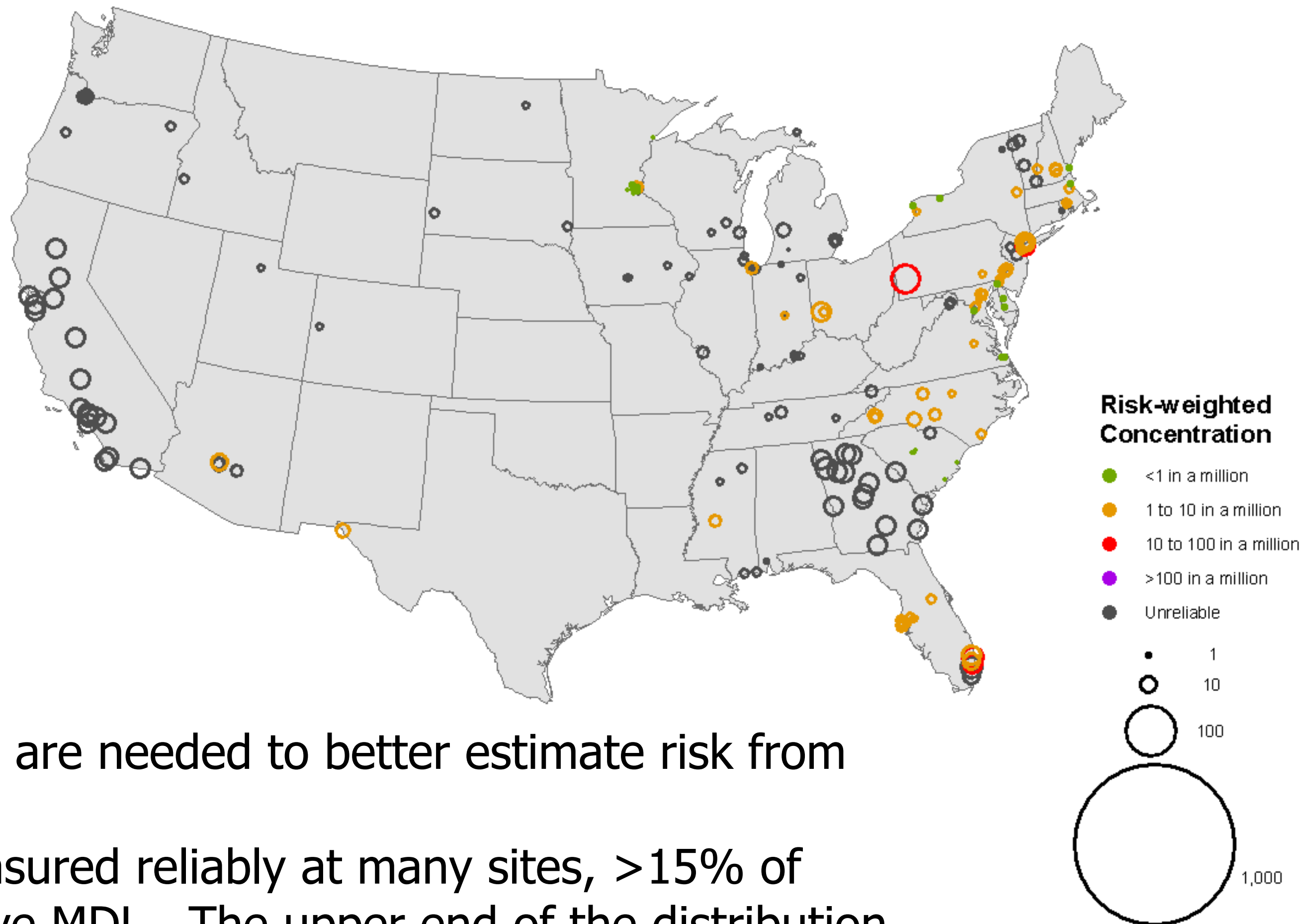
1,3-Butadiene has very high spatial variability.
The highest concentrations are associated with areas with known industrial sources.



A large fraction of sites do not have sufficient MDLs to measure 1,3-butadiene concentrations at the 1-in-a-million risk level.

Maps of Key Risk-Weighted Toxics: 1,4-Dichlorobenzene

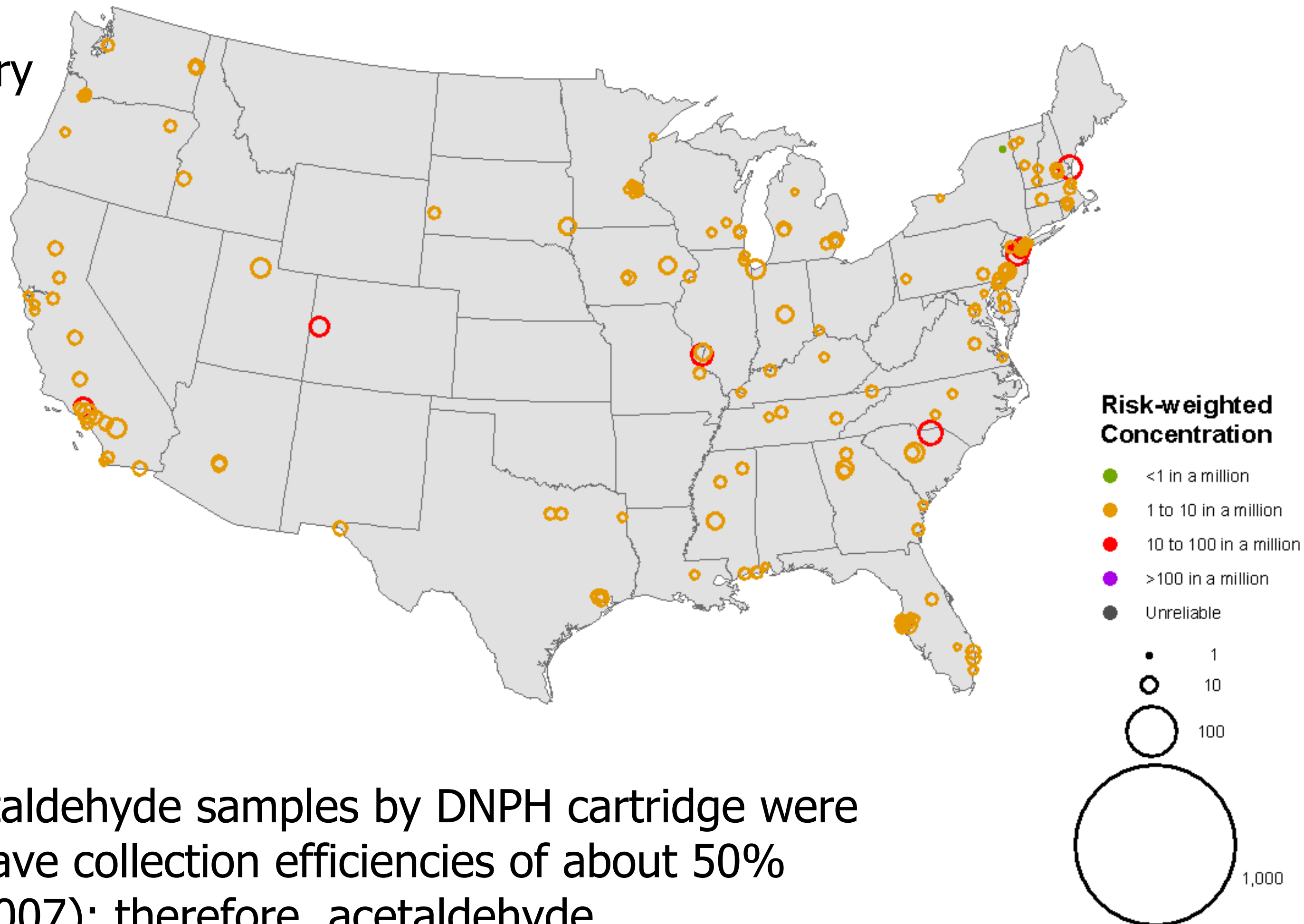
Most monitoring sites can not detect 1,4-dichlorobenzene at the 1-in-a-million (or 10-in-a-million) level.



- Better detection limits are needed to better estimate risk from 1,4-dichlorobenzene.
- Although it is not measured reliably at many sites, >15% of data nationally is above MDL. The upper end of the distribution is also skewed by a large number of monitoring sites with high detection limits in California and Georgia.

Maps of Key Risk-Weighted Toxics: Acetaldehyde

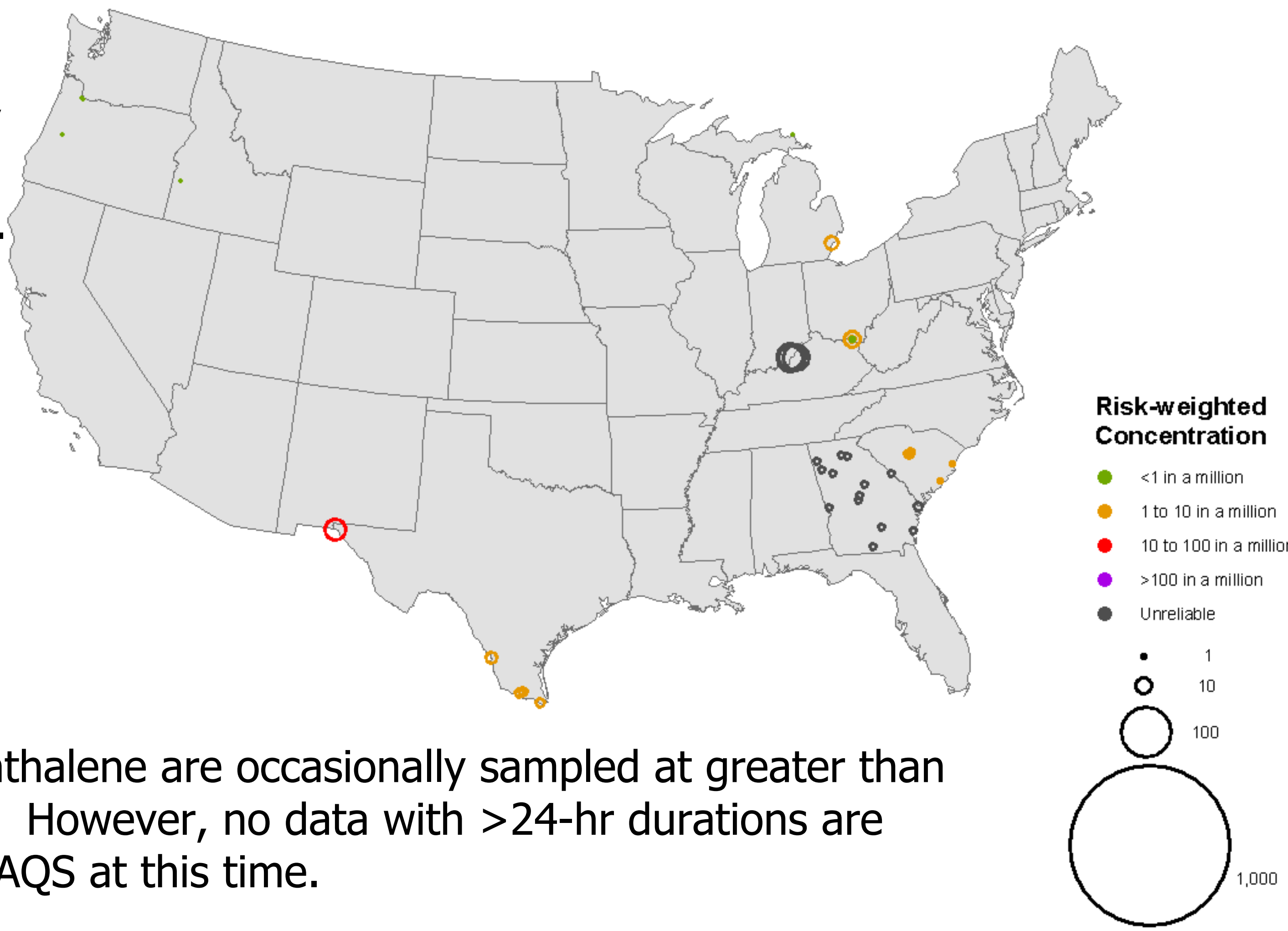
Acetaldehyde has very low spatial variability and only a few sites with over 10-in-a-million risk levels.



Note that 24-hr acetaldehyde samples by DNPH cartridge were recently shown to have collection efficiencies of about 50% (Herrington et al., 2007); therefore, acetaldehyde concentrations (and risk) may be twice the values shown here.

Maps of Key Risk-Weighed Toxics: Naphthalene

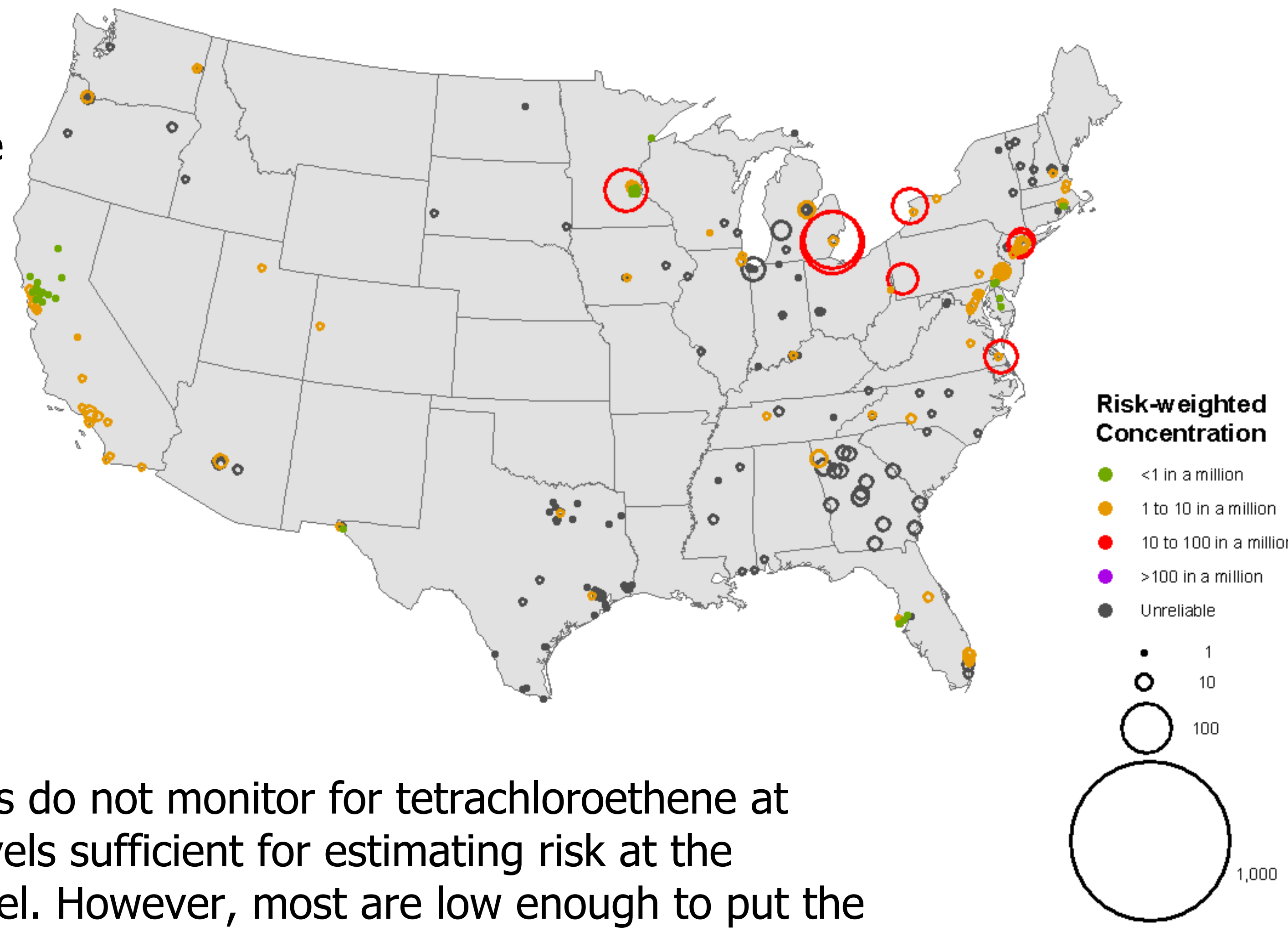
Naphthalene is relatively sparsely monitored and MDLs vary widely.



