Assessment of the Impact of New EPA Limits on Benzene in Gasoline on Ambient Benzene Concentrations

October 2015

Municipality of Anchorage
Department of Health and Human Services

Phase 2 EPA Mobile Source Air Toxics Rule (MSAT2) 2007

- Limits on gasoline benzene content
  - <0.62% by volume (with averaging, trading and banking)
  - <1.3% by volume for individual refiners 
- Cold temperature NMHC emission standards for vehicles
- Portable fuel container permeability standards

Measure benzene concentrations in Anchorage air before and after the EPA-mandated reduction of benzene content in gasoline

- Phase 1 (pre-implementation)
  Oct 22, 2008 – Oct 16, 2009
- Phase 2 (post-implementation)
  Jan 4, 2013 – Dec 30, 2013

Also measured changes in the ambient concentrations of other VOCs, PAHs, CO and PM-2.5.

Why Anchorage?

- CO concentrations are among the highest in the U.S. Vehicle cold start emissions are a large contributor to CO.
- Benzene content in Anchorage gasoline was about 5%, three to four times higher than commonly found in U.S.
- Anchorage is isolated and nearly all gasoline is supplied by a single local refiner.
- Emission inventory suggested that fuel combustion engines (nearly all gasoline) account for 96% of benzene emissions.

Monitoring

- Gasoline sampling at retailers (bi-monthly, quarterly)
- Ambient sampling:
  - Sampling site located in a residential neighborhood in central Anchorage
  - 24-hour integrated sample collected every 6 days:
    - Benzene and other VOCs
    - PAHs
    - CO
    - PM-2.5
- Protocols repeated in Phase 1 and 2

Gasoline sampling and analysis

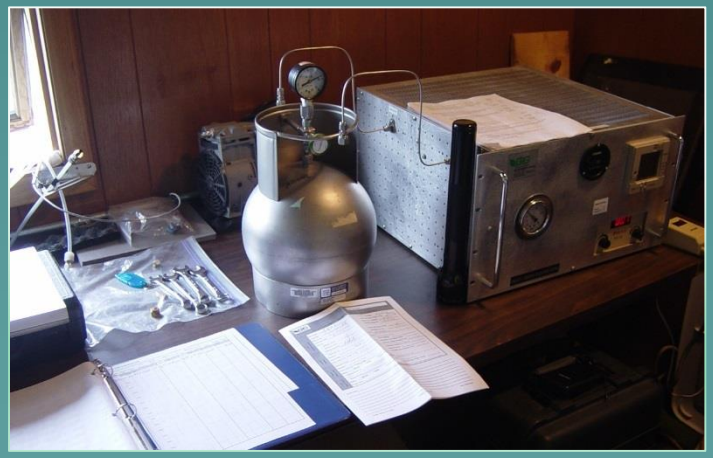
Sampling

- Six largest retailers, one to three gas stations per retailer
- Separate samples for regular and premium grades
- 850 ml sample, stainless steel container, iced immediately after collection
- Transported to University of Alaska, Anchorage Applied Science and Engineering Lab for analysis

Analysis

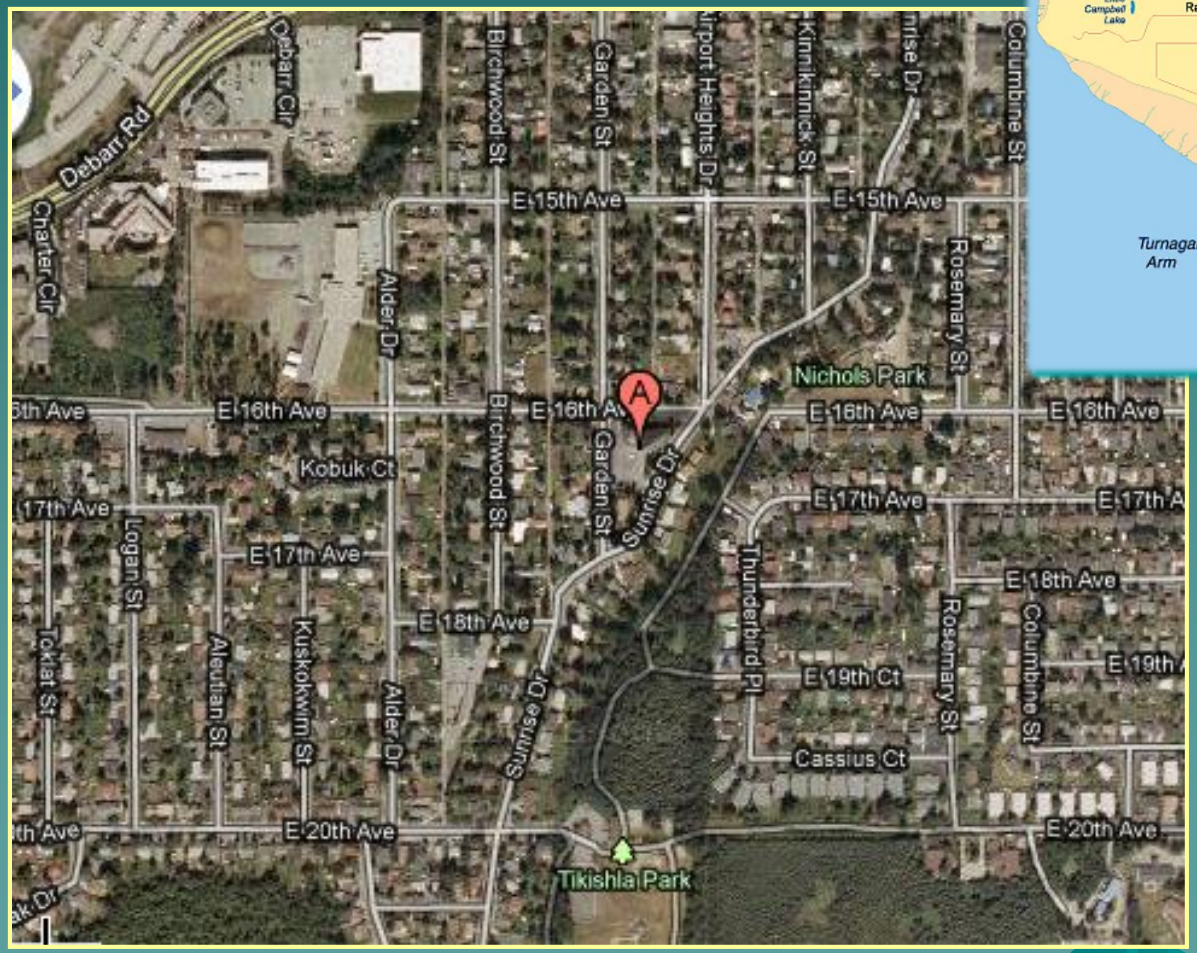
- Samples stored at <5 deg C
- Analyzed within 48 hours of receipt
- 100 meter capillary high resolution chromatograph column
- ASTM Method D6729-14 (2009)

Ambient monitoring



Garden Street Monitor

- residential area
- long-time CO, PM-2.5, and PM-10 SLAMS site with some previous VOC monitoring



