



Contributions to Ozone Formation in the Denver Area

Douglas R. Lawson

“Reducing Ozone in the Denver Region”

Workshop sponsored by

Regional Air Quality Council/Colorado Air Quality Control Commission

October 2, 2002

Outline of Presentation

- Disclaimer
- Background
- Chemistry of Ozone Formation
- Sources of Ozone Precursors
 - Emission Inventories
 - Ambient Studies
- Fuel Formulations
- Vehicle Emissions
- Summary

Disclaimer

Statements and data given in this presentation are not those of the Colorado Air Quality Control Commission, only those of the presenter. These conclusions are subject to change as additional high quality data become available.

— — — — —

Data, findings and conclusions are those from research studies and calculations of the presenter [from Max Planck, "A new scientific truth does not triumph by convincing its opponents and making them see the light, but rather because its opponents die out (*Lawson addition: or retire*), and a new generation grows up that is familiar with it."]

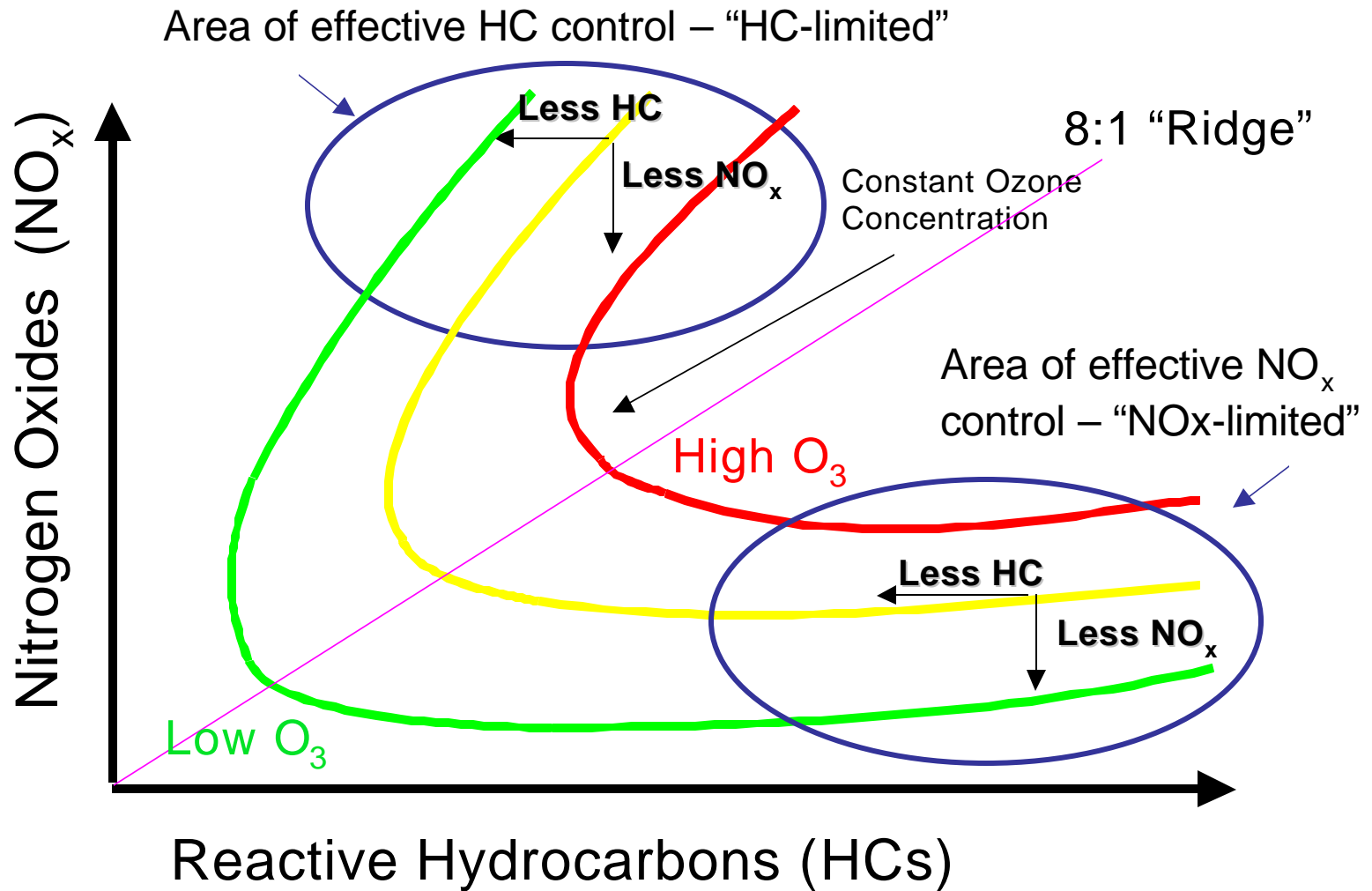
Background

- The Denver area has made very slow progress toward reducing ambient ozone over the years. Why not more and better progress?