- SVOCs like naphthalene are occasionally sampled at greater than 24-hr durations. However, no data with >24-hr durations are available in the AQS at this time.

Maps of Key Risk-Weighted Toxics: Tetrachloroethylene

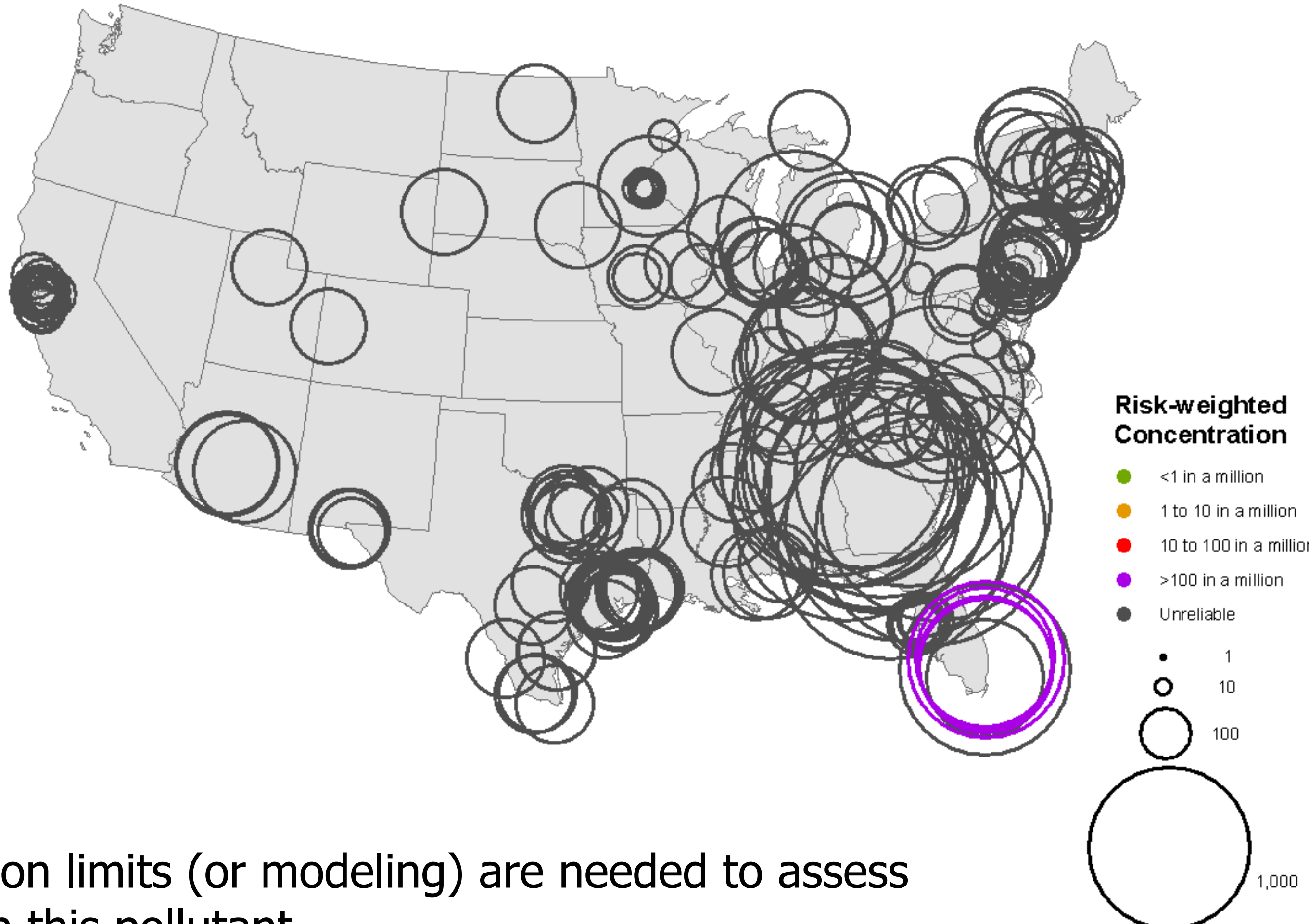
The risk associated with tetrachloroethylene is usually close to 1-in-a-million, with the exception of a few hot spots.



Again, many sites do not monitor for tetrachloroethene at concentration levels sufficient for estimating risk at the 1-in-a-million level. However, most are low enough to put the risk levels below 5-in-a-million.

Maps of Unreliable Risk-Weighted Toxics: Ethylene Dibromide

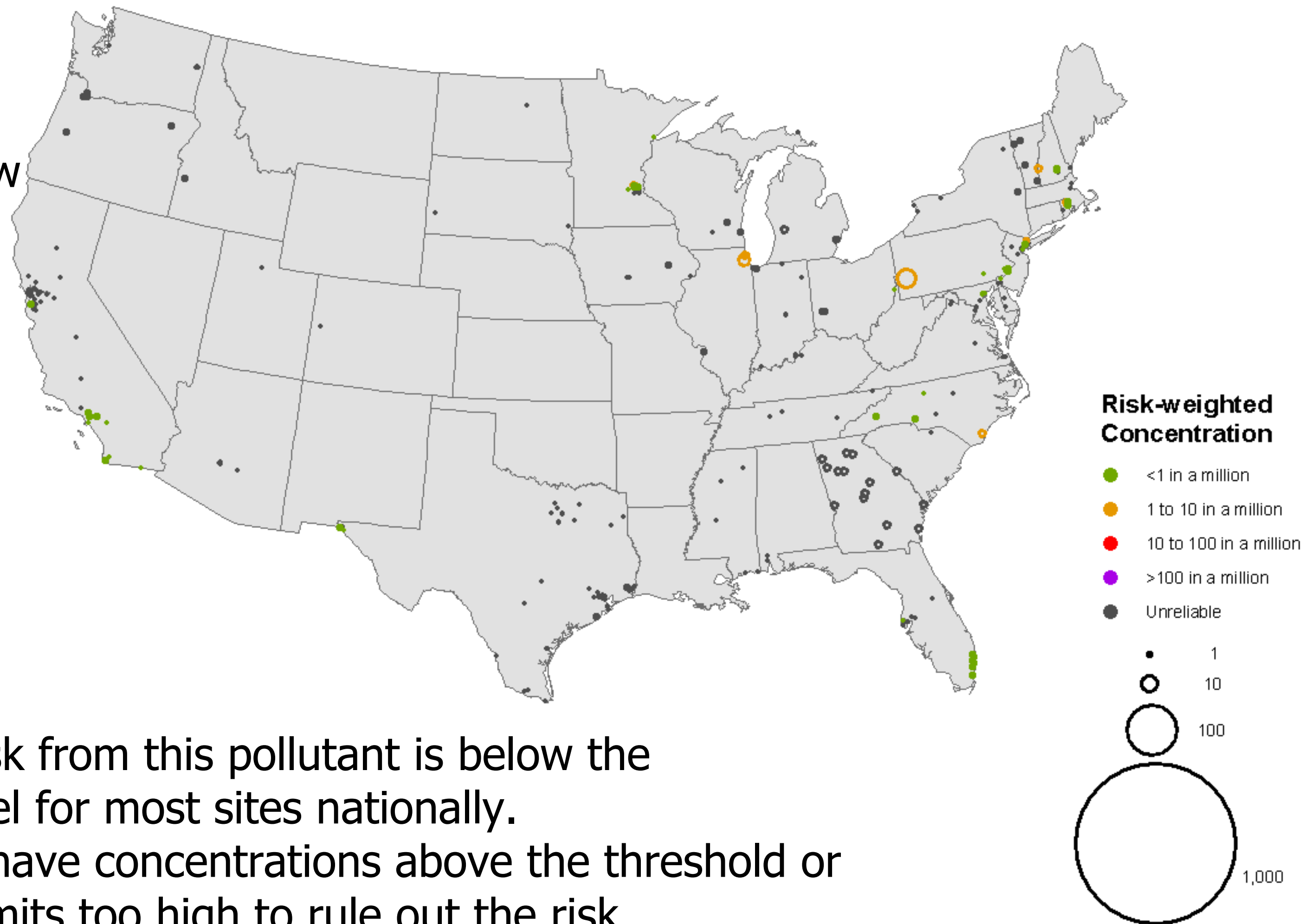
The possible risk associated with ethylene dibromide is very high, because MDLs are a factor of 100 higher than the cancer benchmark.



Much lower detection limits (or modeling) are needed to assess risk associated with this pollutant.

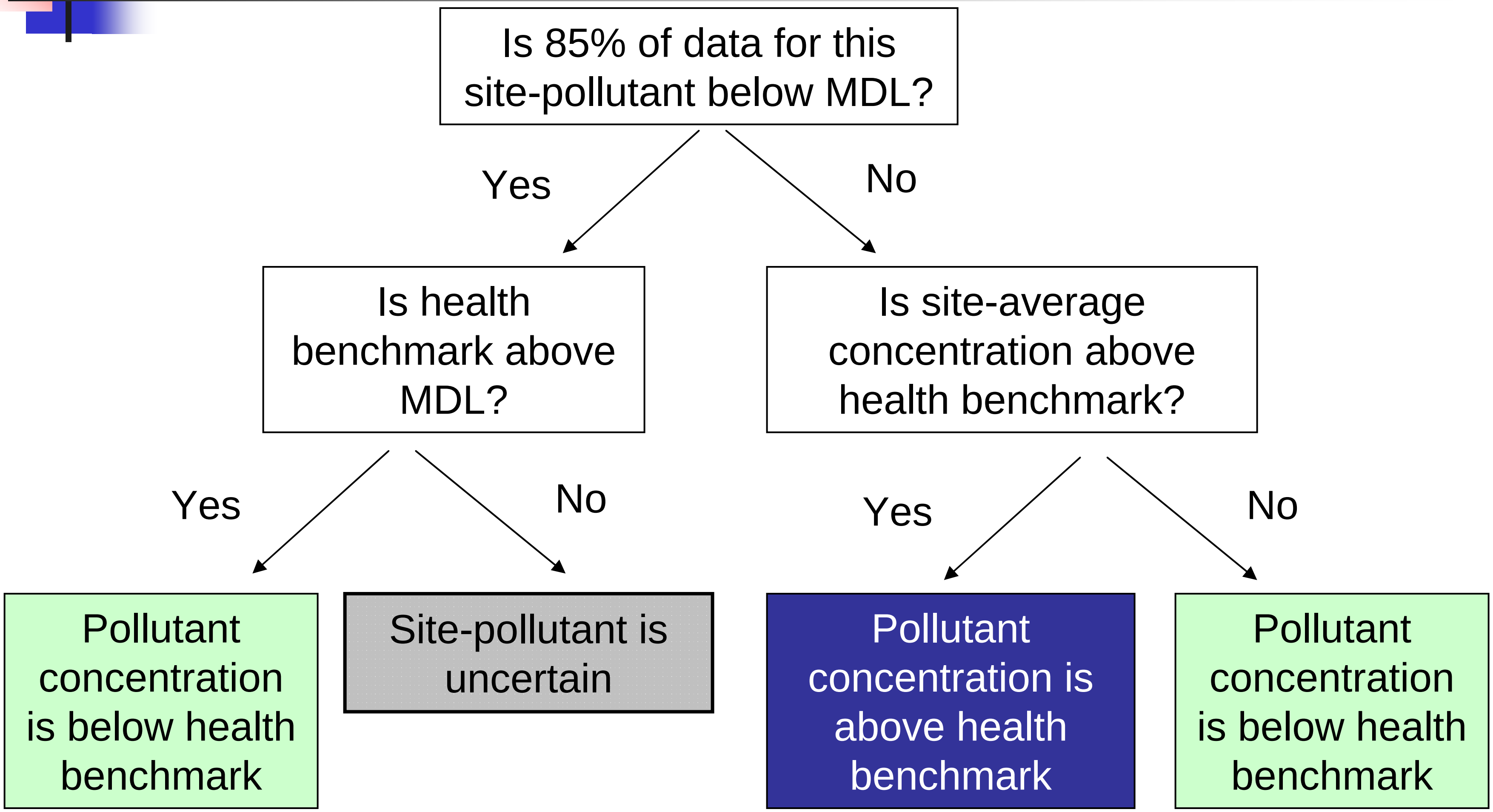
Maps of Low Risk-weighted Toxics: Trichloroethylene

Trichloroethylene concentrations are almost always below MDL, but MDLs are below the cancer benchmark.



- Therefore, the risk from this pollutant is below the 1-in-a-million level for most sites nationally.
- Only a few sites have concentrations above the threshold or have detection limits too high to rule out the risk.

Categorical Risk Screening: Approach



Pollutants Above or Possibly Above 10^{-5} Risk levels at >20% of Sites

Pollutant	Number of sites with concentrations above 10^{-5} cancer risk	Percent of sites with concentrations above 10^{-5} cancer risk	Number of uncertain sites (85% of data below MDL and cancer benchmark below MDL)	Percent of sites above or possibly above 10^{-5} cancer risk
Benzene	113	37	0	37
Acrylonitrile	43	35	41	68
Ethylene Oxide	13	81	3	100
Carbon Tetrachloride	29	10	27	20
Benzyl Chloride	9	8	56	59
1,1,2,2-Tetrachloroethane	12	5	169	80
Hexachlorobutadiene	6	4	59	42
Arsenic TSP	4	5	49	65
1,4-Dichlorobenzene	6	3	35	20
Ethylene Dibromide	6	3	227	100
Arsenic PM_{10}	2	5	12	38
Ethylene Dichloride	4	2	54	23
Cadmium $PM_{2.5}$	1	0	186	72

Counts of sites with <10^{-5} risk are not explicitly shown in this table.