Looking south from Garden Street Monitoring Station in east Anchorage

Acetylene
Acetonitrile
Propylene
Chloromethane
1,3-Butadiene
Acrolein
Benzene
Dichloromethane
Toluene
Methyl Isobutyl Ketone
Styrene
Ethylbenzene
m,p,o-Xylene
n-Octane
Chloroform
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
Dichlorodifluoromethane
Trichlorofluoromethane
Carbon Tetrachloride
Tetrachloroethylene
Dichlorotetrafluoroethane
Trichlorotrifluoroethane

VOC Monitoring

- Method TO-15
- 24-h integrated sample every 6th day
- 6 L Summa canisters
- 23 analytes, five of which are found in significant quantity in Anchorage gasoline
- Shipped to ERG, Inc (EPA contract laboratory) for analysis

PAH Monitoring

Naphthalene

Acenaphthylene

Acenaphthene

Fluorene

Phenanthrene

9-Fluorenone

Fluoranthene

Pyrene

Chrysene

Retene

Benzo (b) fluoranthene

Benzo (e) pyrene

Benzo (g,h,i) perylene

- Method TO-13A
- 24-h sample every 6th day
- Glass fiber filter + XAD resin/PUF cartridge
- 13 analytes
- Shipped frozen to ERG, Inc (EPA contract laboratory) for analysis

CO and PM-2.5 Monitoring

CO

- Trace-level monitor (Thermo Electron Model 48i – TLE)
- Continuous sampling 24/365
- Exceeded Federal Reference Method requirements
- Added attention to collection of accurate low concentration data

PM-2.5

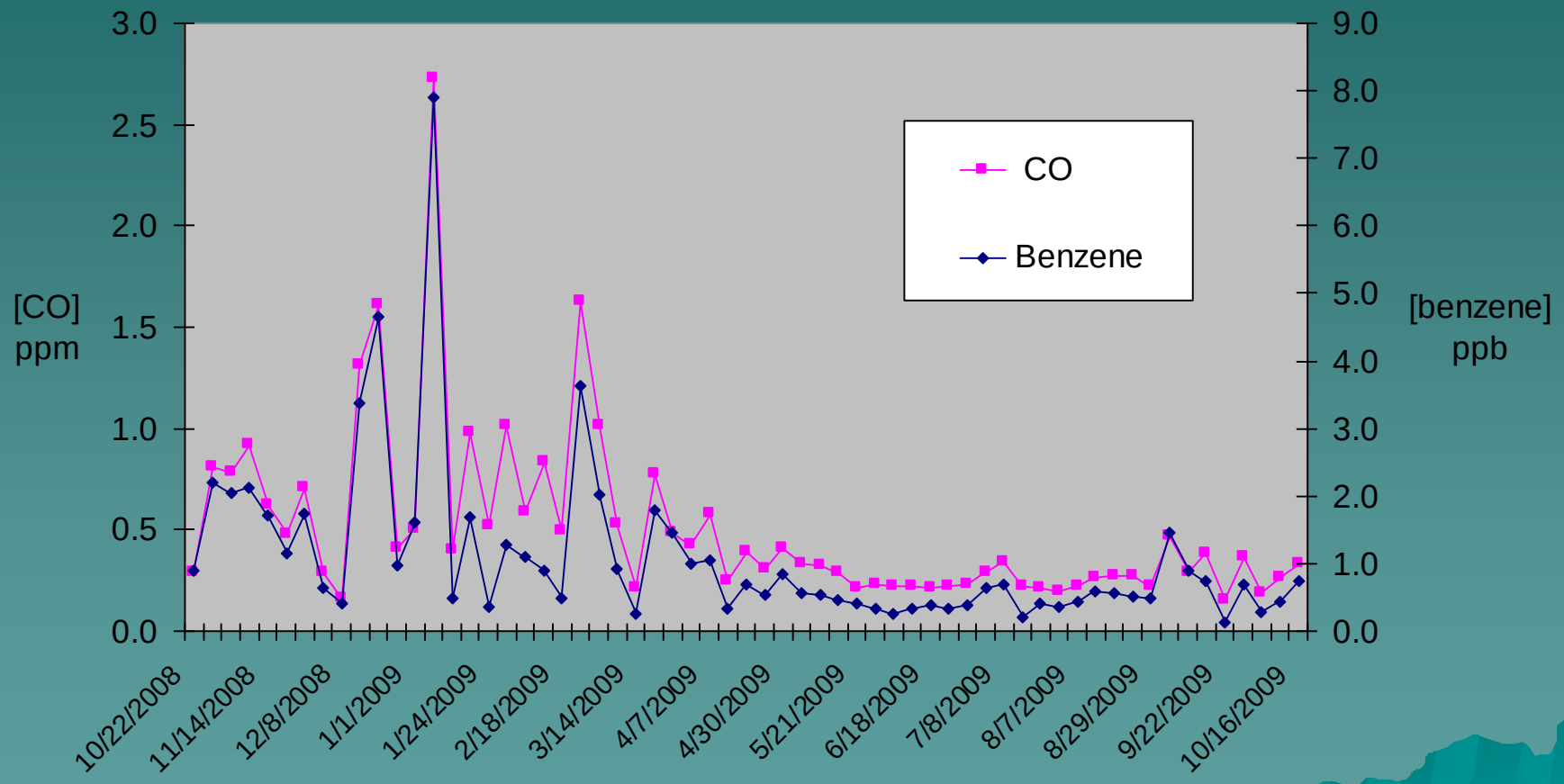
- Met-One BAM-1020 (beta attenuation)
- Continuous sampling 24/365
- Met Federal Equivalent Method requirements