- We came perilously close to exceeding the 0.08 ppm ozone standard this summer. Why aren't we doing better?
- Debates have raged for years regarding which pollutant (or both) is the less costly and more effective one to reduce for reducing ambient ozone – hydrocarbons (HC, NMHC, VOC, or ROG) or nitrogen oxides (NO_x, most of which is emitted as NO).


Chemistry of Ozone Formation


- The precursors to ozone formation are VOCs (volatile organic compounds), NO_x (nitrogen oxides), and CO (carbon monoxide)
- Metro Denver area is most likely VOC-limited
- Presentation focus on VOCs
- 1999 National Research Council report on ozone-forming potential of reformulated gasoline:
 - Disproportionate amount of ozone precursor emissions from mobile sources come from a small number of high-emitting vehicles
 - Motor vehicle CO emissions contribute ~20% of the ozone-forming potential from mobile sources

Ozone Isopleth Plot (EKMA Diagram)



From NREL's Weekend Ozone Studies in Los Angeles:

 = Mean Wednesday
 ± 1 sigma

 = Mean Sunday
 ± 1 sigma

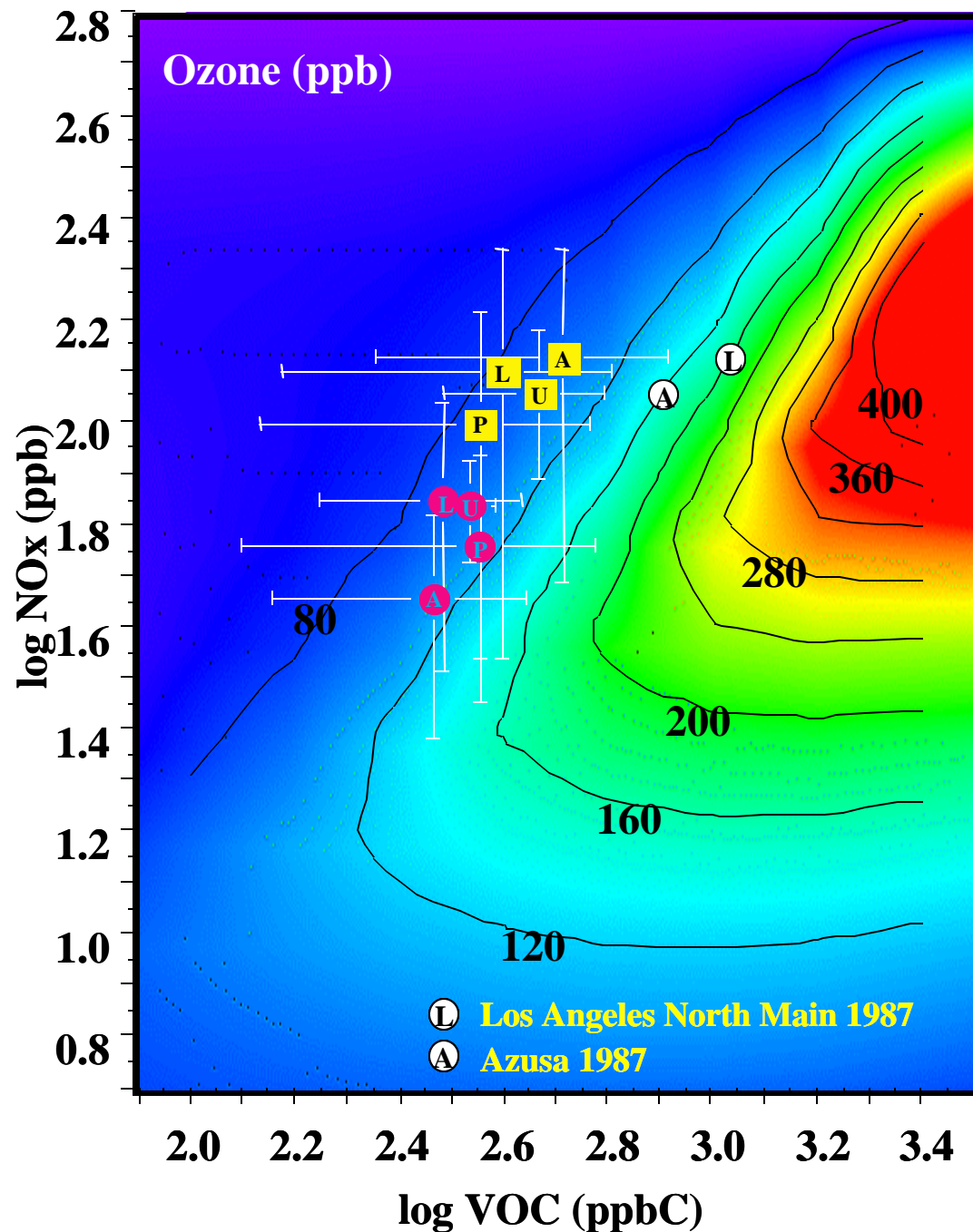
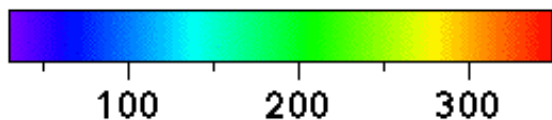
L.A. Monitoring Stations