Pollutants Above or Possibly Above 10^{-6} Risk at >50% of Sites

Pollutant	Number of sites	Number of sites with concentration above 10^{-6} cancer risk	Percent of sites with concentrations above 10^{-6} cancer risk	Number of uncertain sites (85% of data below MDL and cancer benchmark below MDL)	Percent of sites above or possibly above 10^{-6} cancer risk
Benzene	305	304	100	0	100
Acetaldehyde	161	160	99	0	99
Carbon Tetrachloride	278	237	85	41	100
Ethylene Oxide	16	13	81	3	100
1,3-Butadiene	276	193	70	82	100
Arsenic $PM_{2.5}$	432	288	67	46	77
Arsenic PM_{10}	37	22	59	14	97
Nickel PM_{10}	35	20	57	3	66
Acrylonitrile	124	64	52	60	100
Arsenic TSP	82	33	40	49	100
Tetrachloroethylene	271	99	37	137	87
Cadmium PM_{10}	36	13	36	8	58
Naphthalene	39	13	33	20	85
1,4-Dichlorobenzene	202	66	33	104	84
Nickel TSP	101	26	26	57	82
Cadmium TSP	105	16	15	60	72
Benzyl Chloride	110	14	13	78	84
Hexachlorobutadiene	153	12	8	136	97
1,1,2,2-Tetrachloroethane	226	12	5	213	100
1,2-Dichloropropane	227	12	5	178	84
Vinyl Chloride	252	11	4	177	75
Ethylene Dichloride	251	9	4	239	99
1,1,2-Trichloroethane	211	6	3	202	99
Ethylene Dibromide	233	6	3	227	100
Cadmium $PM_{2.5}$	261	5	2	256	100
Dibenzo[A,H]Anthracene	30	0	0	19	63

Counts of sites with $<10^{-6}$ risk are not explicitly shown in this table.

Quantifying Our Confidence in Toxics of Concern

- A weighted method was created to quantify the level of confidence that a specific pollutant is usually measured at or above a level of concern.
- Using our 10^{-6} risk screening results, we weight the values above 10^{-6} as 1, the values below 10^{-6} as -1, and uncertain values as 0.
- We then sum the results across sites.
- We have the highest confidence in pollutants with higher magnitudes (positive or negative).

Determining which Pollutants are Most Likely above the 10^{-6} Level Nationally

Pollutant Name	# sites	Fraction rank	Weighted Rank
Benzene	305	1.0	305
Carbon Tetrachloride	278	0.9	237
Arsenic PM2.5	432	0.5	200
1,3-Butadiene	276	0.6	179
Acetaldehyde	161	1.0	159
Tetrachloroethylene	271	0.3	74
Acrylonitrile	124	0.5	64
Arsenic TSP	82	0.4	33
1,4-Dichlorobenzene	202	0.2	31
Arsenic PM10	37	0.6	21
Nickel TSP	101	0.2	18
1,1,2,2-Tetrachloroethane	226	0.1	13
Ethylene Oxide	16	0.8	13
Hexachlorobutadiene	153	0.1	11
Naphthalene	39	0.3	10
Benzyl Chloride	110	0.1	10
Nickel PM10	35	0.3	9
Ethylene Dibromide	233	0.0	6
Cadmium PM2.5	261	0.0	5
Cadmium TSP	105	0.0	4
1,3-Dichloropropene(Total)	3	1.0	3
Arsenic PM10	3	1.0	3
1,2-Dibromo-3-Chloropropane	6	0.0	0

Pollutant Name	# sites	Fraction rank	Weighted Rank
1,2-Dichloropropane	227	0.0	-1
3-Chloropropene	13	-0.8	-10
Cadmium PM10	36	-0.3	-11
1,4-Dioxane	14	-1.0	-14
Chromium VI TSP	20	-0.8	-16
Benzo(A)Pyrene PM10	18	-1.0	-18
Benzo(B)Fluranthene PM10	18	-1.0	-18
Benzo(K)Fluoranthene PM10	18	-1.0	-18
Dibenz(A-H)Anthracene PM10	18	-1.0	-18
Indeno[1,2,3-Cd] Pyrene PM10	18	-1.0	-18
Dibenzo[A,H]Anthracene	30	-0.6	-19
Benzo[A]Pyrene	30	-0.7	-21
Ethylene Dichloride	251	-0.1	-24
Beryllium PM10	26	-1.0	-26
Benzo[A]Anthracene	30	-1.0	-30
Benzo[B]Fluoranthene	30	-1.0	-30
Benzo[K]Fluoranthene	30	-1.0	-30
Chrysene	30	-1.0	-30
Indeno[1,2,3-Cd]Pyrene	30	-1.0	-30
1,1,2-Trichloroethane	211	-0.2	-37
Beryllium TSP	62	-0.9	-58
Bromoform	94	-0.9	-88
Vinyl Chloride	252	-0.6	-159
Formaldehyde	161	-1.0	-161
1,1-Dichloroethane	224	-0.9	-193
Methyl Tert-Butyl Ether	207	-1.0	-197
Trichloroethylene	266	-0.8	-209
Dichloromethane	275	-0.8	-222
Nickel PM2.5	426	-0.8	-342

Confidence that National Risk-weighted Concentrations are $>10^{-6}$

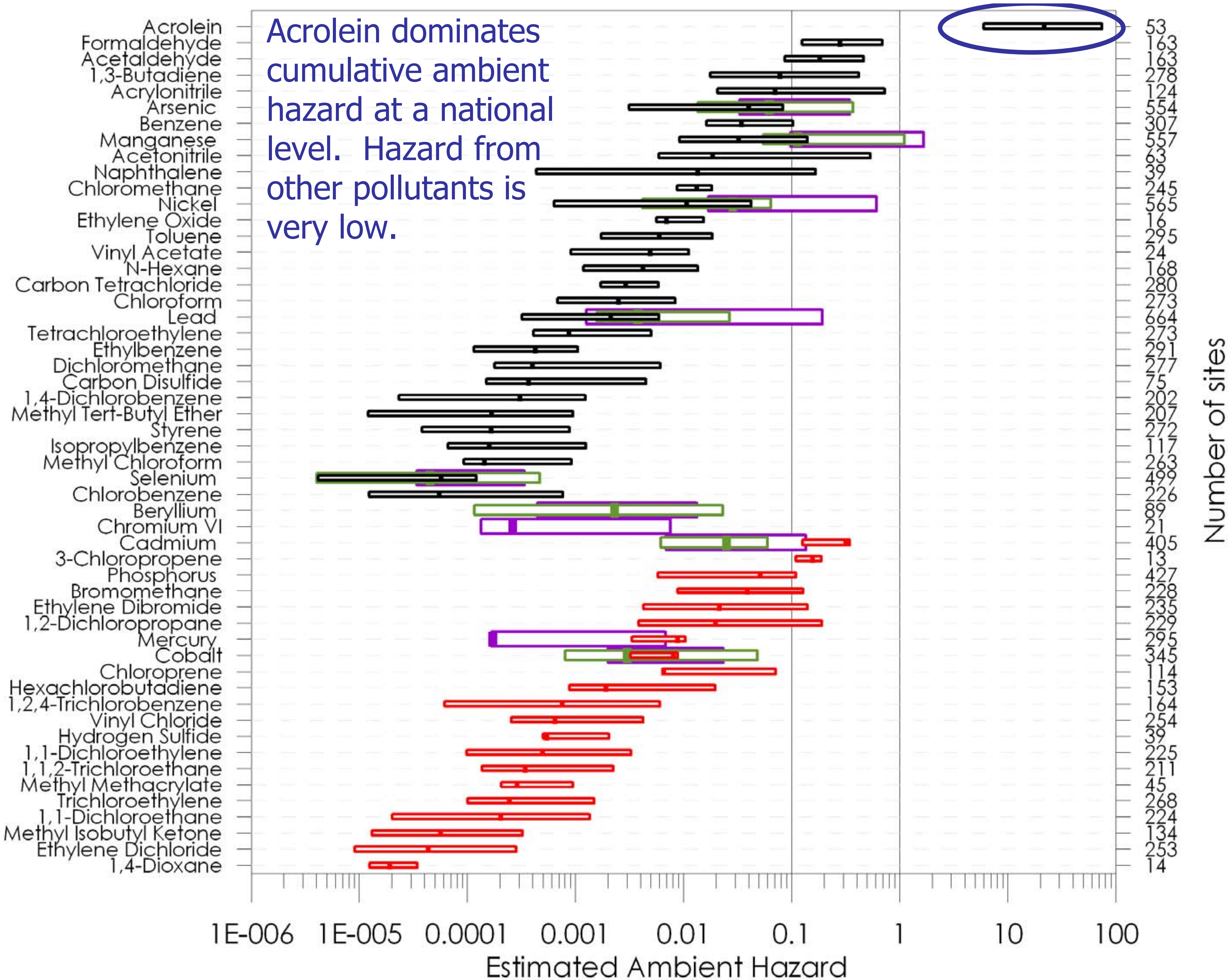
Certain	**Likely**	**Unknown**	**Unlikely**	**Not a national problem**
Benzene	Tetrachloroethylene	Ethylene dibromide	3-Chloroprene	Vinyl Chloride
Carbon tetrachloride	Acrylonitrile	1,1,2,2-tetrachloroethane	Chromium VI	Formaldehyde
Acetaldehyde	1,4-Dichlorobenzene	Hexachlorobutadiene	Individual PAHs	1,1-Dichloroethane
Arsenic	Nickel (TSP and PM10)	Benzyl Chloride	Bromoform	MTBE
1,3-Butadiene	Ethylene oxide	Cadmium	Beryllium	Trichloroethylene
	Naphthalene	1,2-Dichloropropane		Dichloromethane
		Ethylene dichloride		Nickel PM2.5
		1,1,2-Trichloroethane		
		1,3-Dichloropropene		

Noncancer Hazard

- We perform the same basic analyses for chronic hazard using OAQPS reference concentrations as we just showed for the cancer risk.
- An additional acute and subchronic hazard screening was performed on daily and subdaily measurements. Minimum risk levels (MRLs) were used for daily screening values.
- For the estimated ambient hazard, the following definitions are used:

National 5th to 95th percentile distribution of risk

- Well characterized pollutants and $PM_{2.5}$
- PM_{10}
- TSP
- Mostly below detection pollutants
- Median


Acrolein dominates cumulative ambient hazard at a national level. Hazard from other pollutants is very low.
Acrolein
Formaldehyde
Acetaldehyde
1,3-Butadiene
Acrylonitrile
Arsenic
Benzene
Manganese
Acetonitrile
Naphthalene
Chloromethane
Nickel
Ethylene Oxide
Toluene
Vinyl Acetate
N-Hexane
Carbon Tetrachloride
Chloroform
Lead
Tetrachloroethylene
Ethylbenzene
Dichloromethane
Carbon Disulfide
1,4-Dichlorobenzene
Methyl Tert-Butyl Ether
Styrene
Isopropylbenzene
Methyl Chloroform
Selenium
Chlorobenzene
Beryllium
Chromium VI
Cadmium
3-Chloropropene
Phosphorus
Bromomethane
Ethylene Dibromide
1,2-Dichloropropane
Mercury
Cobalt
Chloroprene
Hexachlorobutadiene
1,2,4-Trichlorobenzene
Vinyl Chloride
Hydrogen Sulfide
1,1-Dichloroethylene
1,1,2-Trichloroethane
Methyl Methacrylate
Trichloroethylene
1,1-Dichloroethane
Methyl Isobutyl Ketone
Ethylene Dichloride
1,4-Dioxane
53
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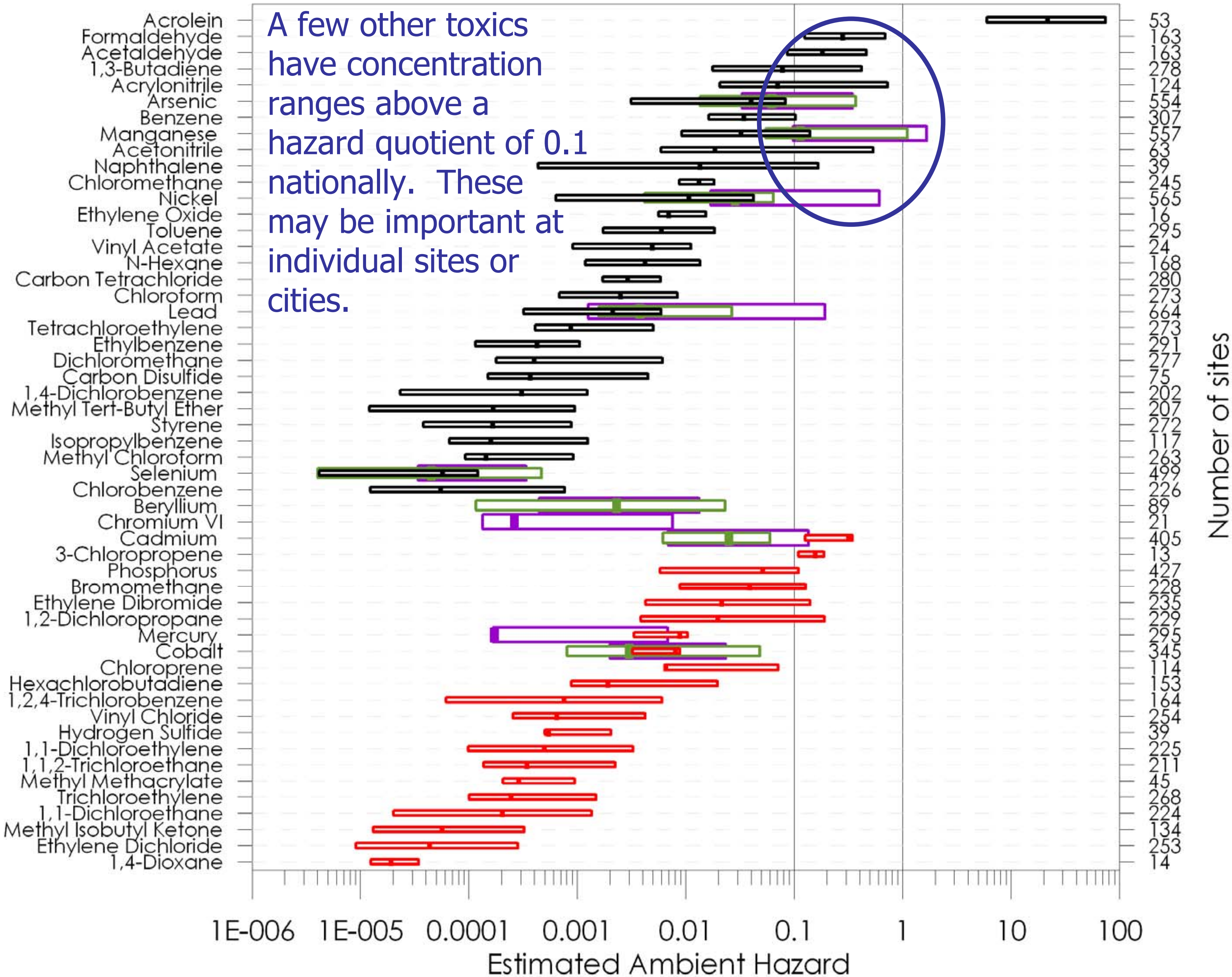
245
565
16
295
24
168
280
273
664
273
291
277
75
202
207
272
117
263
499
226
89
21
405
13
427
228
235
229
295
345
114
153
164
254
39
225
211
45
268
224
134
253
14
Number of sites
1E-006
1E-005
0.0001
0.001
0.01
0.1
1
10
100
Estimated Ambient Hazard