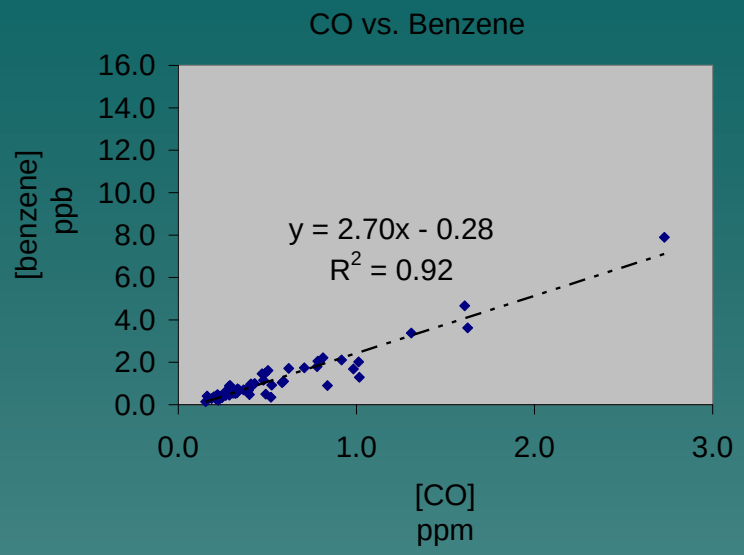
Phase 1 Results

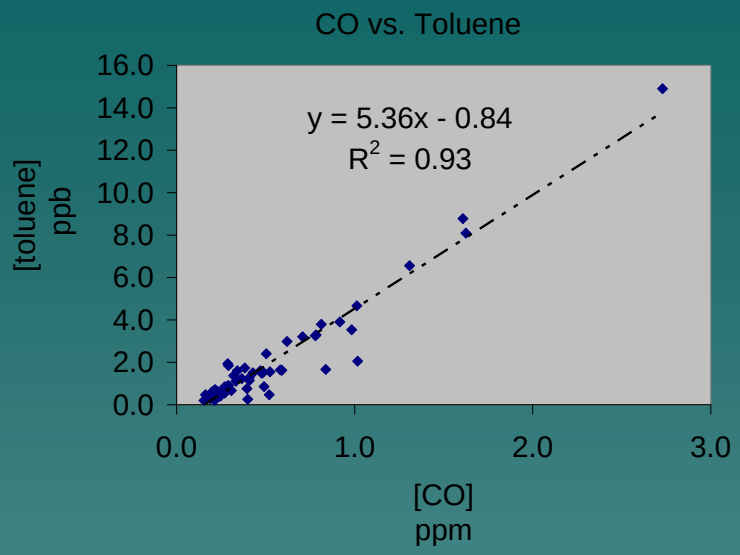
Snapshot of situation before implementation of gasoline benzene standard in Anchorage (Oct 2008 – Oct 2009)

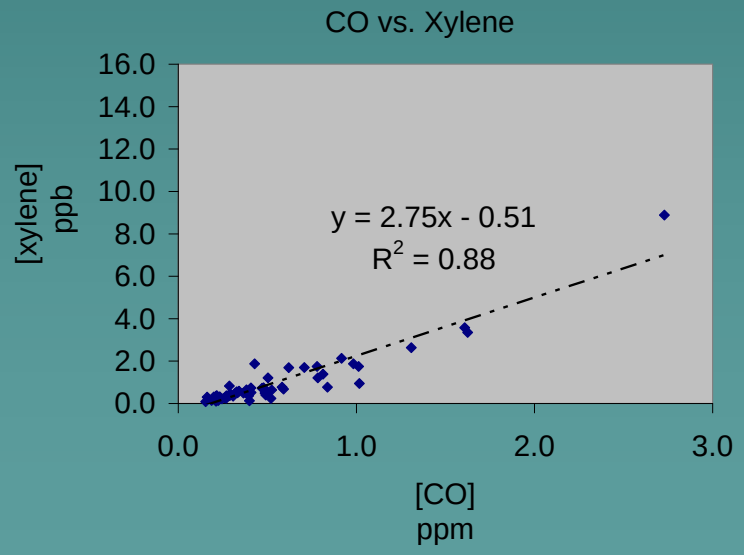
Gasoline benzene content	5.05% (by weight) 4.16% (by volume)
Ambient benzene concentration	0.99 ppbv
Cancer risk (Lifetime exposure)	High estimate = 1:40,000 Low estimate = 1:140,000

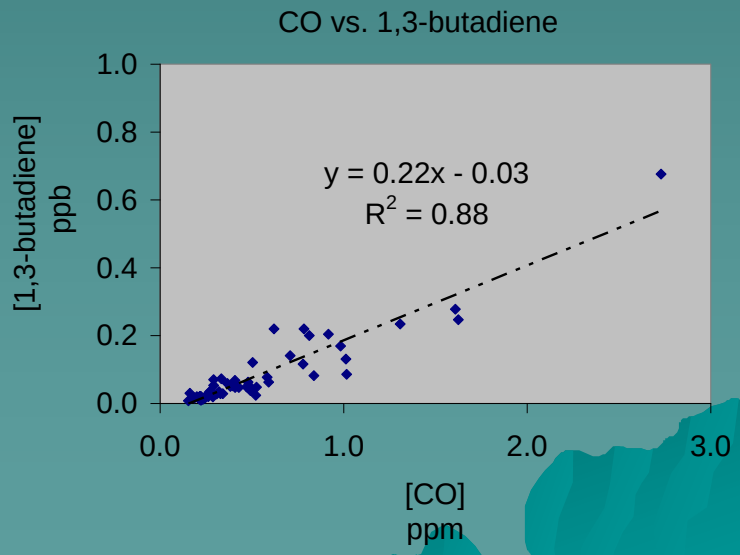
Ambient benzene and other VOCs were highly correlated with CO and highest in winter



