A Note on Vehicle Refueling Emissions

By Paolo Zannetti

The EnviroComp Institute (www.envirocomp.org)

zannetti@envirocomp.org

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These slides were taken from a US EPA site:

https://www.epa.gov/sites/production/files/2017-11/documents/vehicle_refueling_emissions.pdf

presenting Refueling Emission Inventories and Regulatory Policy. The presentation was prepared by Glenn W. Passavant, Ingevity Corporation, North Charleston, SC.

Vehicle Refueling Emissions

Refueling Emission Inventories and Regulatory Policy

US EPA Emissions Inventory Conference
Baltimore, MD

August 2017

Glenn W. Passavant
Ingevity Corporation
North Charleston, SC

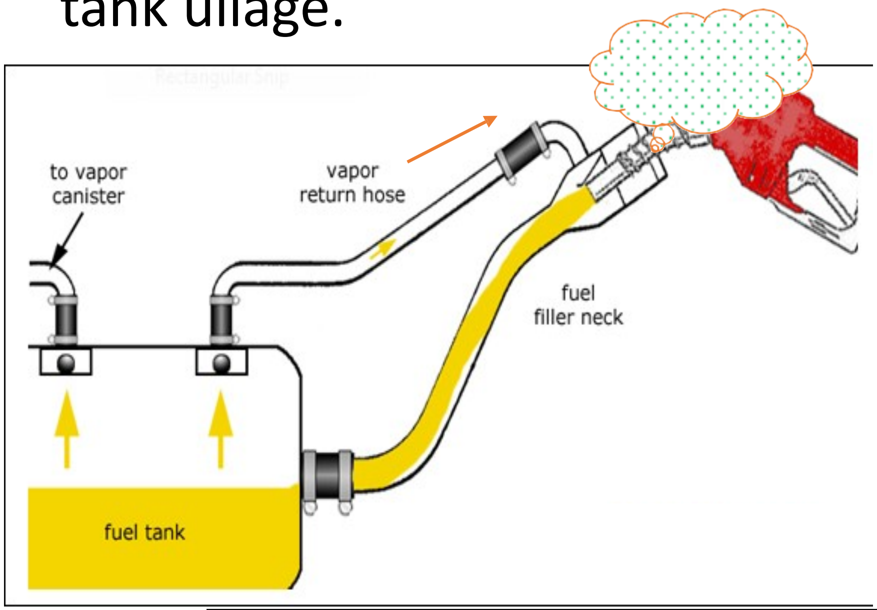
Overview

- What are vehicle refueling emissions?
- What hydrocarbon compounds are in refueling emissions?
- Why should we care about refueling emissions?
- What factors affect the per vehicle refueling emission rate?

- Case 1: USA
- Case 2: China
- Case 3: EU
- Case 4: Brazil

What are vehicle refueling emissions?

- VOC vapor and entrained droplets displaced from the fuel tank ullage.