A – Azusa

L – Los Angeles, N. Main

P – Pico Rivera

U – Upland



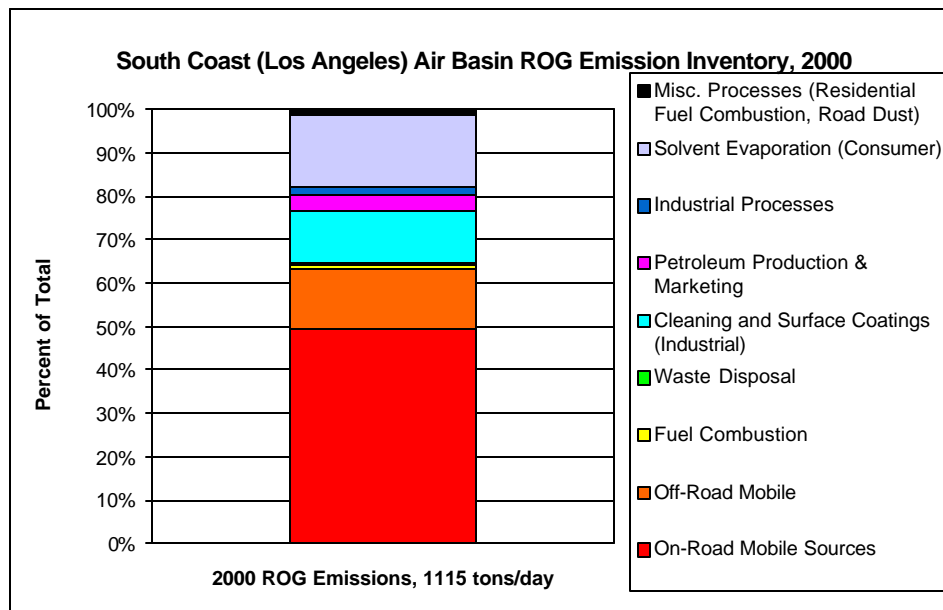
Denver's Weekend Ozone Effect

- Patrick Reddy has shown that the Denver area's ozone is as high or higher on weekends than on weekdays. This phenomenon has been observed in other urban U.S. locations.
- Areas experiencing the weekend ozone effect are hydrocarbon-limited; i.e., hydrocarbon controls are the most effective way to reduce ambient ozone. NO_x controls will increase ambient ozone in urban locations.
- Weekend Ozone Effect in Denver can provide insight as to control measures that would reduce ambient ozone levels. What do we know about changes in HC and/or NO_x emissions on weekends relative to weekdays?