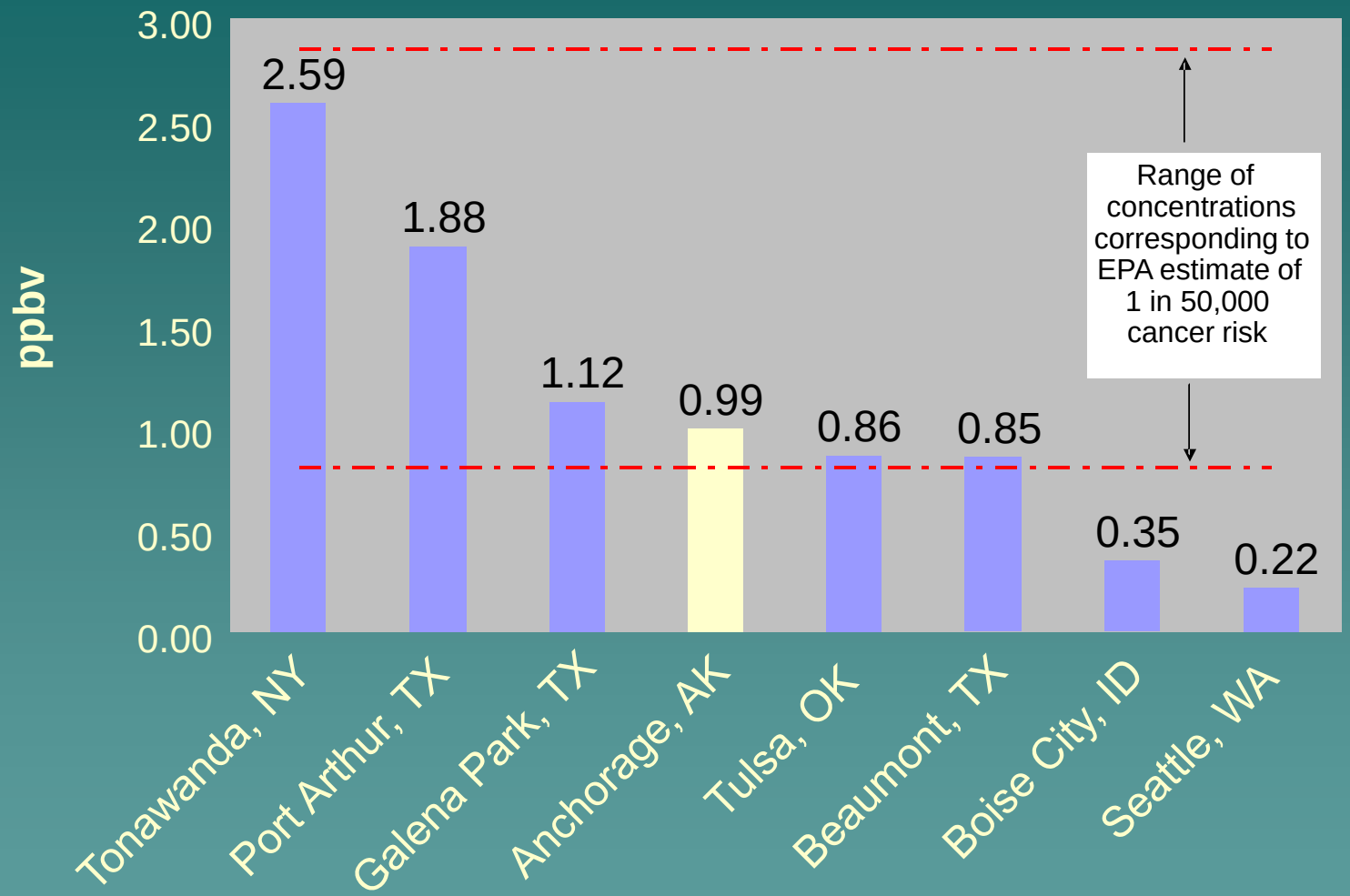

CO vs. Benzene
[benzene] ppb
y = 2.70x - 0.28
R2 = 0.92
[CO] ppm
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0.0
1.0
2.0
3.0


CO vs. Toluene
[toluene] ppb
y = 5.36x - 0.84
R2 = 0.93
[CO] ppm
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0.0
1.0
2.0
3.0


CO vs. Xylene
[xylene] ppb
y = 2.75x - 0.51
R2 = 0.88
[CO] ppm
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0.0
1.0
2.0
3.0


CO vs. 1,3-butadiene
[1,3-butadiene] ppb
y = 0.22x - 0.03
R2 = 0.88
[CO] ppm
1.0
0.8
0.6
0.4
0.2
0.0
0.0
1.0
2.0
3.0

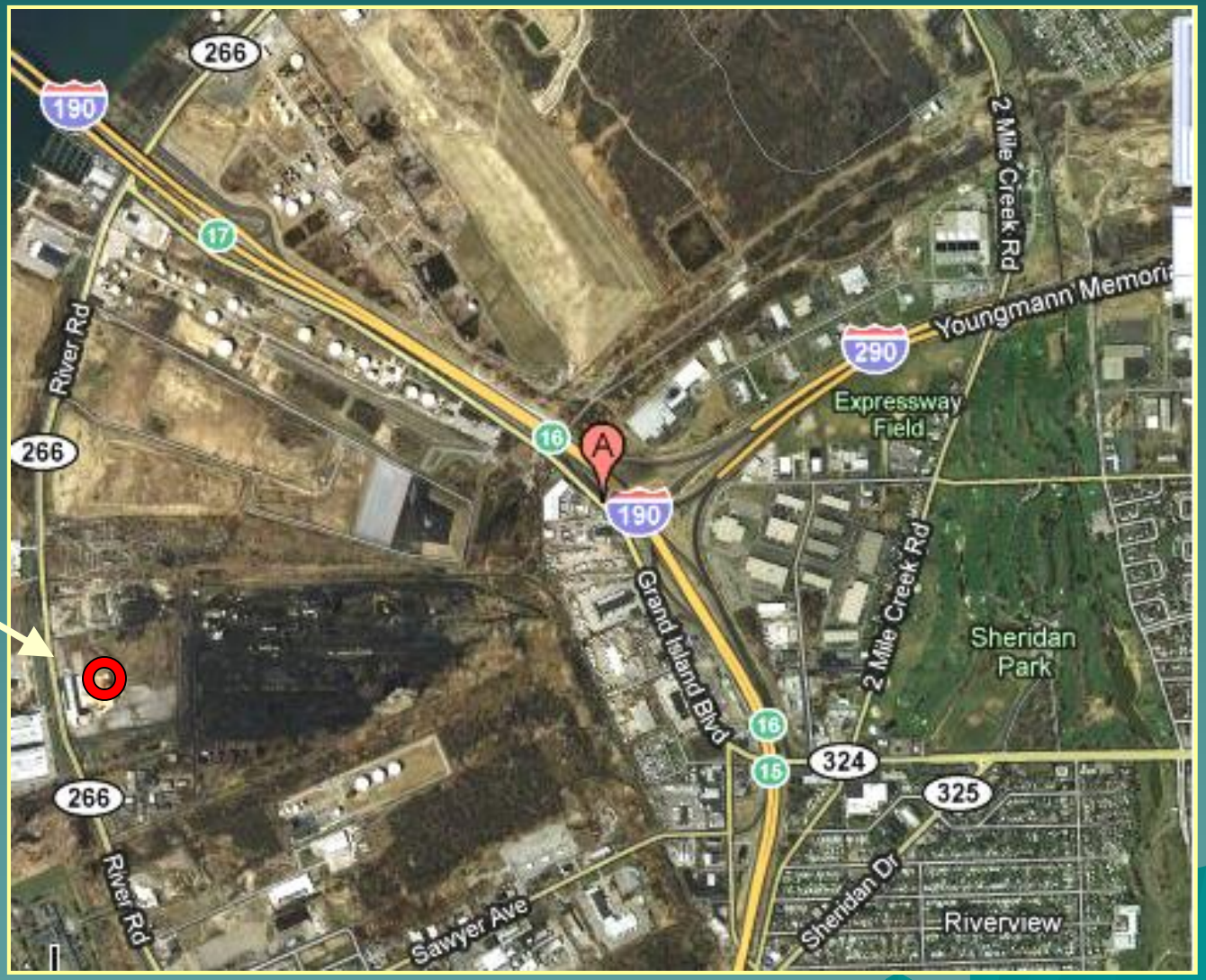
Comparison of Mean Ambient Benzene Concentrations