A few other toxics have concentration ranges above a hazard quotient of 0.1 nationally. These may be important at individual sites or cities.
Acrolein
Formaldehyde
Acetaldehyde
1,3-Butadiene
Acrylonitrile
Arsenic
Benzene
Manganese
Acetonitrile
Naphthalene
Chloromethane
Nickel
Ethylene Oxide
Toluene
Vinyl Acetate
N-Hexane
Carbon Tetrachloride
Chloroform
Lead
Tetrachloroethylene
Ethylbenzene
Dichloromethane
Carbon Disulfide
1,4-Dichlorobenzene
Methyl Tert-Butyl Ether
Styrene
Isopropylbenzene
Methyl Chloroform
Selenium
Chlorobenzene
Beryllium
Chromium VI
Cadmium
3-Chloropropene
Phosphorus
Bromomethane
Ethylene Dibromide
1,2-Dichloropropane
Mercury
Cobalt
Chloroprene
Hexachlorobutadiene
1,2,4-Trichlorobenzene
Vinyl Chloride
Hydrogen Sulfide
1,1-Dichloroethylene
1,1,2-Trichloroethane
Methyl Methacrylate
Trichloroethylene
1,1-Dichloroethane
Methyl Isobutyl Ketone
Ethylene Dichloride
1,4-Dioxane
53
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163
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124
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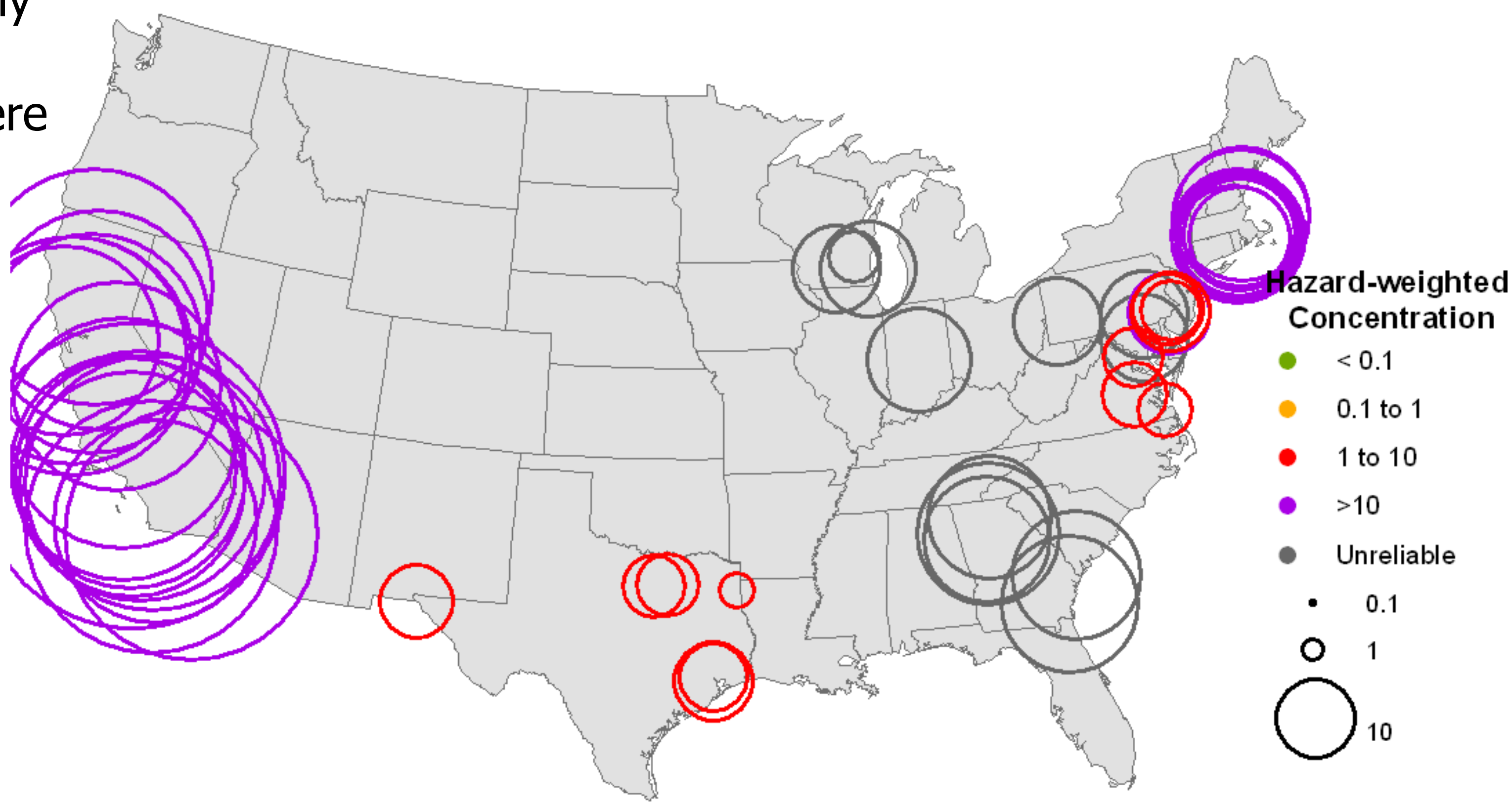
273
664
273
291
277
75
202
207
272
117
263
499
226
89
21
405
13
427
228
235
229
295
345
114
153
164
254
39
225
211
45
268
224
134
253
14
Number of sites
1E-006
1E-005
0.0001
0.001
0.01
0.1
1
10
100
Estimated Ambient Hazard

Maps of Key Hazard-Weighted Toxics: Acrolein

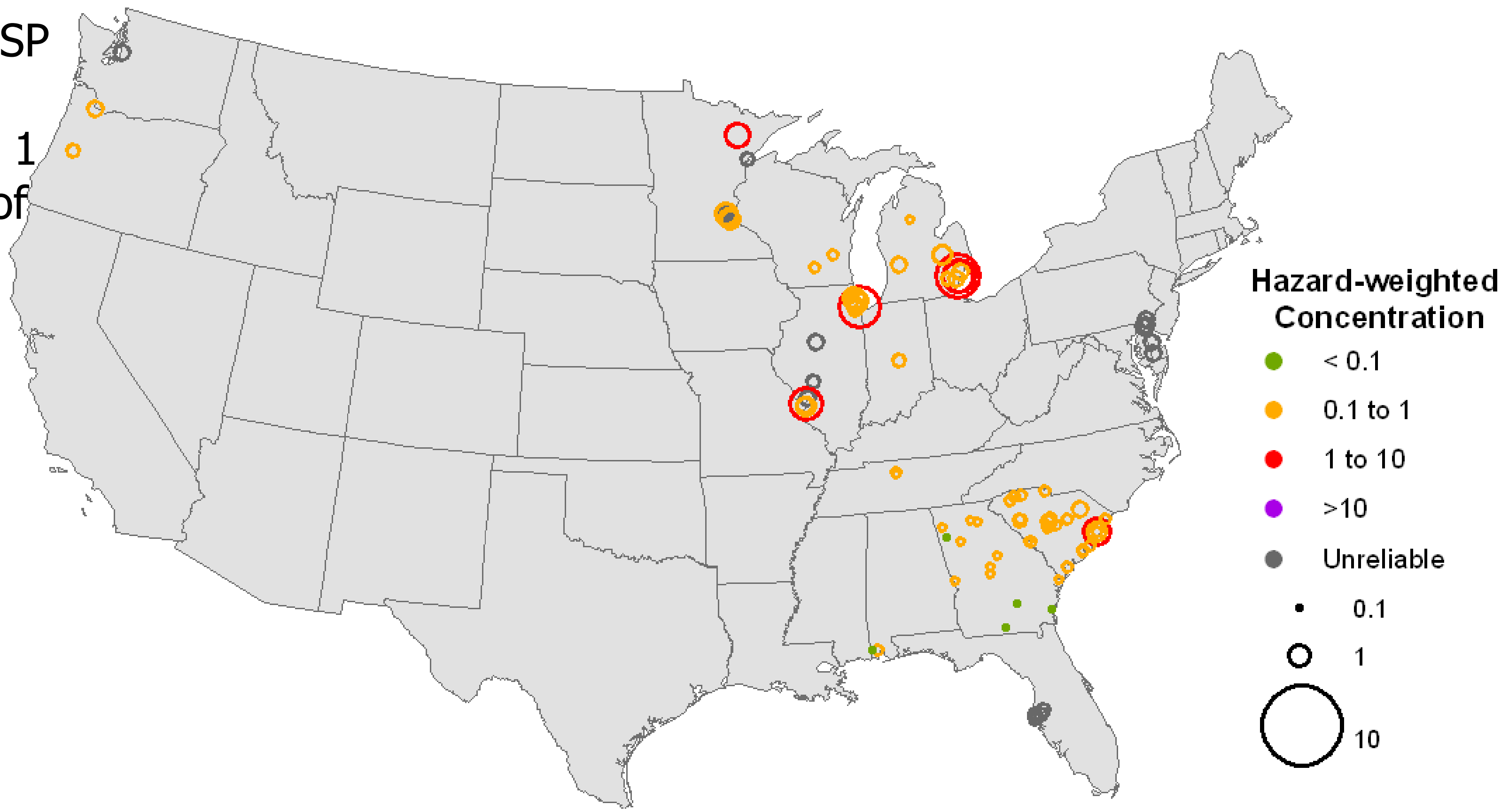
Acrolein is typically above a hazard quotient of 1 where measured.



Note that these values are individually unreliable as shown in Phases I and II of the National Data Analysis. However, newer, more reliable measurements show similar concentration ranges (we'll show this later).

Maps of Key Hazard-Weighted Toxics: Manganese TSP

Manganese TSP has a hazard quotient over 1 in a number of individual locations.



Note that measurements of manganese in smaller size fractions (i.e., PM_{10} and $PM_{2.5}$) have lower concentrations than the larger TSP.

Maps of Key Hazard-Weighted Toxics: Formaldehyde

Formaldehyde is almost always above a hazard quotient of 0.1, but is only rarely above 1.

Only the Indiana site has an obvious nearby emissions source that would account for the higher annual average concentrations.

Pollutants Above or Possibly Above 1.0 Hazard-weighted Concentrations at >1% of Sites

Pollutant	Number of sites	Number of sites above reference concentration	Percent of sites above reference concentration	Uncertain sites (85% of data below MDL and reference concentration below MDL)	Percent of sites above or possibly above reference concentration
Acrolein	53	41	77	12	100
Manganese TSP	96	8	8	6	15
Manganese PM_{10}	26	1	4	0	4
Acetonitrile	63	2	3	0	3
Formaldehyde	161	4	2	0	2
Acrylonitrile	124	3	2	0	2
1,3-Butadiene	276	4	1	0	1
Nickel TSP	101	1	1	6	7

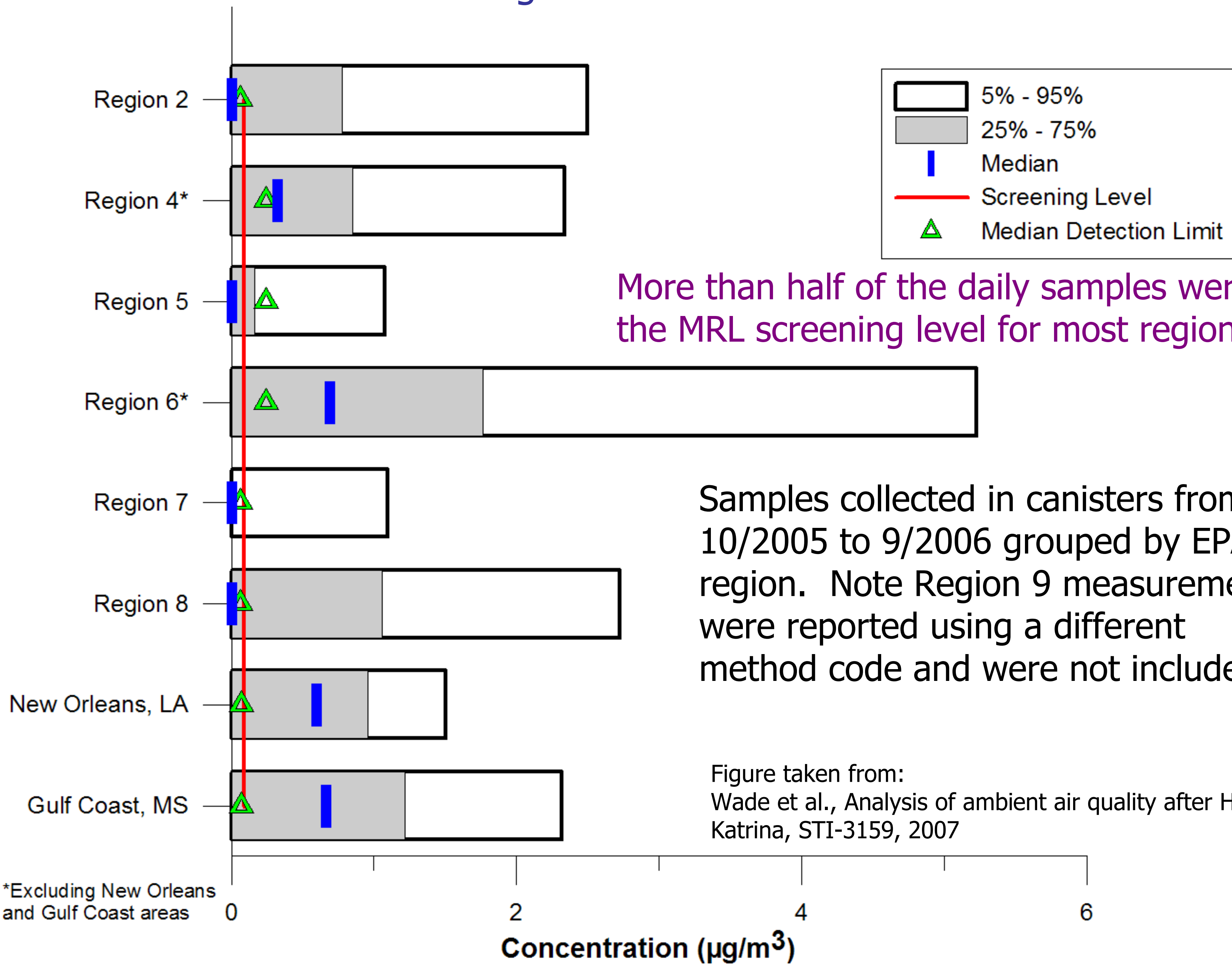
Counts of sites with <1.0 hazard quotient are not explicitly shown in this table.

Which Toxics Are Most Important? Acute Hazard Screening

Daily and subdaily measurements were compared to acute screening levels (2000-2005):

- Acrolein concentrations exceeded MRLs more than 50% of the time at most sites.
- Formaldehyde concentrations exceeded MRLs about 0.3% (1 out of 300 samples) of the time.
  - Formaldehyde concentrations may be an acute problem in some localities.
  - Some of these locations coincided with the high chronic values on the previous map, but 23 other sites had at least one high value that exceeded the MRL on at least one occasion.
- Pollutants with an exceedance rate below 0.01% (1 in 10,000 samples):
  - Benzene, tetrachloroethylene, acetaldehyde, dichloromethane, bromomethane, chloromethane, 1,2-dichloropropane, 1,4-dichlorobenzene, acrylonitrile, chloroethane, chloroform, hydrogen sulfide, methyl chloroform, MTBE, phosphorous, toluene, trichloroethylene, vinyl chloride, and xylenes.
  - These results are extreme statistical outliers and should not be overinterpreted due to possible data quality issues.
- These results primarily mirror the chronic hazard results.

Acrolein concentrations are above the MRL using new canister methods in all regions in which it has been measured.



*Excluding New Orleans and Gulf Coast areas

More than half of the daily samples were above the MRL screening level for most regions.

Samples collected in canisters from 10/2005 to 9/2006 grouped by EPA region. Note Region 9 measurements were reported using a different method code and were not included.