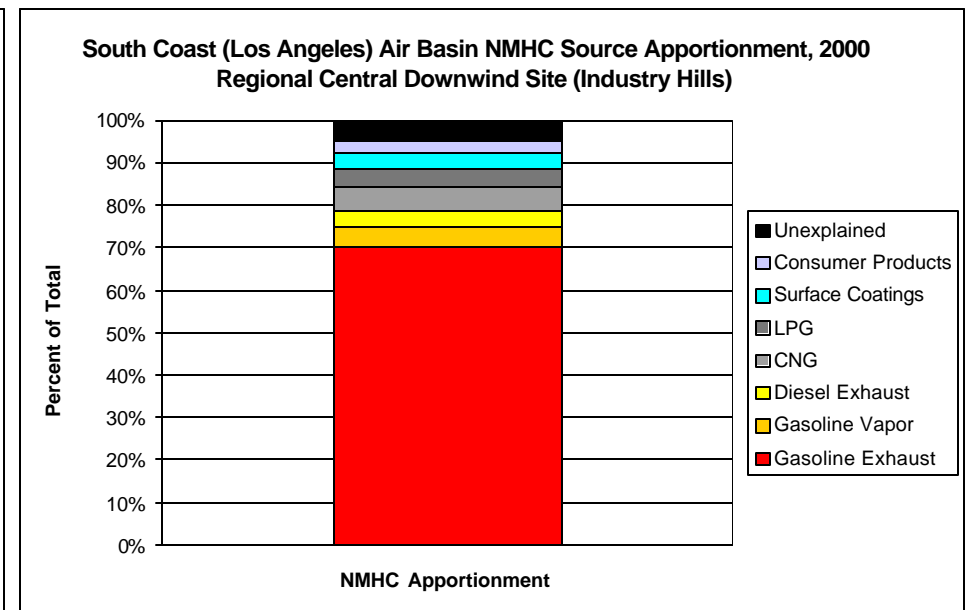
What are the sources
of
ambient hydrocarbons?

Differences between Emission Inventories and Source Apportionment of Ambient HC Data Los Angeles, Year 2000 Data