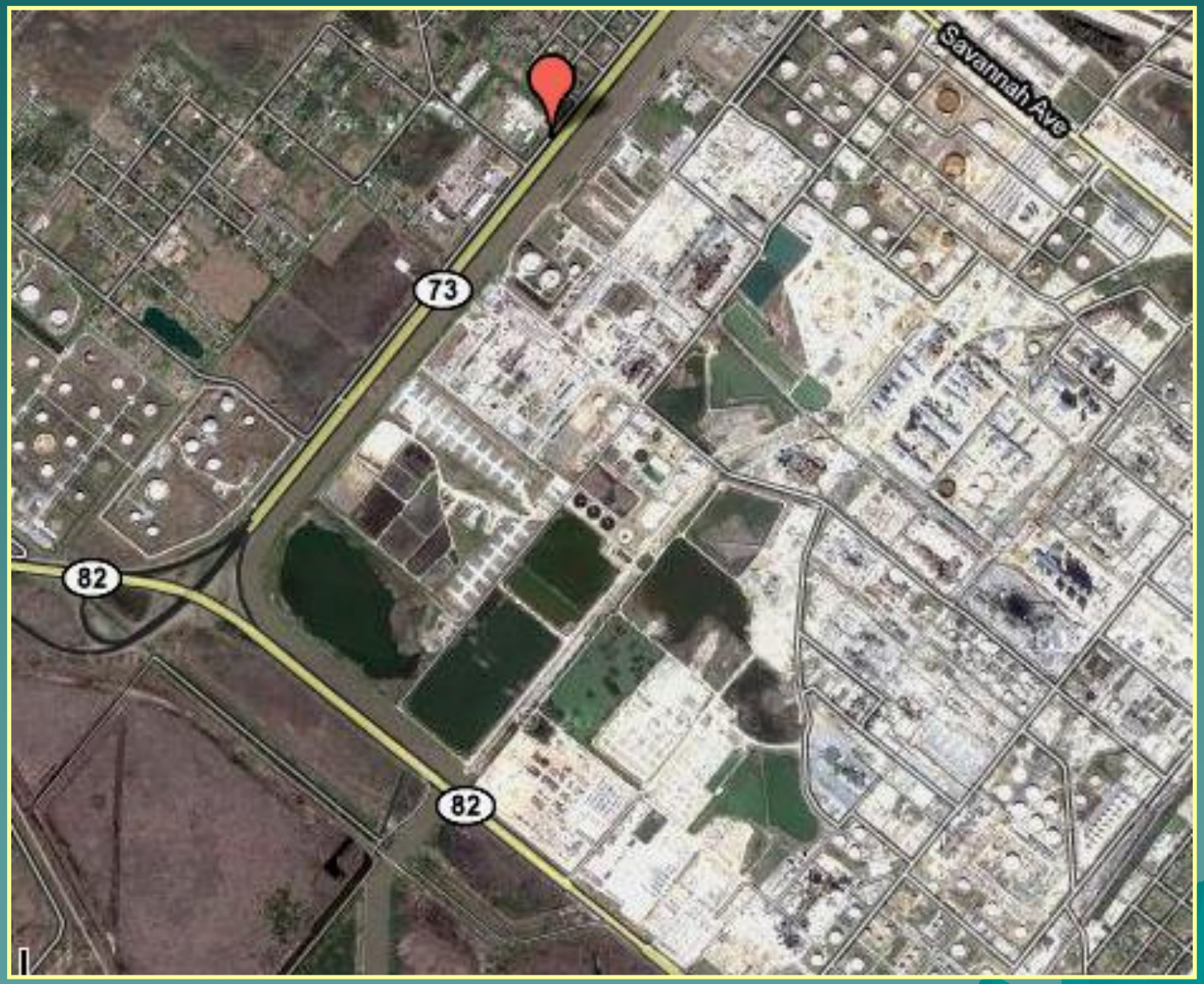
Anchorage Phase 1 results (2008-09) compared with 2008 data from other cities.

Tonawanda, NY 2.5 ppb (99th percentile)

Tonawanda Coke
90.8 tons/yr
benzene

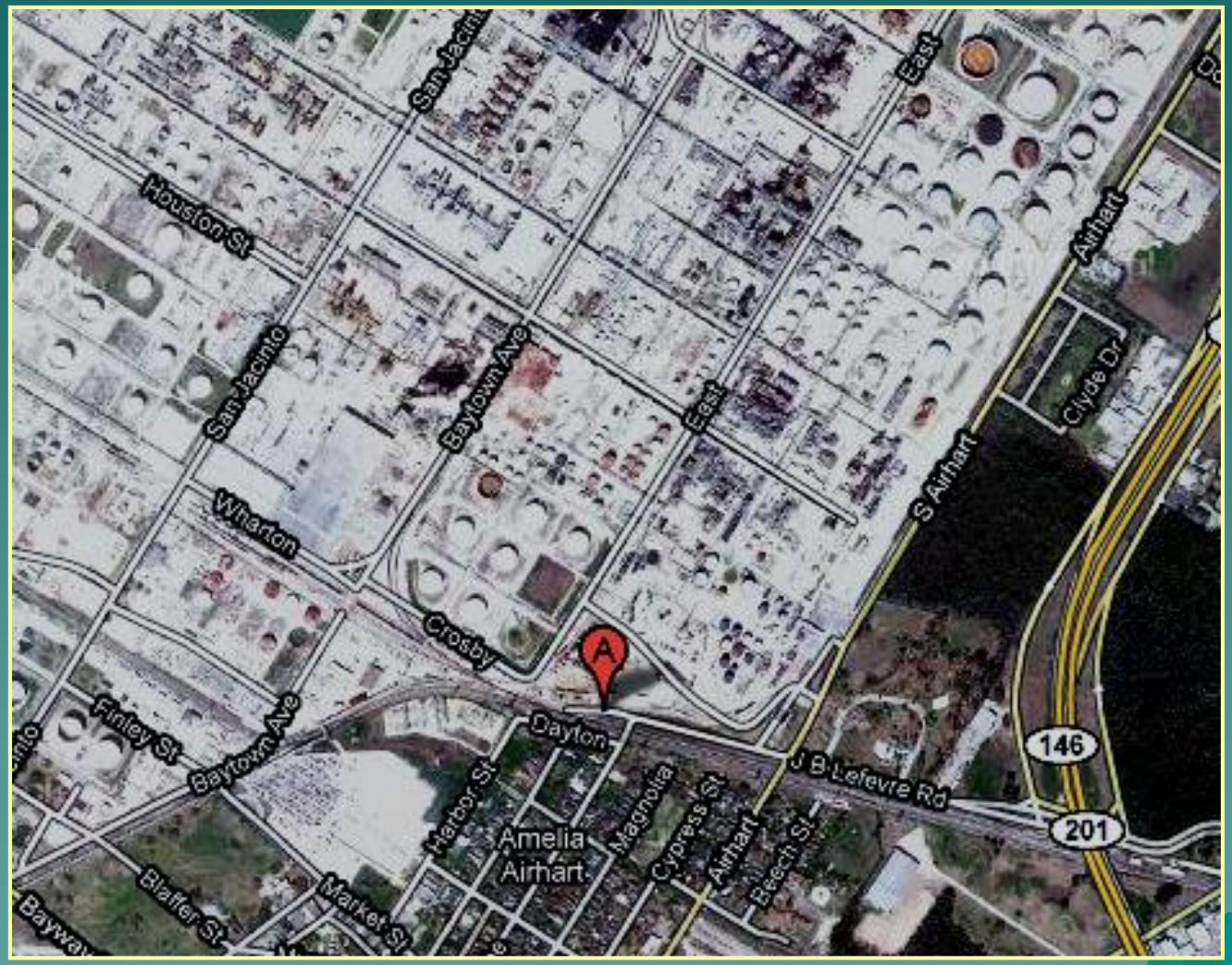


Port Arthur, TX 1.9 ppb (99th percentile)



Galena Park, TX 1.1 ppb (98th percentile)

Baytown/Houston, TX 1.0 ppb (97th percentile)



Tulsa, OK 0.9 ppb (95th percentile)