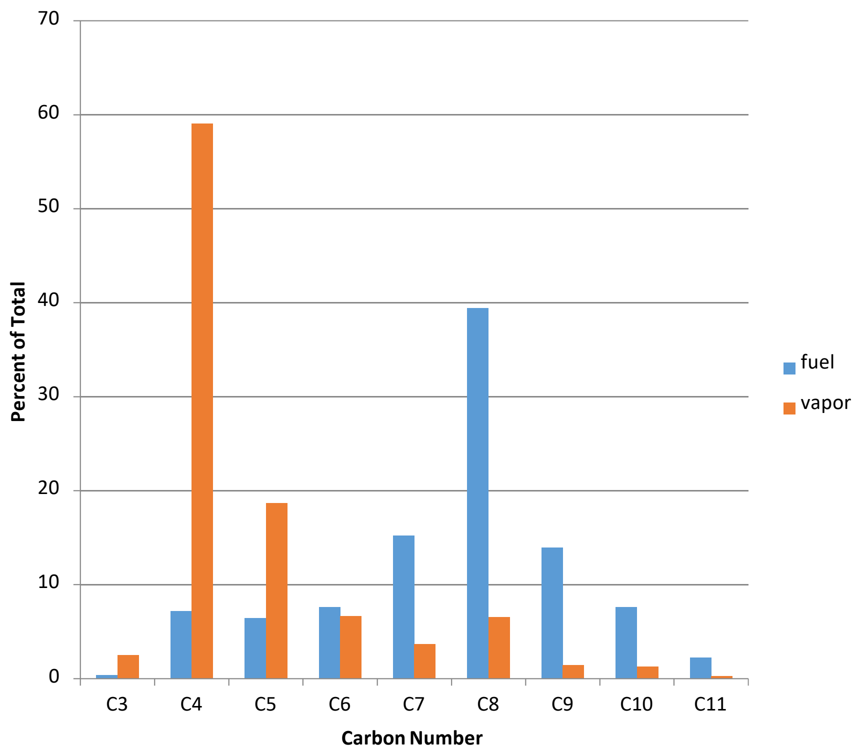


- Any fuel spilled during the refueling event.

Mostly of concern for volatile liquid fuels (>2 psi RVP)

VOC Composition of Refueling Emissions

- Refueling vapors are dominated by (C4 and C5) compounds (butanes and pentanes); liquid gasoline is dominated by a variety of heavier (C6 to C9) compounds.
- Addition of ethanol changes vapor composition but it remains dominated by lighter weight compounds (C5 or less).



SAE Paper 880712 : "Factors Influencing the Composition and Quantity of Passenger Car Refueling Emissions - Part II"

Why Control Refueling Emissions? – O_3 Reactivity

- Ozone is formed through photochemical interactions of VOCs and NOx. Many different VOCs are emitted into the atmosphere, each reacting at different rates and with different reaction mechanisms.
- The differences in rates of ozone formation are referred to as the ozone "reactivity" of the VOCs and are quantified through Reactivity Adjustment Factors (RAFs).
- Ozone RAFs have been determined for each VOC.
- The lighter weight compounds which are dominant in gasoline vapor are moderately reactive. However, they represent such a large fraction of the total emission mass, that reducing lighter ends through RVP control is a major ozone reduction strategy.
- In this sample, C4-C5 compounds represent 65% of ozone forming potential emissions from gasoline vapor.
- VOCs, such as aromatic compounds. also form secondary organic aerosols ($PM_{2.5}$). The fraction of aromatic compounds varies with gasoline grade.

* SAE Paper 860086: "Composition of Vapor Emitted from a Vehicle Gasoline Tank During Refueling"

** 17 CCR 94700 : "Maximum Incremental Reactivity Values for Compounds - 2010"

Compound	mass % liquid*	mass % vapor*	CA ARB RAF**	mass vapor % wtd RAF
propane	0.06	1.9	0.49	0.65%
n-butane	5.27	47.6	1.15	38.30%
n-pentane	1.21	3.1	1.31	2.84%
n-hexane	1.28	0.9	1.15	0.72%
isobutane	0.45	6.1	1.23	5.25%
isopentane	4.92	17.6	1.45	17.86%
2,2-dimethylbutane	0.01	0.7	1.17	0.57%
2,3-dimethylbutane	2.2	2.6	0.97	1.76%
2-methylpentane	1.81	1.9	1.5	1.99%
3-methylpentane	1.28	1.2	1.8	1.51%
2,4-dimethylpentane	1.78	0.9	1.55	0.98%
3,3-dimethylpentane	3.79	1.2	1.2	1.01%
3-methylhexane	1.3	0.4	1.61	0.45%
2,2,4-trimethylpentane	9.12	2.2	1.2	1.85%
2,3,4-trimethylpentane	5.41	0.7	0.96	0.47%
methylcyclopentane	0.47	0.3	2.06	0.43%
2-methyl-1-butene	0.16	0.5	6.4	2.24%
cis-2-butene	0.07	0.5	14.24	4.98%
trans-2-butene	0.03	0.5	15.16	5.30%
cis-2-pentene	0.21	0.5	10.38	3.63%
toluene	18.01	2.3	4	6.44%
benzene	2.9	1.5	0.72	0.76%