Emission Inventory Data

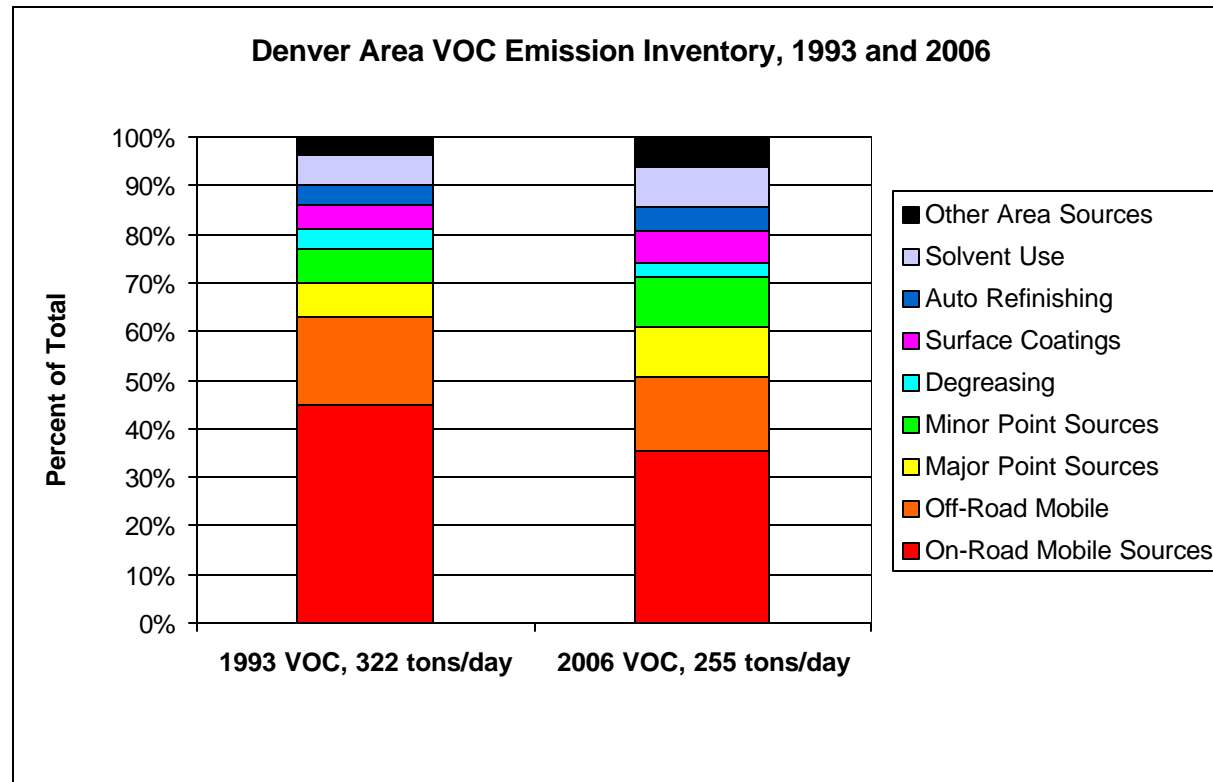


Ambient Source Apportionment Data



Observation: On a proportional basis, there are significantly more "gasoline-like" HCs in the ambient samples than estimated by the emission inventory.

Denver Area VOC Emissions

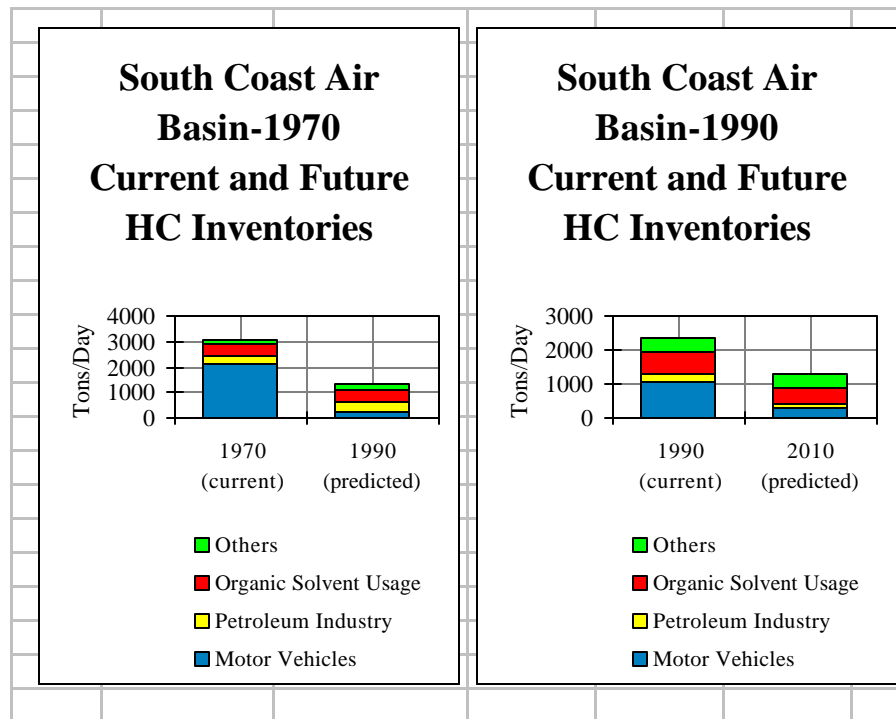


Observation: The inventories suggest that mobile emissions produce about 2/3 of the VOC emissions, and that mobile emissions will be less important in the future.

Question: How reliable are the VOC emission forecasts?

[Casey Stengel quote: "Forecasting is difficult, especially when it involves the future."]

South Coast Air Basin 1970 and 1990 Current and Future HC Emission Inventories



Observation: Current inventories always suggest half or more of the current HC are from mobile sources, and that in the future mobile emissions will be relatively less important than HC emissions from other sources. However, the new base year emissions are always higher than previously predicted, and mobile emissions comprise a greater fraction of the "current" emissions than previously predicted (case in point: MOBILE6 doubles the current CO emissions compared with CO emissions previously predicted by MOBILE5).