Boise, ID 0.35 ppb 75th percentile

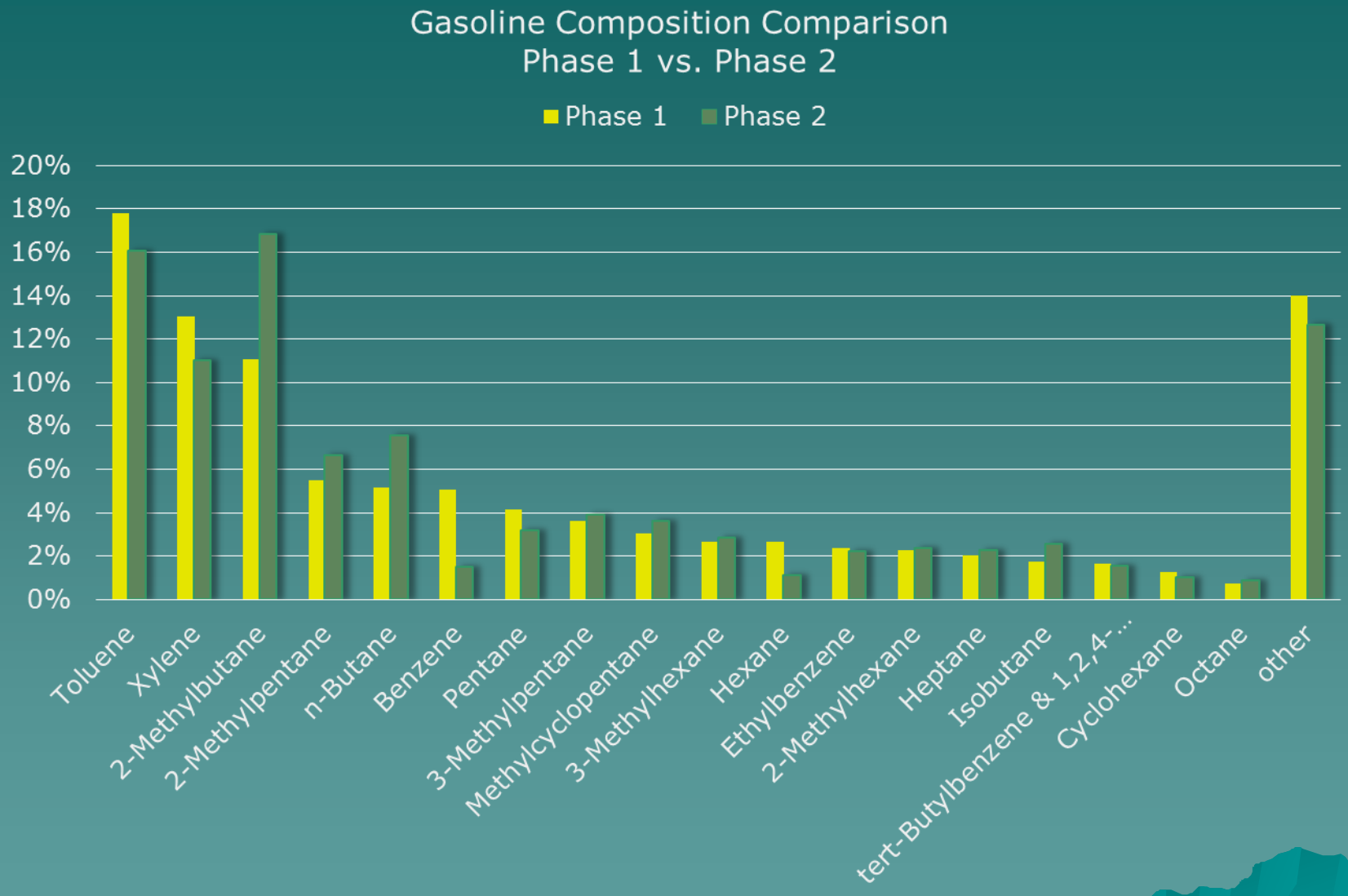
Phase 2

- 3 years after Phase 1
- 6 months after Tesoro Alaska began producing gasoline meeting 1.3% v/v benzene limit.
- Used nearly identical protocols for collection and analysis of ambient samples and gasoline samples from local gasoline retailers.

Phase 2 Results

Gasoline Composition

- Benzene content dropped by 70%
  - 5.05% to 1.53% (by weight)
  - 4.16% to 1.26% (by volume)
- Ethyl benzene, xylene, hexane and a few other components fell slightly
- Butanes increased
- Overall change in gasoline formulation between Phase 1 and 2 was not dramatic


Gasoline Composition Comparison
Phase 1 vs. Phase 2
Phase 1
Phase 2
20%
18%
16%
14%
12%
10%
8%
6%
4%
2%
0%
Toluene
Xylene
2-Methylbutane
2-Methylpentane
n-Butane
Benzene
Pentane
3-Methylpentane
Methylcyclopentane
3-Methylhexane
Hexane
Ethylbenzene
2-Methylhexane
Heptane
Isobutane
tert-Butylbenzene & 1,2,4-…
Cyclohexane
Octane
other

Ambient Concentrations

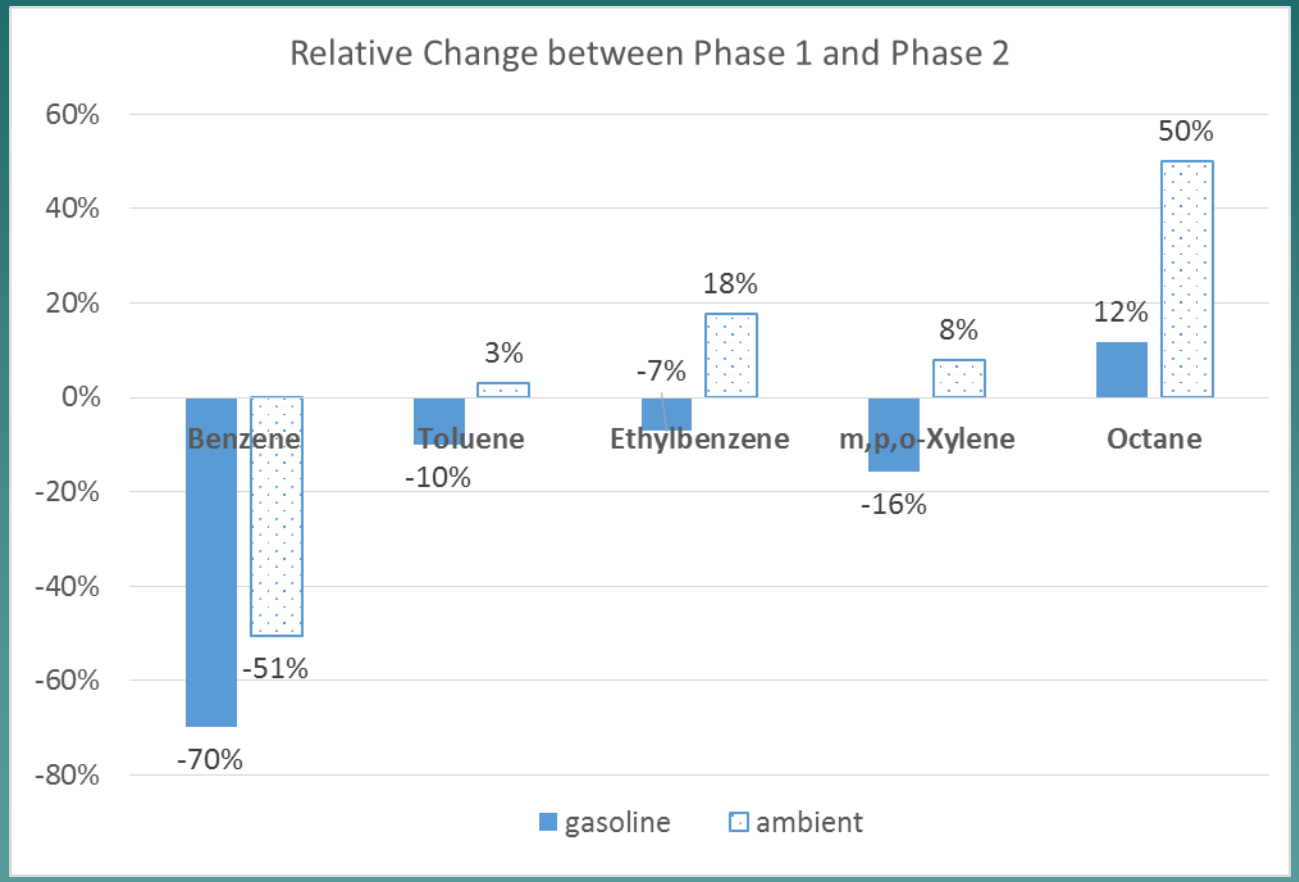
VOCs (ppbv)