Figure taken from:
Wade et al., Analysis of ambient air quality after Hurricane Katrina, STI-3159, 2007

National Toxics of Importance: Summary

Chronic cancer risk-weighted concentrations above 10^{-6} nationally

Certain	Likely	Unknown	Unlikely	Not a national problem
Benzene	Tetrachloroethylene	Ethylene dibromide	3-Chloroprene	Vinyl Chloride
Carbon tetrachloride	Acrylonitrile	1,1,2,2-tetrachloroethane	Chromium VI	Formaldehyde
Acetaldehyde	1,4-Dichlorobenzene	Hexachlorobutadiene	Individual PAHs	1,1-Dichloroethane
Arsenic	Nickel (TSP and PM10)	Benzyl Chloride	Bromoform	MTBE
1,3-Butadiene	Ethylene oxide	Cadmium	Beryllium	Trichloroethylene
	Naphthalene	1,2-Dichloropropane		Dichloromethane
		Ethylene dichloride		Nickel PM2.5
		1,1,2-Trichloroethane		
		1,3-Dichloropropene		

Chronic noncancer hazard-weighted concentrations above 1.0 nationally

Certain	Likely	Unknown	Unlikely	Not a national problem
Acrolein			Formaldehyde	All other monitored toxics
			Manganese (TSP and PM10)	
			1,3-Butadiene	
			Acrylonitrile	

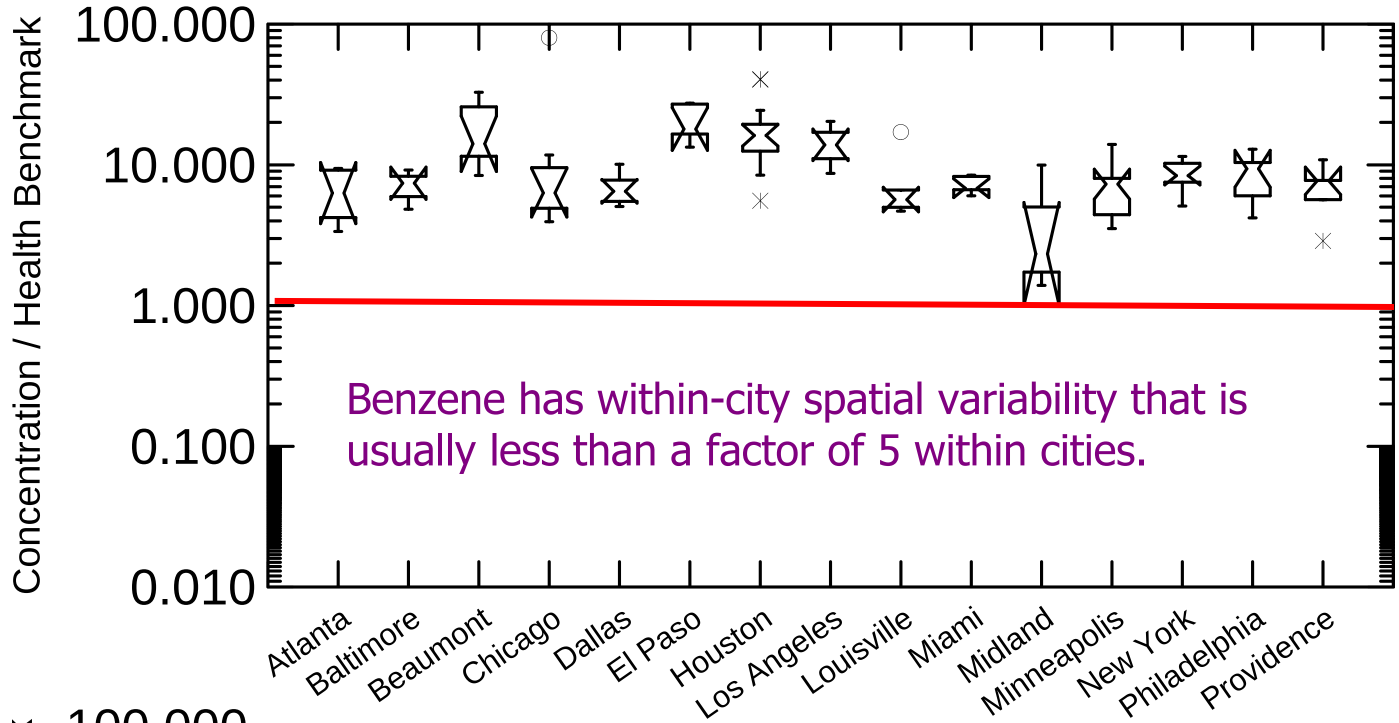
Which Toxics Identified as Problems in NATA 1999 Were Not Available for this Screening?

Pollutants identified as contributors to chronic risk or hazard in NATA 1999 that are not measured directly or reported to AQS:

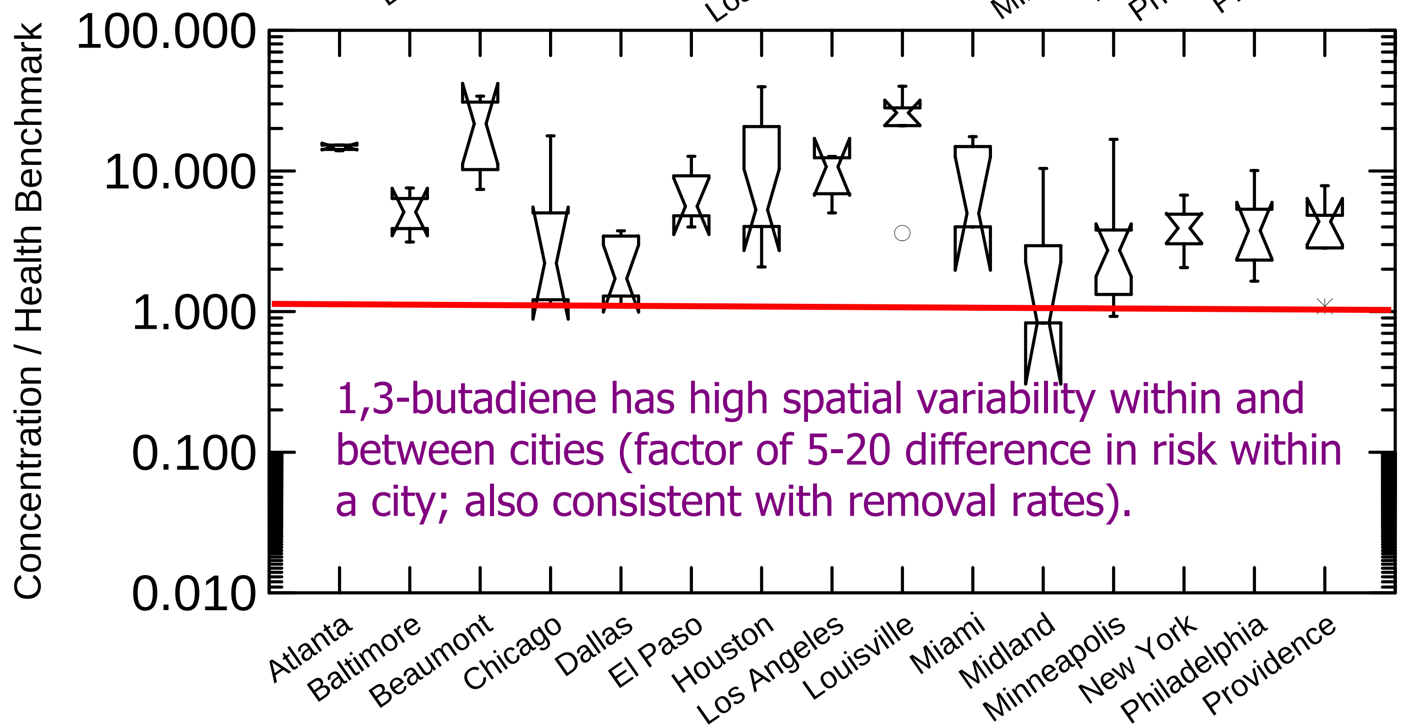
- Particulate organic matter *(usually reported individually, rather than as a sum)*
- Diesel Particulate Matter *(not directly measured; surrogate measurements such as BC are available)*
- Coke oven emissions
- Quinoline
- Triethylamine
- Hydrazine
- Maleic Anhydride

Can We Systematically Compare Risk Burden of Key Monitored Toxics Between Cities?

- The suite of important toxics measured for ambient risk burden is not typically measured at any single site; different networks monitor different subsets of toxics.
- Does the variability of air toxics concentrations within cities result in large differences in risk burden estimates?
- Can we provide spatial uncertainty estimates for risk averages based on the available monitoring data?



The within-city risk burden of individual air toxics demonstrates that individual city risk can be estimated and compared with uncertainties on the order of a factor of 2-5 for most cities.

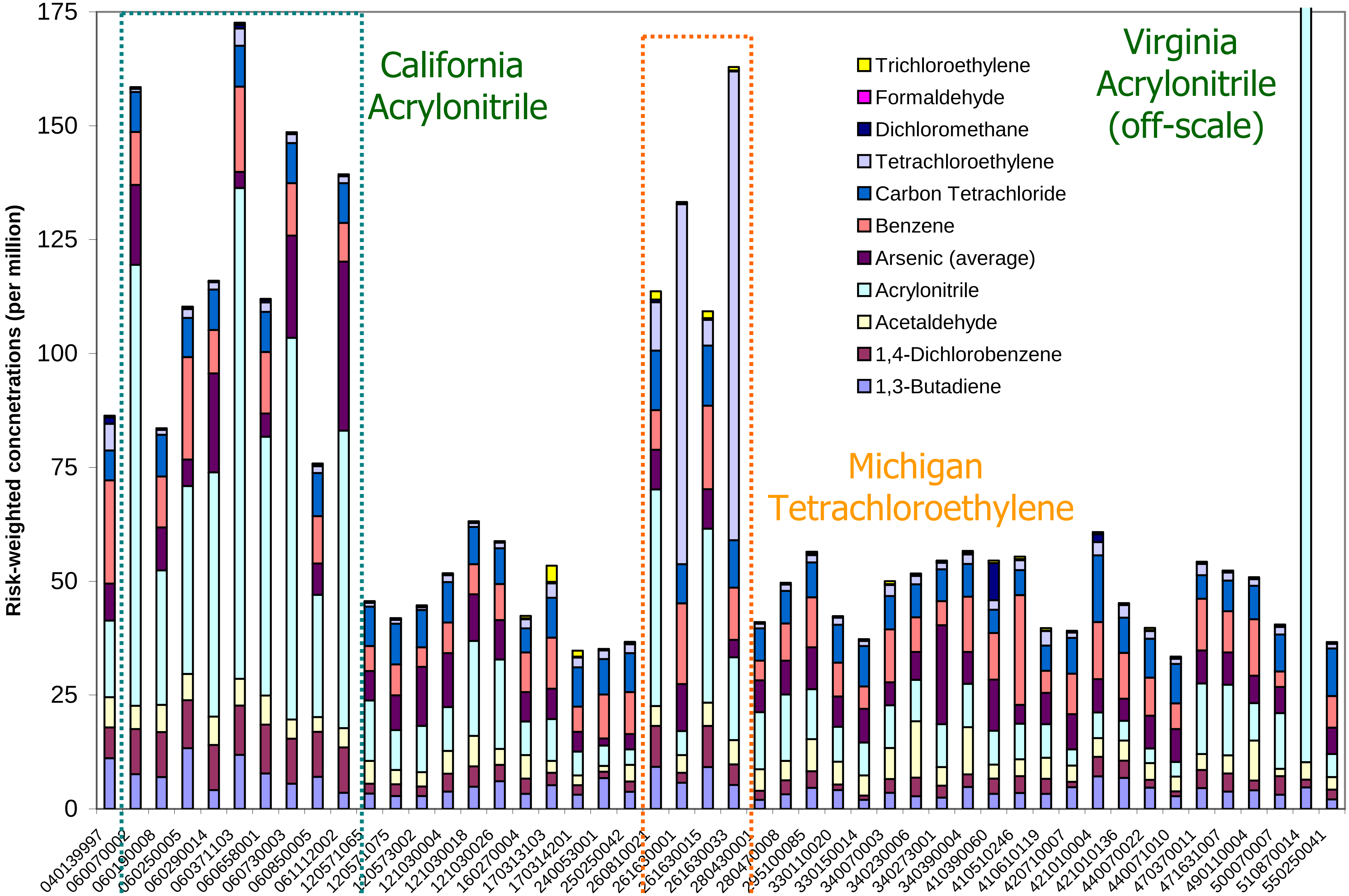


Pollutants with high spatial variability nationally usually have high spatial variability within a city.

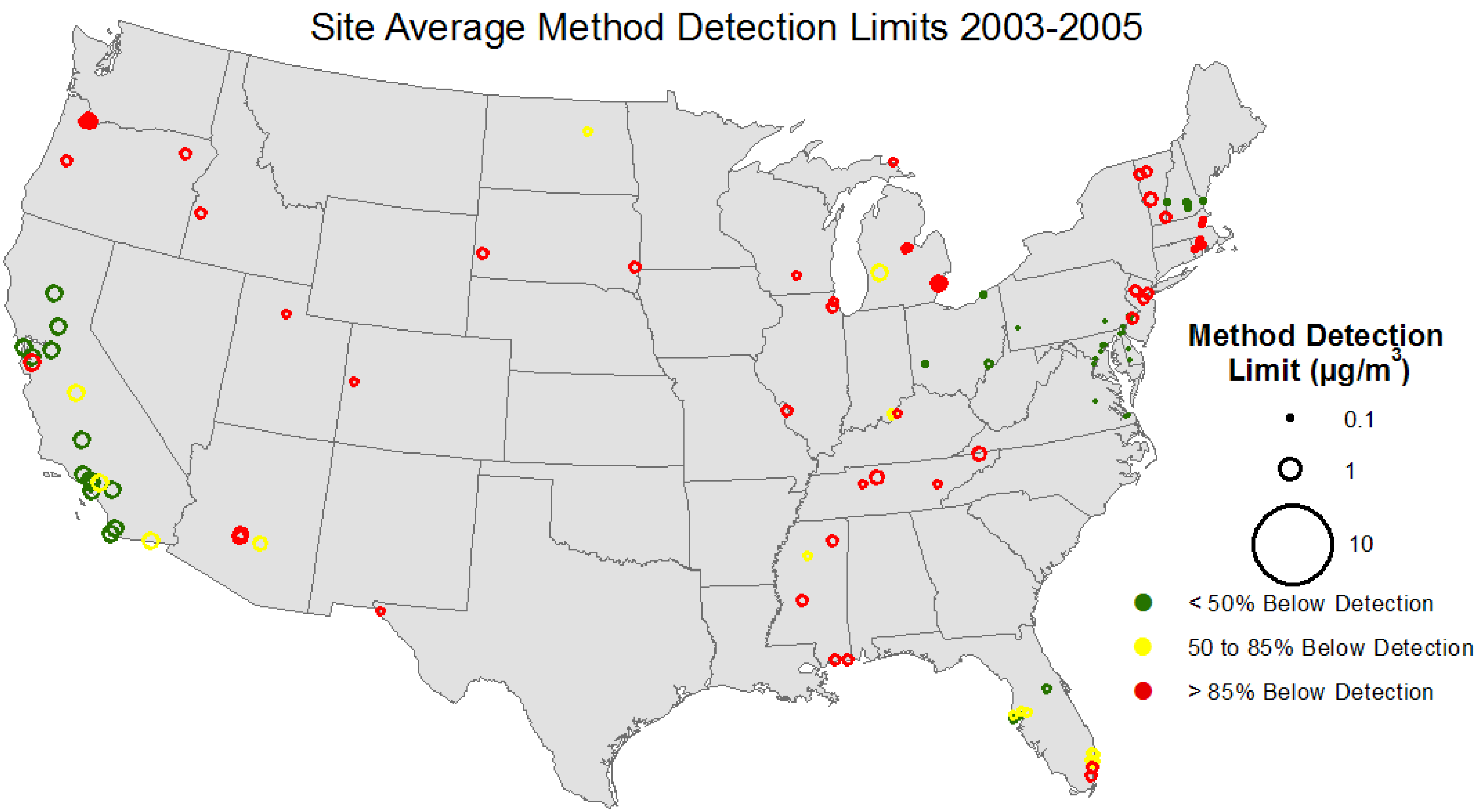
Comparison Of Risk-weighted Concentrations Across Sites

- Risk-weighted site-average concentrations were compared across sites with a common suite of 11 air toxics. These 11 air toxics were chosen because
  - their risk-weighted values were high (e.g., acrylonitrile, benzene, carbon tetrachloride, arsenic, and acetaldehyde) or
  - they were available at the same sites as the risk-driving pollutants (e.g., trichloroethylene, formaldehyde).
- 48 sites measured this suite of toxics between 2003-2005.
- The variability in cumulative risk-weighted concentrations by site were dominated by acrylonitrile and tetrachloroethylene (indicated on next slide by boxes); both these air toxics are further explored in following slides.