Air Toxic Exposures

- Gasoline vapor contains compounds which adversely affect health
- Occupational health impacts for service station attendants:
  - At higher concentrations, gasoline vapor may result in adverse impacts
    - **Symptoms:** irritant, dermatitis, headache, lassitude, blurred vision, dizziness, slurred speech, confusion, convulsions; chemical pneumonitis; possible liver, kidney damage
  - ACGIH 8-hr gasoline vapor TLV is 300 ppm and the 15-min.; STEL is 500 ppm.
  - Even at very low concentrations, benzene vapor may result in adverse impacts
    - Hematotoxicity and potential carcinogen (leukemia)
  - ACGIH 8-hr benzene TLV is 0.50 ppm and the 15-min. STEL is 2.5 ppm.
- Community health impacts
  - No identified chronic exposure standards for gasoline vapor or benzene, only AEGLs.

B. Edokpolo, Q.J. Yu, D. Connell, "Health Risk Characterization for Exposure to Benzene in Service Stations and Petroleum Refineries Environments Using Human Adverse Response Data," Toxicology Reports 2 (2015), pp. 917-927.

Refueling VOC Emission Rates

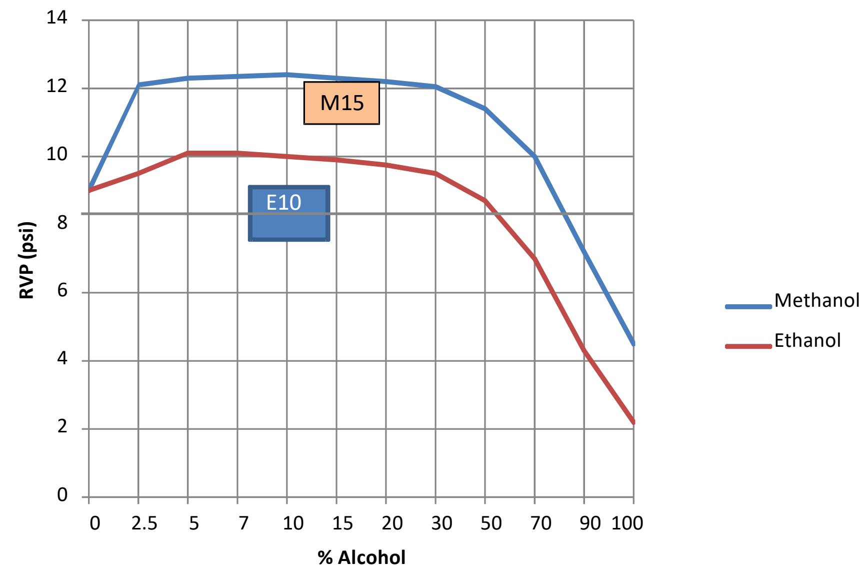
- Between 1972 and 1988 there were at least six studies which evaluated uncontrolled refueling emission rates on a g/gal basis.
- Each study gave a slightly different results depending on the vehicles evaluated and the range of the key experimental factors included such as the vapor pressure and temperatures.
- A 1988 study by the CRC (VE-6) was the most comprehensive. The relationship in the equation below reflects a fill from 10% to 100%. It is the equation used by EPA.

$$g/gal = \exp[-1.2798-0.0049(\Delta T) + 0.0203(T_d) + 0.1315(RVP)]$$

  - Where $\Delta T = (T_{tank}-T_{dispensed})$; temperatures are in °F, RVP is in psi