	Phase 1		Phase 2			
	mean	(1 SE)	mean	(1 SE)	Δ	Δ%
Toluene	1.68	(0.24)	1.73	(0.23)	0.05	3
Benzene	**0.99**	**(0.12)**	**0.49**	**(0.05)**	**-0.51**	**-51**
m,p, o-Xylene	0.77	(0.10)	0.83	(0.11)	0.07	8
Ethylbenzene	0.17	(0.02)	0.20	(0.03)	0.04	22
n-Octane	0.04	(0.00)	0.06	(0.01)	0.02	57
Acetylene	2.45	(0.33)	1.75	(0.22)	-0.70	-28
Propylene	0.68	(0.08)	0.61	(0.07)	-0.07	-10
Chloromethane	0.68	(0.02)	0.53	(0.01)	-0.16	-23
Dichlorodifluoromethane	0.64	(0.02)	0.52	(0.01)	-0.12	-19
Acrolein	0.30	(0.08)	0.25	(0.02)	-0.05	-18
Trichlorofluoromethane	0.29	(0.01)	0.26	(0.00)	-0.04	-12
Dichloromethane	0.16	(0.02)	0.15	(0.01)	-0.01	-4
Carbon Tetrachloride	0.11	(0.01)	0.10	(0.00)	-0.01	-9
Trichlorotrifluoroethane	0.10	(0.00)	0.08	(0.00)	-0.02	-21
Acetonitrile	0.08	(0.01)	0.06	(0.00)	-0.03	-31
1,3-Butadiene	0.07	(0.01)	0.07	(0.01)	0.00	-5
1,2,4-Trimethylbenzene	0.07	(0.01)	0.10	(0.01)	0.03	38
Methyl Isobutyl Ketone	0.03	(0.00)	0.02	(0.00)	-0.01	-27
Styrene	0.03	(0.00)	0.03	(0.00)	0.00	12
1,3,5-Trimethylbenzene	0.03	(0.00)	0.03	(0.00)	0.00	12
Tetrachloroethylene	0.03	(0.01)	0.02	(0.00)	-0.01	-43
Chloroform	0.02	(0.00)	0.02	(0.00)	-0.01	-28
Dichlorotetrafluoroethane	0.02	(0.00)	0.02	(0.00)	0.00	-15
Total VOC	**9.45**	**-0.87**	**7.96**	**-0.73**	**-1.49**	**-16**

Benzene down 51%

Negligible change in 1,3-butadiene

Relationship between change in gasoline content and change in ambient concentration



PAHs (ng/m³)

	Phase 1		Phase 2			
	mean	(1 SE)	mean	(1 SE)	Δ	Δ%
Naphthalene	65.30	(6.78)	58.50	(7.15)	-6.77	-10
Phenanthrene	6.45	(0.47)	5.71	(0.54)	-0.74	-11
Fluorene	3.60	(0.24)	2.60	(0.36)	-0.93	-26
Acenaphthylene	2.54	(0.50)	2.24	(0.59)	-0.3	-12
Acenaphthene	2.30	(0.27)	2.50	(0.32)	0.17	7
Pyrene	1.60	(0.26)	2.27	(0.16)	0.67	42
Retene	1.42	(0.12)	0.92	(0.33)	-0.5	-35
Fluoranthene	1.38	(0.15)	1.65	(0.14)	0.28	20
9-Fluorenone	0.95	(0.10)	1.20	(0.12)	0.24	25
Chrysene	0.37	(0.05)	0.30	(0.08)	-0.07	-18
Benzo (b) fluoranthene	0.35	(0.05)	0.25	(0.08)	-0.1	-28
Benzo (g,h,i) perylene	0.23	(0.03)	0.13	(0.05)	-0.1	-44
Benzo (e) pyrene	0.16	(0.02)	0.12	(0.04)	-0.05	-27
Total PAH	**86.60**	**(8.38)**	**79.39**	**(9.25)**	**-7.21**	**-8**

How much of the decline in ambient benzene concentration can be attributed to the new gasoline benzene standard?

Other factors could have contributed to the decline.

Possible factors influencing change in ambient benzene concentration

1. **Reduction of gasoline benzene content**
2. Overall improvements in motor vehicle emission control technology between Phase 1 and 2
3. Differences in ambient temperature and weather
4. Other?

Drop in CO concentrations between Phase 1 and 2 suggest that other factors could have been in play.

- Mean ambient CO fell by 13%
- Mean ambient temperature 1.2 °C higher during Phase 2