Cumulative Risk-weighted Concentrations By Site



California's Acrylonitrile MDLs Are High, but Data Are Usually Above Detection



California's Acrylonitrile MDLs Are High, but Data Are Usually Above Detection

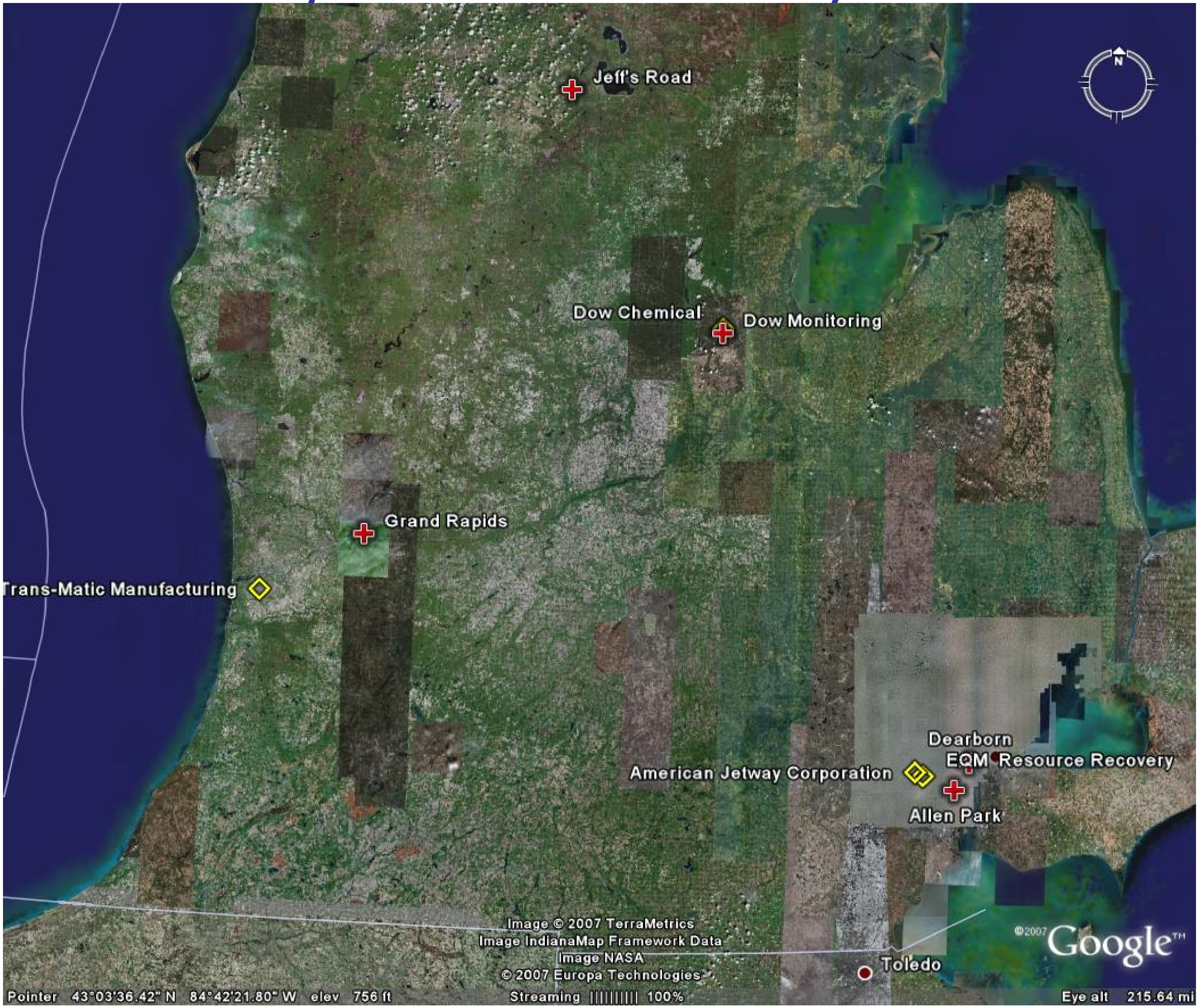
- California's MDL from 2003-2005 was typically about 0.65 $\mu g/m^3$.
- The 10^{-6} cancer benchmark for acrylonitrile is 0.0147 $\mu g/m^3$.
- Risk-weighted concentrations from California must exceed 22-in-a-million (MDL/2 substitution), which is above the values at almost all other sites.
- More than half the samples of acrylonitrile in California were reported above MDL, leading to risk values >50-in-a-million at most sites.
- Why are concentrations of acrylonitrile in California higher than the rest of the country?

Acrylonitrile to Benzene Ratios Are Also High in California; Is this Reasonable?

- Concentration ratios provide information on the age of air masses and can indicate if pollution is locally emitted or transported.
  - Ratios of acrylonitrile to benzene concentrations at sites in California ranged from 0.2 to 1.0, with two-thirds of the sites above 0.5.
  - The national median ratio of acrylonitrile to benzene was 0.1, and the 80th percentile was 0.25.
  - Ratios of emissions from the 1999 NEI indicated that acrylonitrile was emitted at 1/100th the rate of benzene nationally and in California.
  - The highest ratios of acrylonitrile to benzene in California were at sites associated with fresh emissions; lower emissions were found in the downwind areas.

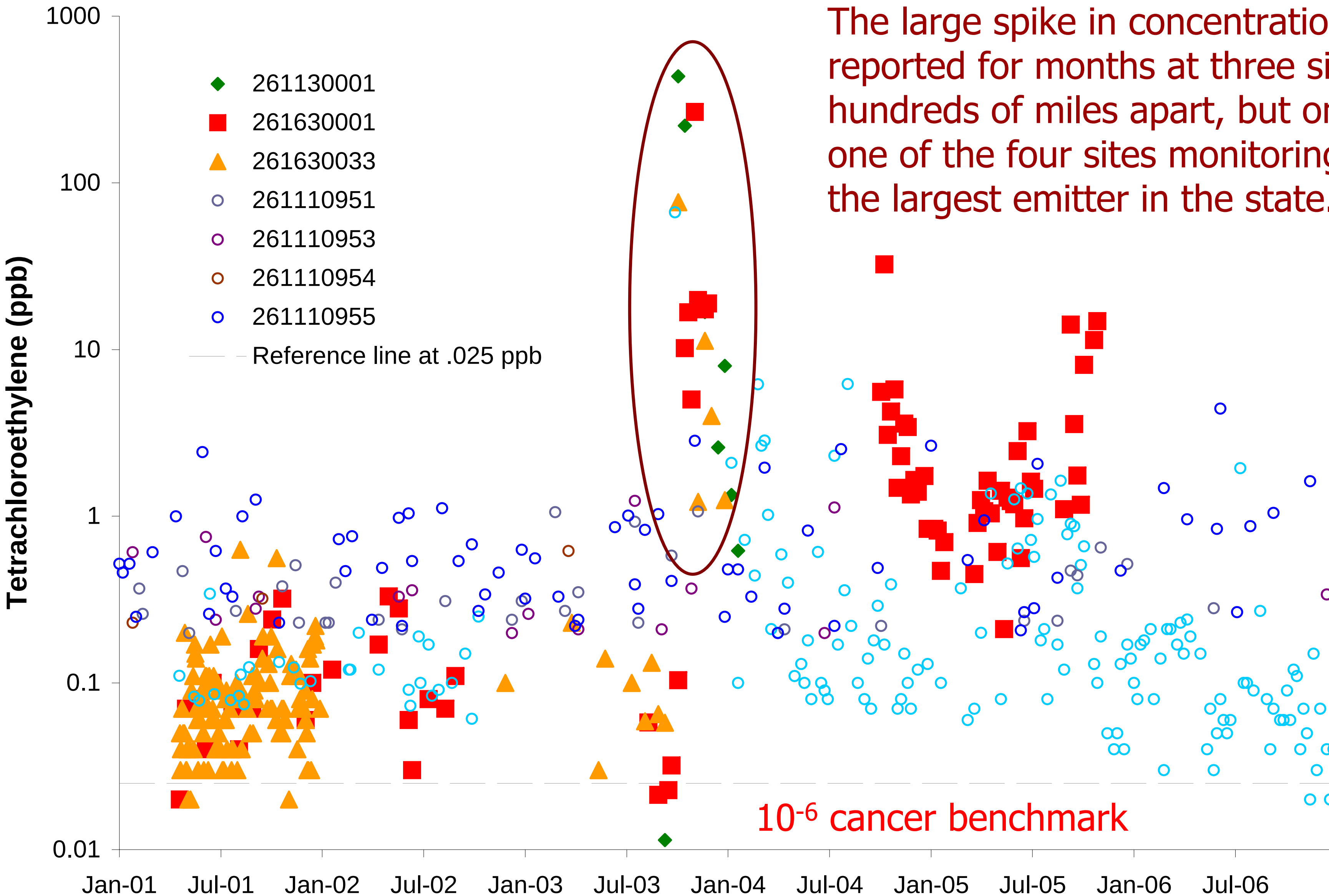
    This is the opposite of what we would expect because acrylonitrile has a substantially longer atmospheric residence time than benzene. We would expect higher ratios in the downwind areas due to contributions from transport.
- The California acrylonitrile data are not consistent with our expectations from concentration ratios, emissions ratios, or other national measurements. Therefore, these data appear suspect; additional investigation is needed to better understand acrylonitrile values in California.

Michigan Tetrachloroethylene



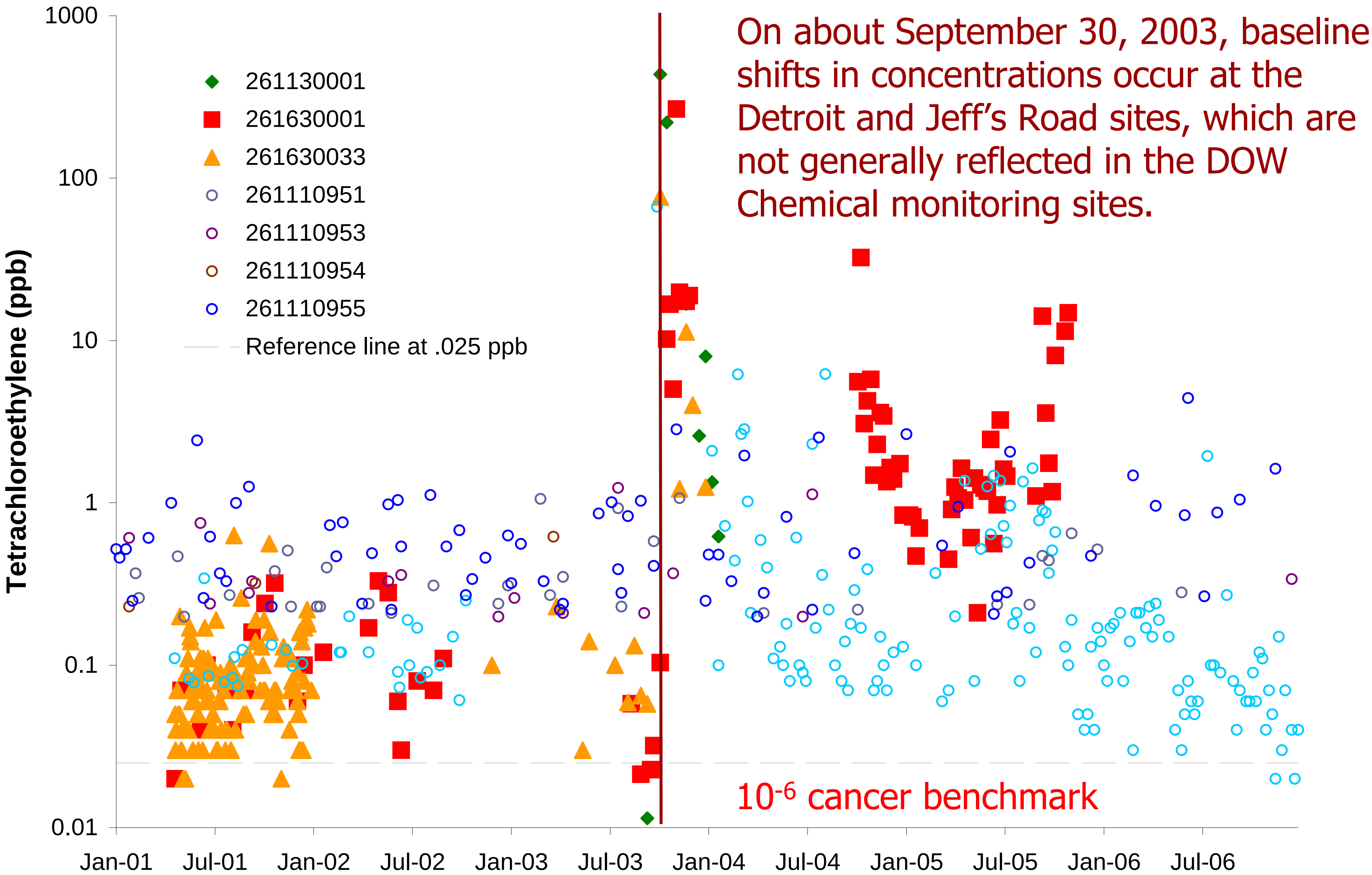
Red crosses are monitoring sites, yellow diamonds are major emissions sources in the toxics release inventory.

Michigan Tetrachloroethylene Time Series



The large spike in concentrations is reported for months at three sites hundreds of miles apart, but only at one of the four sites monitoring near the largest emitter in the state.