HC Emissions Summary

- Current HC speciation does not match the current inventory HC speciation in Los Angeles. This is a problem. What about the Denver area?
- Ambient HC speciation need to match the inventory, so that we might know how and where to make the most effective and least costly emission reductions to reduce ozone.
- The projected HC (and CO) emission reductions for mobile source emissions, have fallen way short of projections. What about HC from MOBILE6 for the Denver area? What do we know about the accuracy of MOBILE6 outputs? What can we do to request more accountability from EPA regarding MOBILE outputs?

Questions regarding accuracy/reliability of the Denver Area emission inventory

- How accurate is the output from the MOBILE6 model? We need to know!
- How accurate are the other large emission components in the Denver area inventory?
- Lawn and Garden Equipment/Logging (L&G/L)
 - In Denver area, L&G/L emits 28 tons/day in 1993; in all of California L&G equipment emits 75 tons/day. Why such a large discrepancy?
- How accurate are the estimates for degreasing, coatings, and solvent use? And can we observe compounds from these HC sources in Denver's ambient data?

Observation: We need to know the accuracy of the emission estimates in Denver's inventory for the important HC emission categories before reliable control strategies can be adopted. Can the Workgroup help in this area?

Source of Most HC Emissions

- Mobile sources
- Gasoline-powered vehicles; only a small amount from Diesels
- Most of the exhaust HC comes from just a few vehicles
- Amount of HC from evaporative and refueling losses, as well as other nontailpipe sources is highly uncertain and open to conjecture. MOBILE6 suggests nontailpipe HC emissions are about $1/3$ those from the exhaust.
- Gasoline is the “parent material” of HC emissions, leading to strategies to modify fuel composition

Effects of Reformulated Fuels

- "...California introduced Phase 2 RFG in the spring of 1996. In contrast to what was expected, the observed on-road emissions of HCs and the reactivity of the emissions did not significantly change following the implementation of the new fuel." – Gertler *et al.*, *JAWMA*, vol. 49, pp. 1339-1346 (1999). These results have been confirmed by researchers at UC Berkeley.
- In the Denver area, reducing the RVP of gasoline actually increases the reactivity or ozone-forming potential of the fuel.

Observation: It is not the fuels that are the problem, it is the cars that are the problem.

Ozone-forming potential of lower RVP summer fuel

	Base Fuel	CARB MIR,	Base Fuel,		Low RVP Fuel,
Compound	Weight Fraction	1998	Total Reactivity	Weight Fraction	Total Reactivity
ethene	0	9.97	0.00	0	0.00
acetylene	0	1.23	0.00	0	0.00
ethane	0	0.35	0.00	0	0.00
propene	0	12.44	0.00	0	0.00
n-propane	0	0.64	0.00	0	0.00
isobutane	0.27	1.56	0.42	0	0.00
1-butene	0	10.8	0.00	0	0.00
n-butane	3.03	1.44	4.36	0	0.00
t-2-butene	0.06	14.52	0.87	0	0.00
c-2-butene	0.07	13.8	0.97	0	0.00
isopentane	10.01	1.93	19.32	10.31	19.90
1-pentene	0.3	8.16	2.45	0.31	2.52
n-pentane	6.67	1.74	11.61	6.87	11.95
isoprene	0.01	11.47	0.11	0.01	0.12
t-2-pentene	0	10.63	0.00	0	0.00
c-2-pentene	0.29	10.63	3.08	0.30	3.18
2,2-dimethylbutane	0.34	1.52	0.52	0.35	0.53
cyclopentane	0.04	2.61	0.10	0.04	0.11
2,3-dimethylbutane	2.1	1.31	2.75	2.16	2.83
2-methylpentane	4.61	2.07	9.54	4.75	9.83
3-methylpentane	2.8	1.5	4.20	2.88	4.33
2-methyl-1-pentene	0	4.42	0.00	0	0.00
n-hexane	3.84	1.69	6.49	3.96	6.68
methylcyclopentane	0	2.4	0.00	0	0.00
2,4-dimethylpentane	1.25	1.85	2.31	1.29	2.38
benzene	3.21	1.00	3.21	3.31	3.31
cyclohexane	0.54	1.96	1.06	0.56	1.09
2-methylhexane	1.66	1.78	2.95	1.71	3.04
2,3-dimethylpentane	2.48	1.78	4.41	2.55	4.55
3-methylhexane	1.96	2.22	4.35	2.02	4.48
2,2,4-trimethylpentane	3.87	1.69	6.54	3.99	6.74