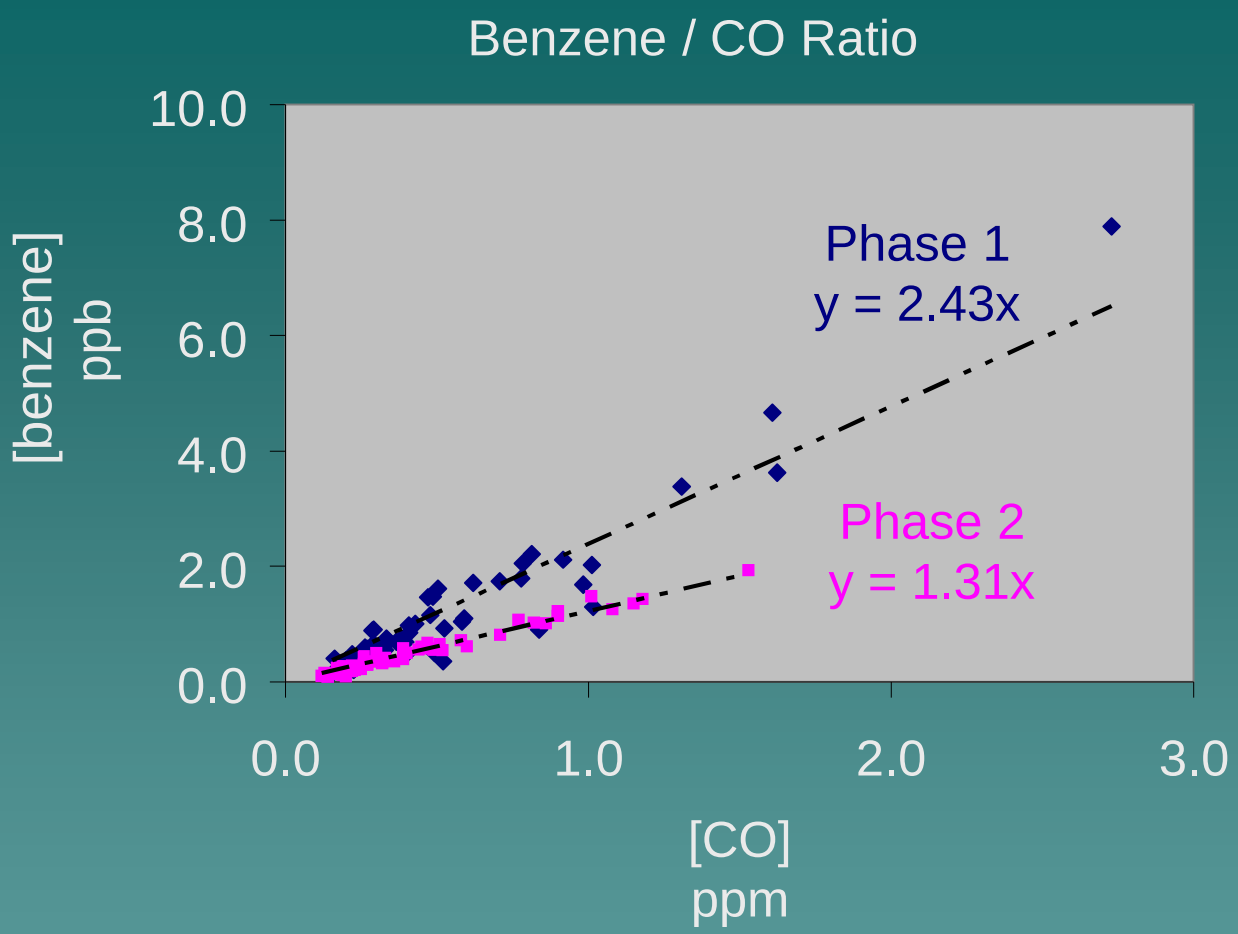
How do we distinguish these effects from "real" reductions from gasoline benzene standard?

Use ratio between ambient VOCs and CO to normalize for the effect of motor vehicle fleet improvements, ambient temperature and weather effects.

We assume:

- Motor vehicle fleet improvements have a similar effect on emissions of CO, benzene and many other VOCs
- Ambient temperature influences emissions of CO, benzene, and other motor vehicle-related VOCs in roughly the same manner (cold start effect is similar)
- Weather / atmospheric dispersion has similar effect on ambient pollutant levels

Assumptions above are predicated on underlying assumption that the changes in gasoline composition between Phase 1 and Phase 2 had no impact on CO emissions

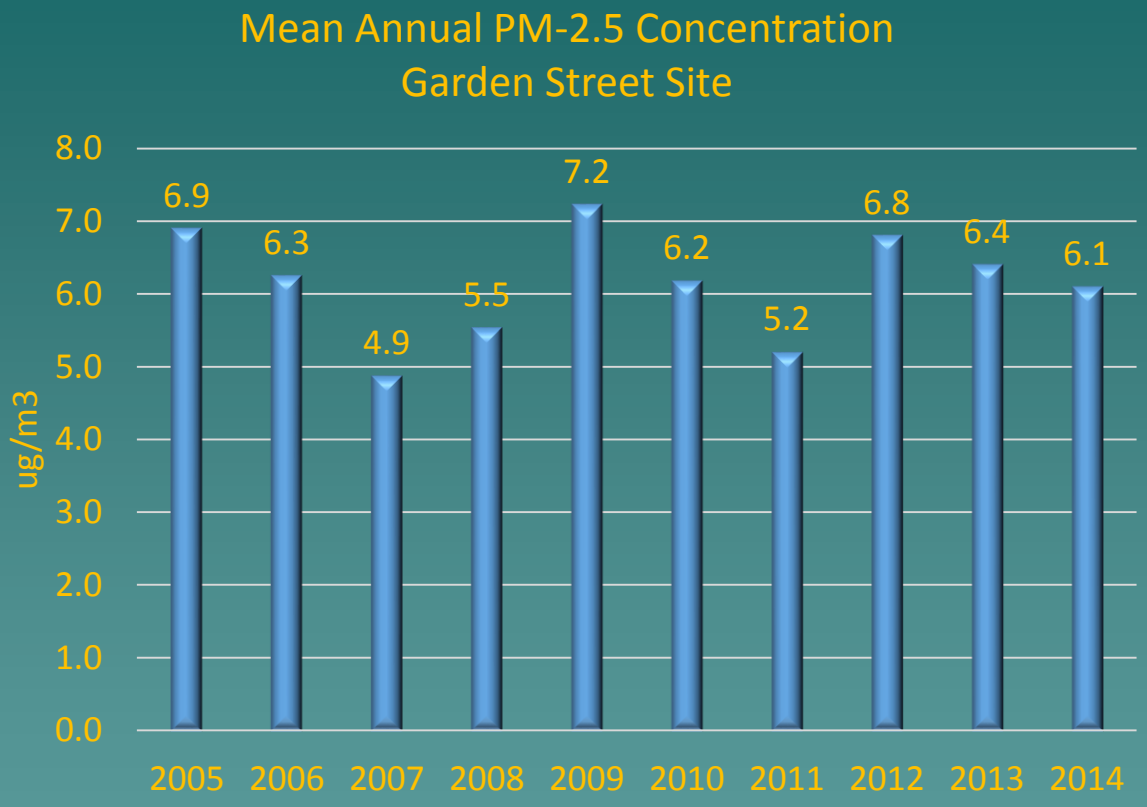


	Phase 1	Phase 2	Δ
Ambient benzene	0.99 ppb	0.49 ppb	-51%
Benzene/CO ratio	2.43	1.31	-46%

Conclusions

- Gasoline benzene content dropped by 70% (5.05% to 1.53% by weight)
- Ambient benzene fell by 51%; most of the decline (46%) attributed directly to benzene reduction in gasoline.
- The change in the benzene / CO ratio (46%) was not proportionate to the reduction in gasoline benzene content (70%).
  - Some tailpipe benzene emissions may be formed during combustion process from other gasoline components (e.g., toluene, ethyl benzene, xylene)
- Concentrations of ambient ethyl benzene, toluene, and xylene increased slightly even though gasoline content was reduced.
- Negligible impact on ambient 1,3-butadiene
- Impact on PM-2.5 and PAHs negligible / unclear

- Mean PM-2.5 concentration declined by 26% between Phase 1 and Phase 2.
- Large year-to-year variation in annual mean suggests that other factors are influencing PM-2.5 concentration
- Single year variations as great as 31% have occurred in other years.



A few words on a companion indoor air study that was never completed ….

Distribution of average annual benzene concentrations by percentile in Anchorage homes with attached garages (2008-2009).