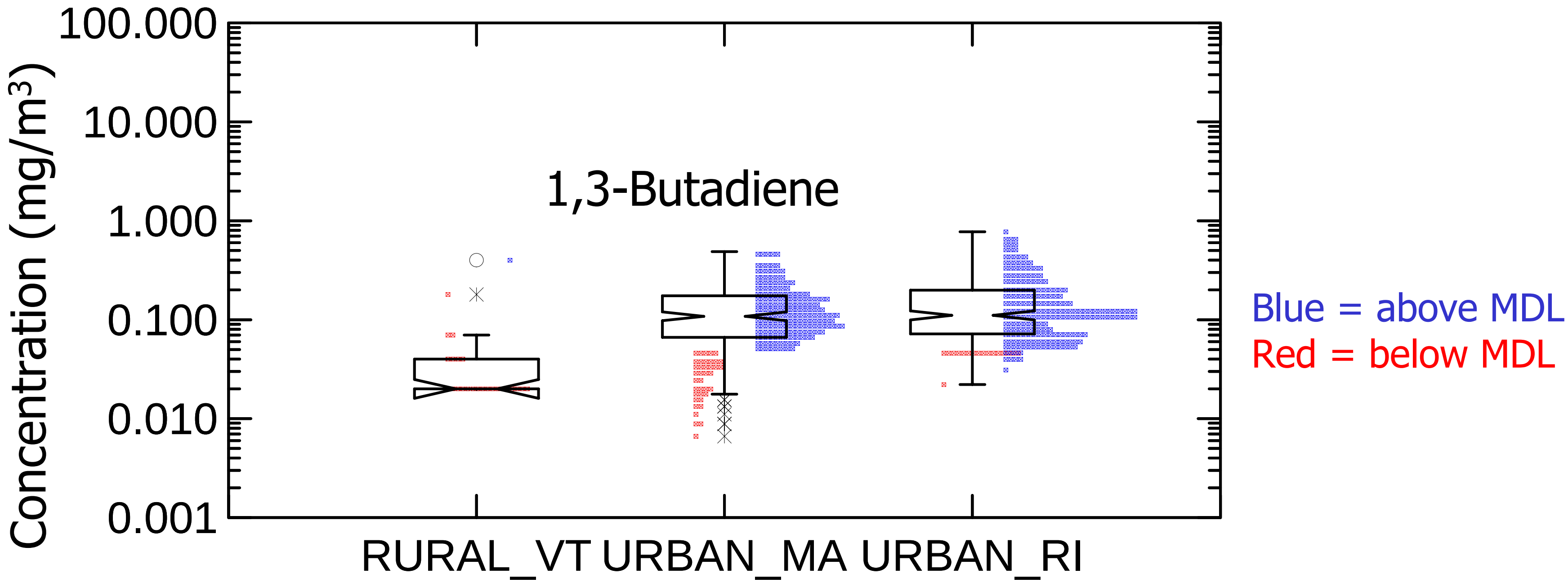
Michigan Tetrachloroethylene Time Series



Spatial and Temporal Variations in Michigan Tetrachloroethylene

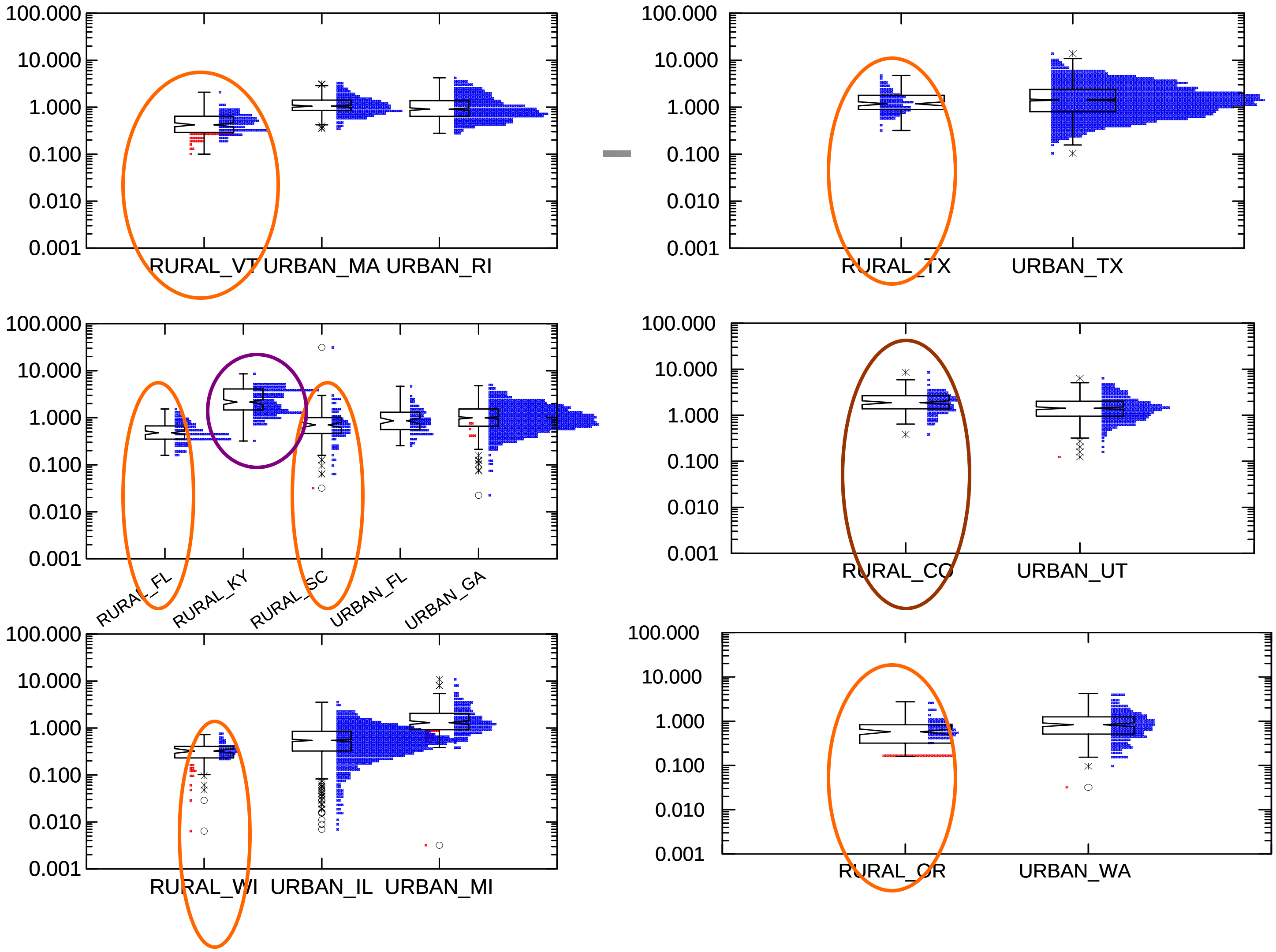
- After September 2003, tetrachloroethylene had multiple incidences of concentrations at >25 times the 1-in-a-million benchmark level at multiple sites in Michigan that are not particularly close to large emissions sources of tetrachloroethylene.
- This period of high concentrations occurred at sites hundreds of miles apart, and lasted multiple months.
- These concentrations are far higher than at other sites in the United States.
- Are these concentrations reflective of ambient concentrations of tetrachloroethylene? No nearby sources were identified, nor is it likely that transported concentrations would be that high and not be seen elsewhere.
- Additional investigation is needed by local analysts familiar with the sites and measurements.

Urban-rural Comparison Approach and Example Figure



- Three sites from an EPA region are displayed on a logarithmic scale.
- The blue and red “dots” are dot-density plots showing the distribution of 24-hr concentrations at each site that are above and below the MDL, respectively.
- The box plots show some key summary statistics on the concentrations for each site.
  - The notch indicates the median concentration.
  - The edges of the notch indicate the 95% confidence intervals in the median concentration.
  - The box indicates the interquartile range (25th and 75th percentile).
  - The whiskers indicate 1.5* the interquartile range.
- The notches indicate that the median concentration reported at the rural site is statistically significantly lower than at the urban sites (confidence intervals do not overlap).
  - However, the MDL is higher at the rural site (>0.2 for rural versus 0.05 mg/m^3 for urban sites).

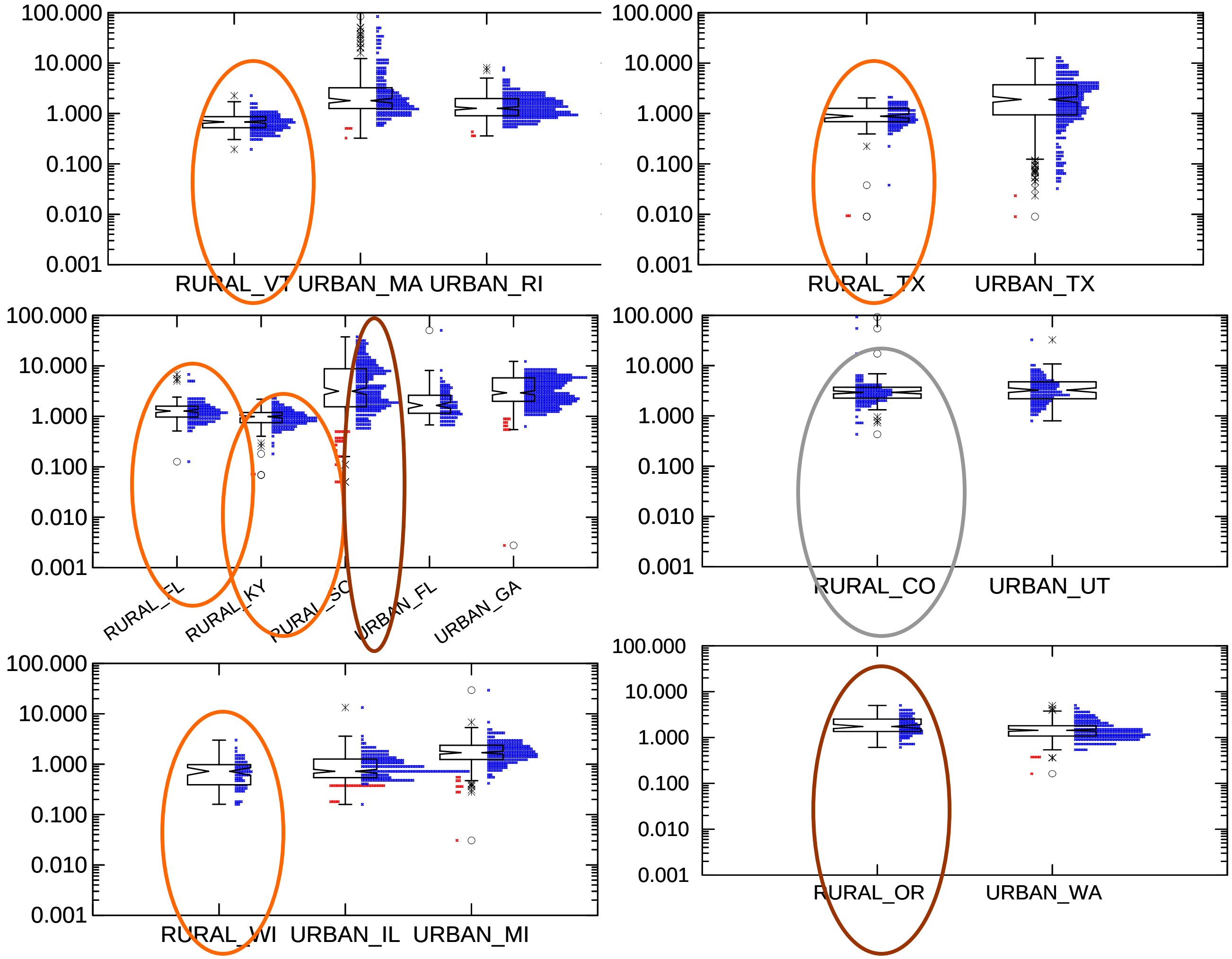
Urban-rural Comparison for Benzene (μg/m³)



Orange = lower rural concentrations
Brown = higher rural concentrations
Purple = Hazard, KY reporting issue

Most rural sites have lower concentrations of benzene than urban sites, as expected.

Urban-rural Comparison for Acetaldehyde (μg/m³)



Some rural sites have lower concentrations of benzene than urban sites, as expected.

Orange = lower rural concentrations
Brown = higher rural concentrations
Gray = No significant difference

What Are the Implications when Estimating Risk for Rural Areas Compared with Urban Areas?

- Cumulative risk- and hazard-weighted concentrations will usually be significantly lower in rural areas. However, the cumulative values will be above levels of concern.
- Primary pollutants will usually have lower concentrations in rural areas.
  - This assumes the rural area is not downwind of major sources or cities.
  - The magnitude of difference between urban and rural concentrations depends on the lifetime of the pollutant.
  - Key air toxics that fall into this category include
    - Benzene, 1,3-butadiene, arsenic, nickel, chromium, tetrachloroethene, naphthalene, cadmium, and 1,4-dichlorobenzene.
    - Ethylene dibromide, 1,1,2,2-tetrachloroethane, benzyl chloride, hexachlorobutadiene, ethylene dichloride, 1,2-dichloropropane, vinyl chloride, trichloroethylene, and POM.
- Secondary pollutants may or may not have lower concentrations in rural areas.
  - These pollutants are sometimes higher in rural areas and there is less difference between urban and rural concentrations than for pollutants that react quickly.
  - Key air toxics that fall into this category include formaldehyde, acetaldehyde, and acrolein.
- Very long-lived pollutants are the same in urban and rural areas.
  - Carbon tetrachloride is the only key toxic that falls into this category.

Estimating Risk From Remote Background Concentrations

- Comparing remote background concentrations with OAQPS cancer benchmarks, the only pollutants known to be above health benchmarks are benzene and carbon tetrachloride:
  - Carbon tetrachloride is approximately 9 times the OAQPS cancer benchmark.
  - Benzene ranges from 1.2 to 2.5 times the OAQPS cancer benchmark.
  - Total quantifiable risk from remote background concentrations is about 10-in-a-million.
    - Note that non-OAQPS cancer benchmarks of formaldehyde indicate that remote background concentrations contribute 2- to 5-in-a-million risk.
- Many air toxics with unmeasured remote background concentrations and poorly measured urban background concentrations could be above health benchmark levels.
  - Key toxics that may contribute to national concentrations include acrolein, 1,1,2,2-tetrachloroethane, acrylonitrile, ethylene oxide, and ethylene dibromide.
  - Models could be used to estimate the remote background concentrations of these toxics.

Are Ozone, PM, and Toxics High in the Same Places?

- Air toxics should be considered along with criteria pollutants to effectively target control strategies to address multiple air quality problems.
- While ozone and particle pollution are regulated by the NAAQS, air toxics impacts are characterized by the amount of cancer risk they pose and by their noncancer hazard.
- The following slides step through an analysis of the “nexus” of pollutants.

Nexus of Pollutants Analysis

A suite of nine widely measured air toxics were compared to ozone and $PM_{2.5}$ nonattainment areas.

2003-2005 site averages for each pollutant were used to calculate Core Based Statistical Area (CBSA*) averages.

CBSA average concentrations converted to risk-weighted concentrations by dividing by 1-in-a-million cancer benchmarks. CBSA average risk-weighted concentrations were examined by pollutant and cumulatively.

A total of 62 CBSAs had data for all nine air toxics considered to perform this analysis.

Nonattainment areas by county for 8-hr ozone and $PM_{2.5}$ were acquired from the EPA AirData web site. Because CBSA boundaries do not always correspond with nonattainment area boundaries, CBSAs were considered to be nonattainment if any of their member counties were in nonattainment areas.