Factors Affecting the VOC Emission Rate

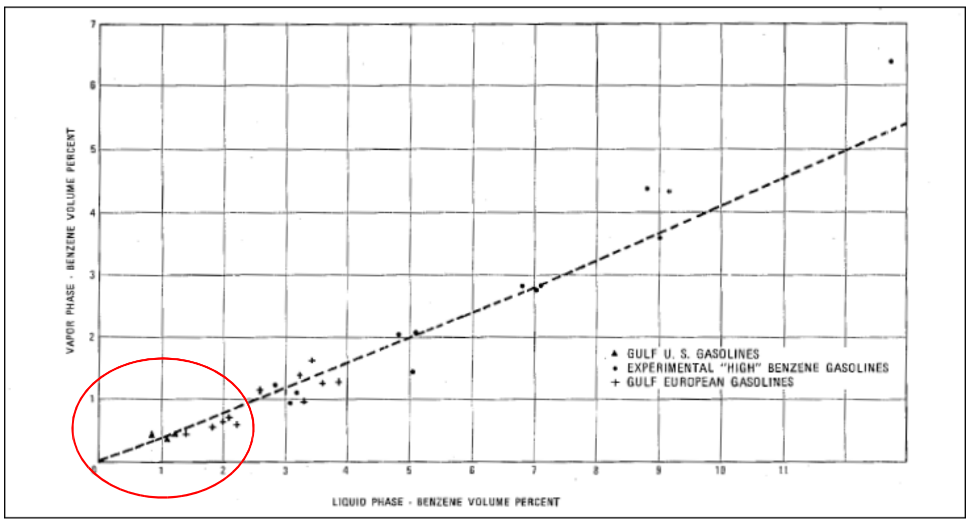
- Three primary factors:
  - Reid vapor pressure (RVP) of fuels
  - Dispensed fuel temperature T_d
  - Tank fuel temperature T_t
- Several secondary factors:
  - Dispensing rate
  - Tank and fillpipe configuration
  - Initial volume of fuel in tank and volume dispensed
- Ethanol/methanol blends affect RVP. RVP control is needed.



SAE Paper 852116, "Volatility Characteristics of Gasoline-Alcohol and Gasoline-Ether Fuel Blends".

Benzene Refueling Emission Rate

Largely dependent on volume % benzene in liquid fuel. (mass % = 0.85 vol %)



Bz (g/gal) = 0.052 (vol% Bz liquid)

Observations

- Based on headspace equilibrium measurements, 1% benzene in liquid yields 0.43% in vapor or 4300 ppmv.
- At STP, this converts to 13737 mg/m^3 or about 0.05 g benzene/gallon.
- Limited data from vehicle testing suggests that benzene emission rate is also affected by any entrained droplets and vapor shrinkage or growth.*

HOWARD E. RUNION (1975) Benzene in Gasoline, American Industrial Hygiene Association Journal, 36:5, 338-350

* See SAE Paper 861559: Factors Influencing Benzene Emissions from Passenger Cart Refueling, October 1986.

Spillage

- Spillage is generally divided into four categories.
  - Pre-fill nozzle handling by the operator
  - Pre-mature shut-off spit back
  - End of fill event well back and topping off
  - Post-fill nozzle handling by the operator

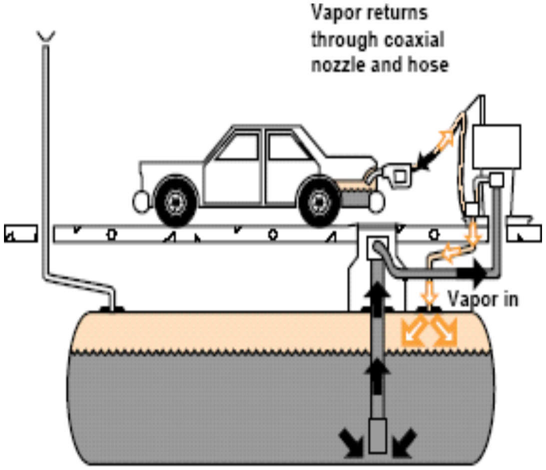
SAE 720931: An Investigation of Passenger Car Refueling Losses