	Base Fuel	CARB MIR,	Base Fuel,		Low RVP Fuel,
Compound	Weight Fraction	1998	Total Reactivity	Weight Fraction	Total Reactivity
n-heptane	1.62	1.43	2.32	1.67	2.39
methylcyclohexane	0.34	2.11	0.72	0.35	0.74
2,3,4-trimethylpentane	1.68	1.52	2.55	1.73	2.63
toluene	15.93	4.19	66.75	16.41	68.75
2-methylheptane	0.66	1.54	1.02	0.68	1.05
3-methylheptane	0.74	1.78	1.32	0.76	1.36
n-octane	0.59	1.24	0.73	0.61	0.75
ethylbenzene	2.82	2.97	8.38	2.90	8.63
m,p-xylene	10.45	7.75	80.99	10.76	83.42
styrene	0	2.52	0.00	0	0.00
o-xylene	3.94	7.83	30.85	4.06	31.78
n-nonane	0.31	1.07	0.33	0.32	0.34
isopropylbenzene	0.19	2.48	0.47	0.20	0.49
n-propylbenzene	0.83	2.35	1.95	0.85	2.01
m-ethyltoluene	2.56	7.2	18.43	2.64	18.98
p-ethyltoluene	1.11	7.2	7.99	1.14	8.23
1,3,5-trimethylbenzene	1.31	11.1	14.54	1.35	14.98
o-ethyltoluene	0.9	7.2	6.48	0.93	6.67
1,2,4-trimethylbenzene	4.11	7.49	30.78	4.23	31.71
n-decane	0.02	0.95	0.02	0.02	0.02
1,2,3-trimethylbenzene	0	11.9	0.00	0	0.00
m-diethylbenzene	0.35	6.45	2.26	0.36	2.33
p-diethylbenzene	0	6.45	0.00	0	0.00
n-undecane	0.13	0.82	0.11	0.13	0.11
other identified hydrocarbons	18.01		0.00	18.55	0.00
unidentified hydrocarbons	3.58		0.00	3.69	0.00
methyl-t-butyl ether	0	1.34	0.00	0	0.00
Total Reactivity			370.62		374.91

Note: Weight fraction of species in fuel normalized to 55 PAMS species.

MIR data from CARB website and Kirschtetter et al., ES&T, vol. 33:329-336 (1999).

MIR = maximum incremental reactivity: the maximum weight of ozone formed by adding a compound to the base ROG mixture per weight of compound added, expressed to hundredth of a gram (μ O₃/ μ VOC)

Observation: Lower RVP fuel has 1% higher ozone-forming potential than base fuel. Evaporative emissions from a lower RVP fuel may be lower in some cases than conventional fuel, but their reactivity is higher.

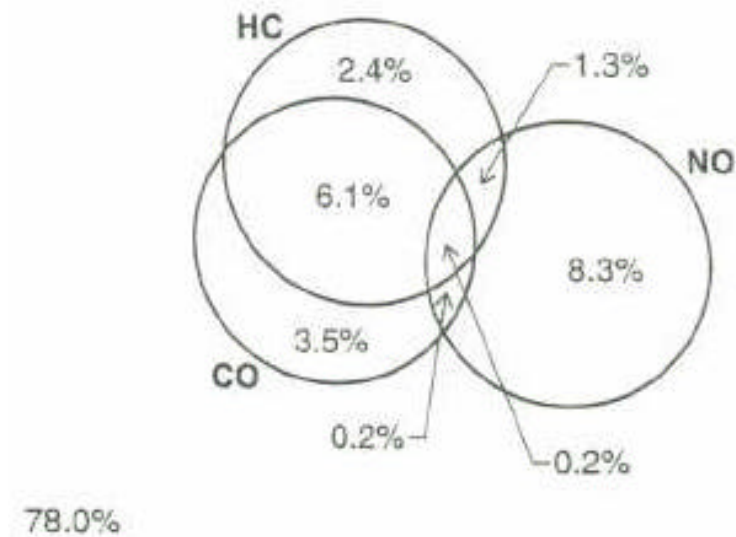
HC Emissions from Gasoline-Powered Vehicles