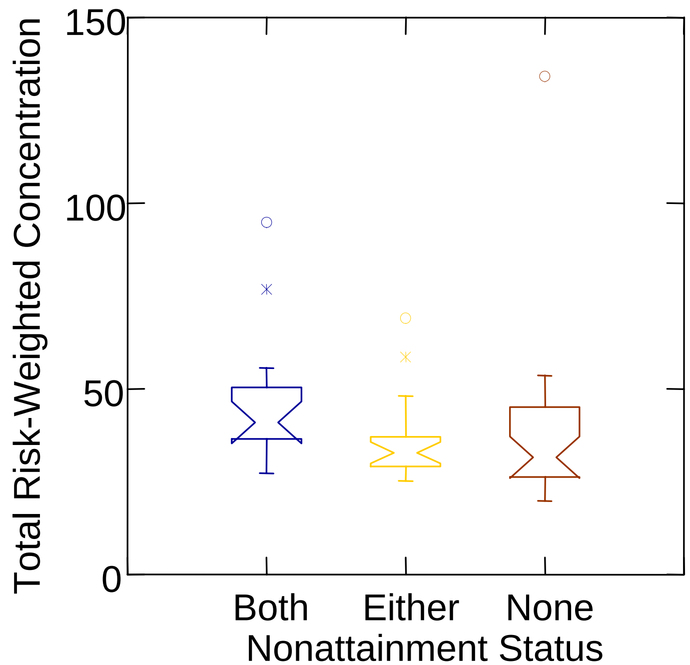
Of the CBSAs considered, only one was designated nonattainment for $PM_{2.5}$ and attainment for ozone. We grouped CBSAs into three categories: in attainment of both standards, in nonattainment for either ozone or $PM_{2.5}$, and in nonattainment for both ozone and $PM_{2.5}$.

*CBSAs include both metropolitan and micropolitan statistical areas

Air Toxics Considered
Benzene
Carbon tetrachloride
1,3-butadiene
Acetaldehyde
Arsenic $PM_{2.5}$
Tetrachloroethylene
Formaldehyde
Dichloromethane
Trichloroethylene

CBSA Count by Category	
Ozone and $PM_{2.5}$	15
Ozone or $PM_{2.5}$	19
Attainment	28

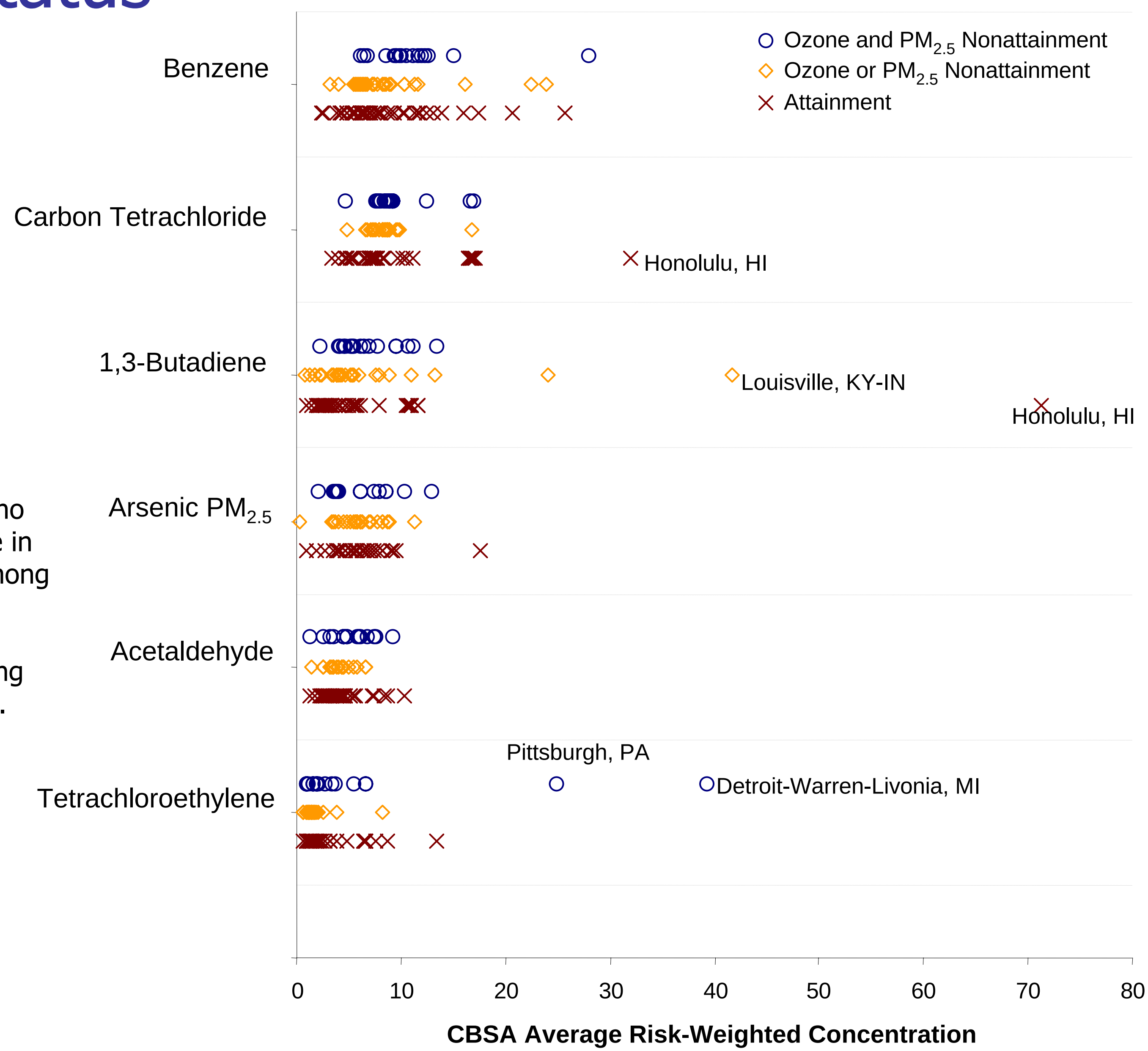
CBSAs in nonattainment for both ozone and $PM_{2.5}$ measure higher cumulative risk-weighted concentrations for these air toxics than CBSAs that are not in violation of both standards.



Comparing Risk-weighted Concentrations and Attainment Status

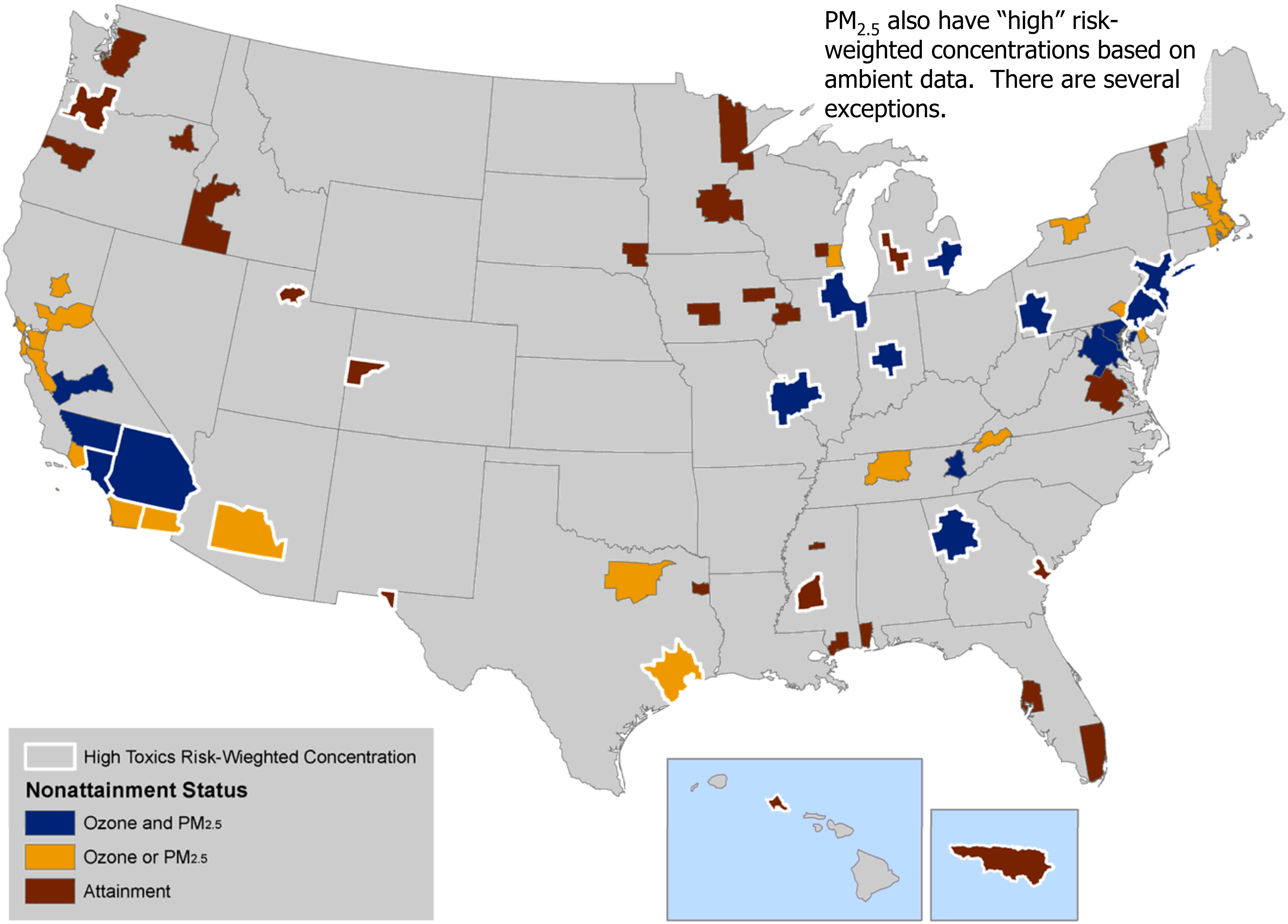
By individual pollutant, there is no statistically significant difference in risk-weighted concentrations among the nonattainment categories.

Only the six air toxics contributing the most to risk are shown here.



Nexus of High CBSA Average Risk-Weighted Concentration and Nonattainment Status

Most of the CBSAs that are nonattainment for ozone and $PM_{2.5}$ also have "high" risk-weighted concentrations based on ambient data. There are several exceptions.



Conclusions and Implications

- Key monitored toxics have been identified and categorized into likely national problems for human health, possible problems for human health (indeterminate based on current monitoring), or not problems.
- Most toxics concentrations have similar spatial variability of primary pollutants like CO and NO_x rather than secondary pollutants like ozone and $PM_{2.5}$. However, many of the most important species from a health perspective are less spatially variable than the typical air toxic.
  - Therefore, fewer monitors may be needed to characterize cumulative risk within cities and efforts could be made to improve detection limits and add measurements of the pollutants of interest.

Conclusions and Implications

- Many national-scale data quality issues remain in the air toxics monitoring network:
  - Most important air toxics are measured at a sufficient number of monitoring sites, but are not measured at concentrations low enough to assess policy-relevant questions. Ethylene oxide and naphthalene are important exceptions that can be monitored in canisters using standard TO-15 methodologies.
  - Monitoring methods have not been required to measure at levels low enough to determine if a pollutant is a health risk or not. Steps have been taken to lower MDLs for the NATTS sites, but this needs to be done for all measurement sites.
  - Differences in concentrations resulting from differences in methods and MDLs across jurisdictional lines confound spatial analyses. Additional guidance or requirements to the states and QA across agencies are likely needed to reduce the differences.

Summary of Toxics Risk Characterization (1 of 5)

- Which air toxics are the most important from a health perspective?
  - Cancer risk, high confidence: Benzene, carbon tetrachloride, arsenic, 1,3-butadiene, acetaldehyde, tetrachloroethylene, acrylonitrile, 1,4-dichlorobenzene, Nickel (TSP and PM_{10}), ethylene oxide, and naphthalene
  - Cancer risk, low confidence: ethylene dibromide, 1,1,2,2-tetrachloroethane, benzyl chloride, hexachlorobutadiene, cadmium, chromium VI, ethylene dichloride, ethylene dichloride, 1,2-dibromo-3-chloropropane, 1,2-dichloropropane, 1,1,2-trichloroethane
  - Noncancer hazard: **Acrolein,** formaldehyde, manganese, 1,3-butadiene, acetaldehyde.

Summary of Toxics Risk Characterization (2 of 5)

- Which air toxics dominate risk and hazard burden nationally?
  - Acrylonitrile, benzene, and carbon tetrachloride contribute more than 10% of cumulative risk-weighted concentrations at most sites. Ethylene oxide contributes more than 10% at the sites where it is measured.
  - Acetaldehyde, 1,3-butadiene, and arsenic contribute more than 5% of cumulative risk-weighted concentrations nationally.
  - Upper limit estimates of risk from pollutants that are poorly characterized indicate that ethylene dibromide, 1,1,2,2-tetrachloroethane, hexachlorobutadiene, and benzyl chloride could all be important. However, emissions of these toxics are low and they are unlikely to contribute substantially to national risk.
  - Acrolein dominates hazard risk, contributing more than 95% of cumulative hazard. Formaldehyde and manganese contribute about 1% each. Others are less than 1%.

Summary of Toxics Risk Characterization (3 of 5)

- Which toxics are possibly problems?
  - Ethylene dibromide, 1,1,2,2-tetrachloroethane, benzyl chloride, hexachlorobutadiene, cadmium, ethylene dichloride — these toxics are prime targets for improved MDLs.
  - Other toxics that need MDL improvement include 1,4-dichlorobenzene, acrylonitrile, tetrachloroethylene, and carbon tetrachloride.
- Which toxics identified as problems by models and emissions inventories are not measured?
  - Particulate organic matter (sum), diesel PM, coke oven emissions, quinoline, triethylamine, hydrazine, and maleic anhydride — only the first two would be expected to be national-scale problems based on their relative emissions levels.
- Which areas appear to have higher risk-weighted concentrations based on key pollutants?
  - California and Michigan had the highest cumulative risk-weighted concentrations based on 11 commonly measured air toxics. However, monitoring issues may be partly responsible for these higher values.

Summary of Toxics Risk Characterization (4 of 5)

- Does risk vary substantially within cities away from sources? Can we predict which pollutants are most likely to contribute to this variation?
  - Pollution does vary within cities by a factor of 5 or more, but this variation is not large enough to alter the interpretation of a pollutant of concern. For example, benzene varies by a factor of 5, but is always above 1-in-a-million risk and often above 10-in-a-million risk.
  - The variation between monitoring sites of risk-weighted concentrations is relatively small among pollutants that are well measured. However, species that are not commonly measured are more likely to be isolated local-scale problems.
- Does risk drop off in rural and remote areas? Is the drop-off large enough to reduce risk below levels of concern? Which pollutants contribute the most to risk in these areas?
  - Yes, risk does drop off in rural and remote areas.
  - Many individual species do drop below levels of concern, but some do not.
  - Carbon tetrachloride contributes the most to risk in remote and rural areas away from local sources.

Summary of Toxics Risk Characterization (5 of 5)

- Is the national monitoring network representative of the United States? What are the inherent biases in our analysis from where monitors are located?
  - The national monitoring network is biased to representing the urban areas of the country, primarily the top 10-20% population counties.
  - Rural and remote areas are far less represented relative to the number of counties with these lower populations.
- Are ozone, PM, and toxics concentrations high in the same areas?
  - Most of the CBSAs that are nonattainment for ozone and $PM_{2.5}$ also have "high" risk-weighted concentrations based on ambient data. However, there are several exceptions.
  - Individual air toxics do not show a strong bias toward increased concentrations in nonattainment areas, but the cumulative risk across common air toxics is 25% higher.

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