- 1 ml spilled gasoline is about 0.7 g of VOC. Even a “drop” is about 0.05 g of VOC.
- For conventional nozzles:
  - EPA’s AP-42 (Chapter 5) estimates spillage at about 0.32 g/gallon dispensed
  - ARB estimates 0.28 g/ gallon dispensed.*
    - For EVR Stage II and conventional nozzles, ARB has nozzle standards to reduce spillage.**
  - API estimates 0.14 g/gallon dispensed.***
- Benzene mass in spilled fuel depends on benzene mass in liquid gasoline.

*ARB Revised Emission Factors for Gasoline Spillage at California Gasoline Dispensing Facilities, December 2013.
** See ARB CP201, CP207 and TPs 201-.2C,.-.2D, and -.2E.
***A Survey and Analysis of Liquid Gasoline Released to the Environment During Vehicle Refueling at Service Stations, API 4498, 1989.

Technology for Refueling Emission Control

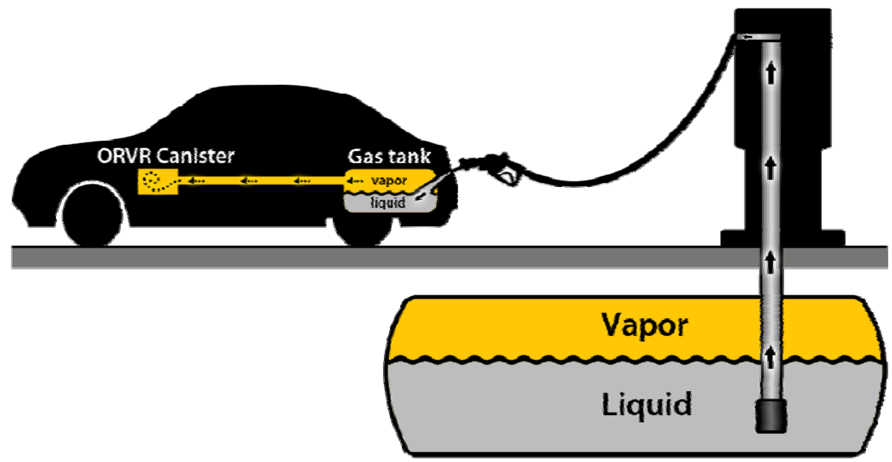
Stage II Vapor Recovery Technology: 70-75% efficiency



Refueling vapors are captured at the vehicle fillpipe outlet using a specially designed fuel nozzle and forced into underground storage tank. In balance-type systems, this returned vapor decreases fuel evaporation in the UST. During fuel delivery, if Stage I control is present, the tank vapors are routed back to the tanker truck as fuel is dropped. Stage II efficiency heavily dependent on user maintenance, inspections, and testing, as well as government oversight.