- Exhaust or tailpipe emissions
 - Cold start – these are being reduced with improved technology
 - Off-cycle emissions – these are being reduced with improved technology
 - High emitters – these are still found on the road, despite our following EPA mandates for emission testing programs
- “Nontailpipe” emissions
 - Many different categories – diurnal, hot soak, running losses, resting losses, refueling, etc. These are being reduced as a result of tighter “nontailpipe” standards.
 - I/M in Denver tests for only 1 category – bad gas caps
- The relative importance of the two types of emissions has not been quantified. EPA’s MOBILE model suggests that “nontailpipe” emissions are more important than a limited number of field studies have suggested [Pierson *et al.*, *JAWMA*, vol. 49, 498-519 (1999)].

Exhaust HC Emissions from Gasoline-Powered Vehicles

- Very skewed emission distribution.
- An old phenomenon; first reported to CARB in 1983.
- Most recent study from Denver by Don Stedman's group: dirtiest 10% of the fleet produced 77% of the HC (Pokharel, Bishop, and Stedman, 2002).
- 3 days of remote sensing at I-25 and 6th Ave. in Jan. 2001.
- ~21,000 valid readings; therefore 2100 vehicles produced 77% of the observed HC emissions. Assuming ~10% of the vehicles were observed more than once, about 1900 vehicles were identified having excessive emissions in only 3 days of remote sensing measurements at one site.
- Most recent study showed that 96% of the vehicles identified as high emitters by remote sensing failed a confirmatory emissions test when pulled over immediately after having been identified by the remote sensor.

How are high emitters' emissions distributed?



Note: figure not drawn to correct proportions

Observation: Amount of overlap from the highest 10% CO, HC, and NO in the light-duty fleet. ASM test cycle data from 12,977 vehicles in California's 1998-99 "random" roadside inspections. Sizes of the overlapping areas not drawn to scale. 78% of the vehicles tested were not in the top 10% for CO, HC, or NO. Source: NRC report on I/M effectiveness.

The Problem of High HC Emitters

Still on the road despite our best efforts to find and fix them with a centralized IM240 program. Reasons (NRC report on effectiveness of I/M programs):

- Up to now, there are no incentives for any state to find them, because the MOBILE model gives unproven emission credits for I/M programs.
- We get emission credits for our I/M program to obtain highway funds.
- I/M programs provide a study of human behavior and the law of unintended consequences.
- Motorists are unwilling/unable to spend the money for adequate repairs. In controlled studies where the motorist is removed from the repair process, I/M repair costs average **at least** 2x the repair costs in I/M programs.
- Some of the vehicles are difficult to repair.
- Insufficient money is being spent on repairs (vehicles are repaired to "pass the test.")
- 23% of the vehicles that fail the IM240 test "disappear" from the program.
- Data from Ohio show that ~7% of the motorists register outside the I/M program area once the program begins. In Colorado, all you have to do is phone the county to obtain a form stating that the vehicle's residence is outside the IM240 region.
- Colorado's vehicle cost repair limit is \$450. Once that money is spent repairing a vehicle, it is excused from the program for another two years.

Summary of Observations

- The Denver area, although having made progress in reducing ambient ozone levels, is too close to violating the ozone standard. We should ask “why?” after all these years of emission control programs.
- Denver experiences the weekend ozone effect, which provides insight regarding pollutant reduction scenarios.
- The Denver area appears to be HC-limited with respect to ozone formation.
- There are discrepancies between ambient studies and HC emission inventories regarding source contributions of HC emissions.
- Emission inventories have always been too optimistic regarding current and future HC emission reductions from mobile sources.
- The majority of the Denver area’s ozone problem comes from HC emissions, which in turn, comes from mobile sources.
- Gasoline reformulation has done little, if anything, to reduce ozone-forming pollution from spark-ignition vehicles (California’s citizens pay 10-20¢ more per gallon than we do for California’ Phase 2 gasoline).
- The majority of on-road exhaust HC emissions comes just a few vehicles. These are the “low-hanging fruit.”
- Remote sensing is the silver bullet.

Disclaimer

Statements and data given in this presentation are not those of the Colorado Air Quality Control Commission, only those of the presenter. These conclusions are subject to change as additional high quality data become available.