ORVR Technology – 98% efficiency

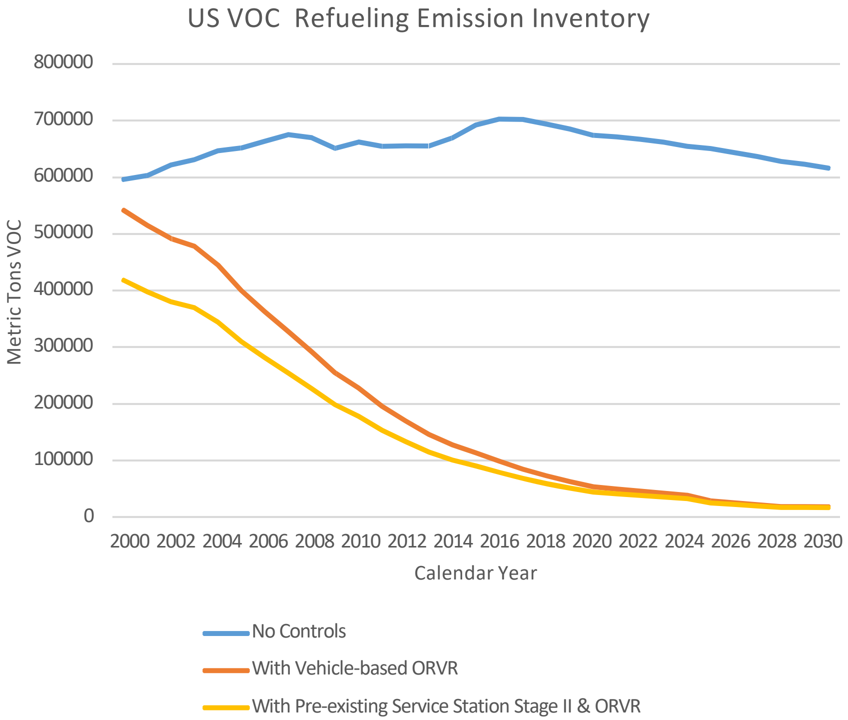
Onboard refueling vapor recovery systems capture displaced vapors

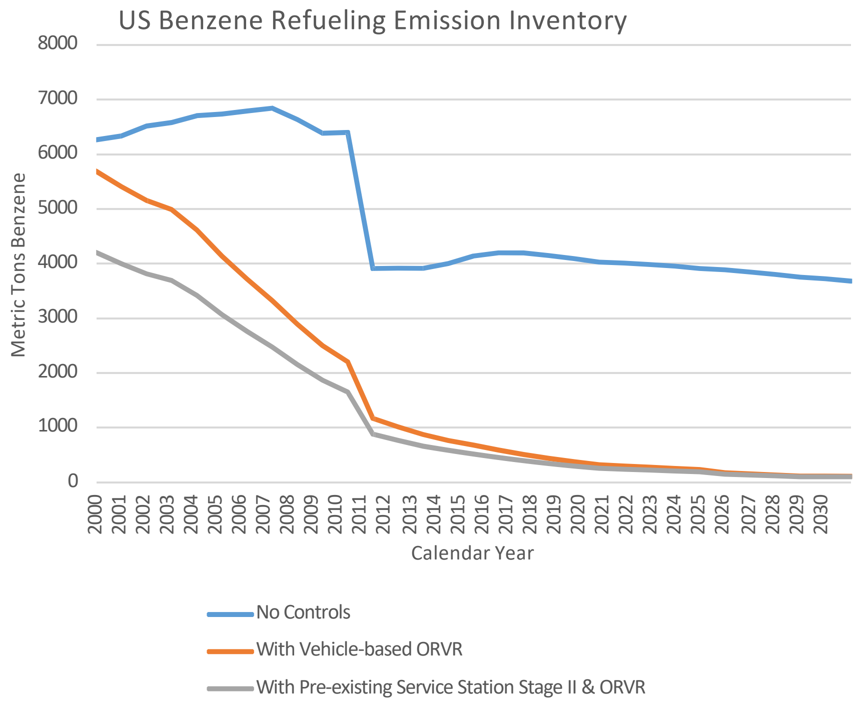


Refueling vapors are blocked from escaping through the fill pipe and instead captured on the vehicle's activated carbon canister. The canister is purged during vehicle driving, and the vapor is burned as fuel. ORVR technology is integrated with vehicle's current evaporative control system hardware. ORVR designs also reduce spillage during refueling. ORVR is applicable to all types of gasoline-powered highway vehicles.

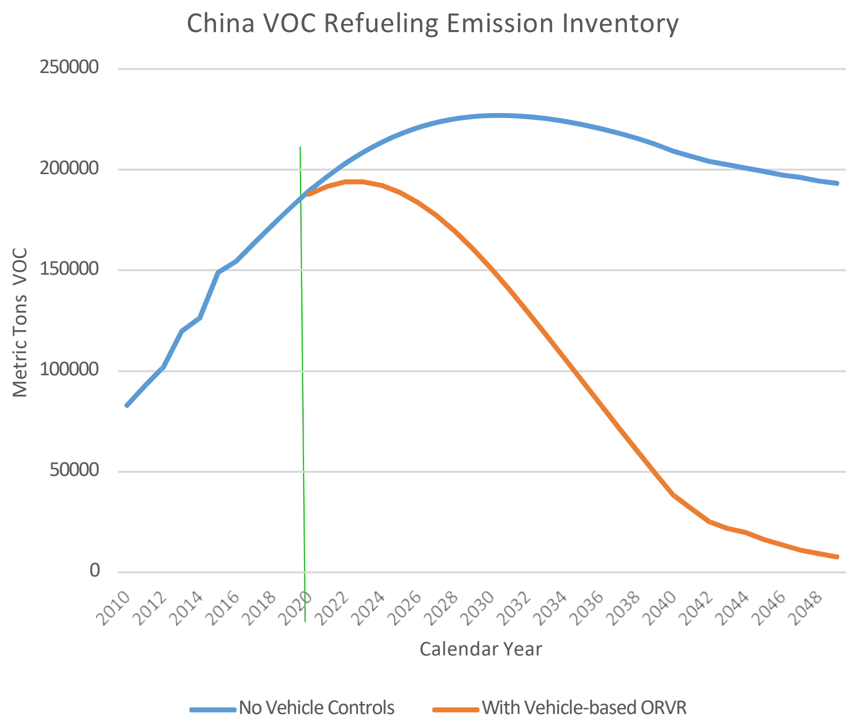
Case Evaluations

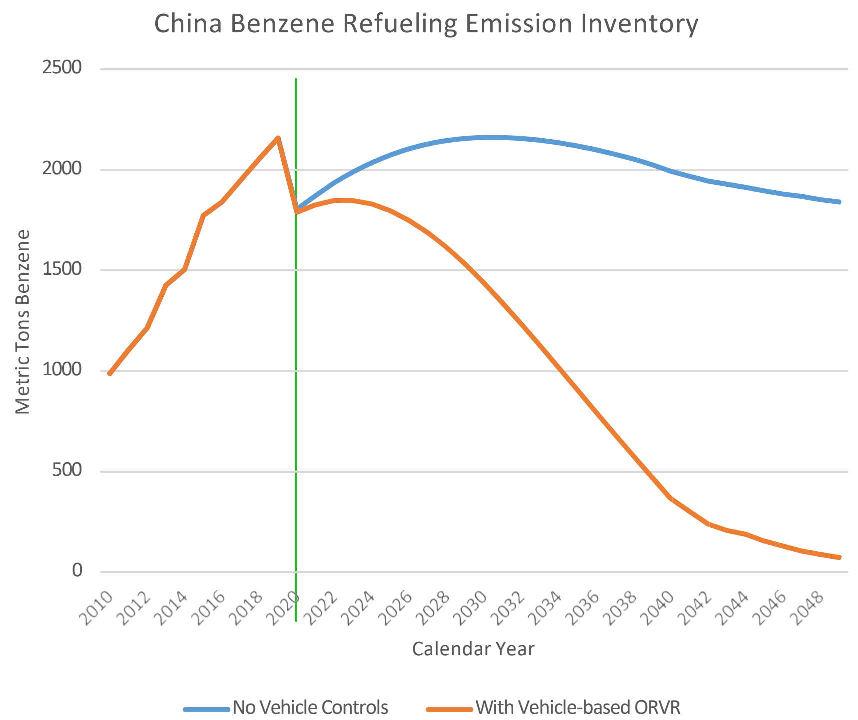
Case 1: The US (mature fuel and technology control programs)





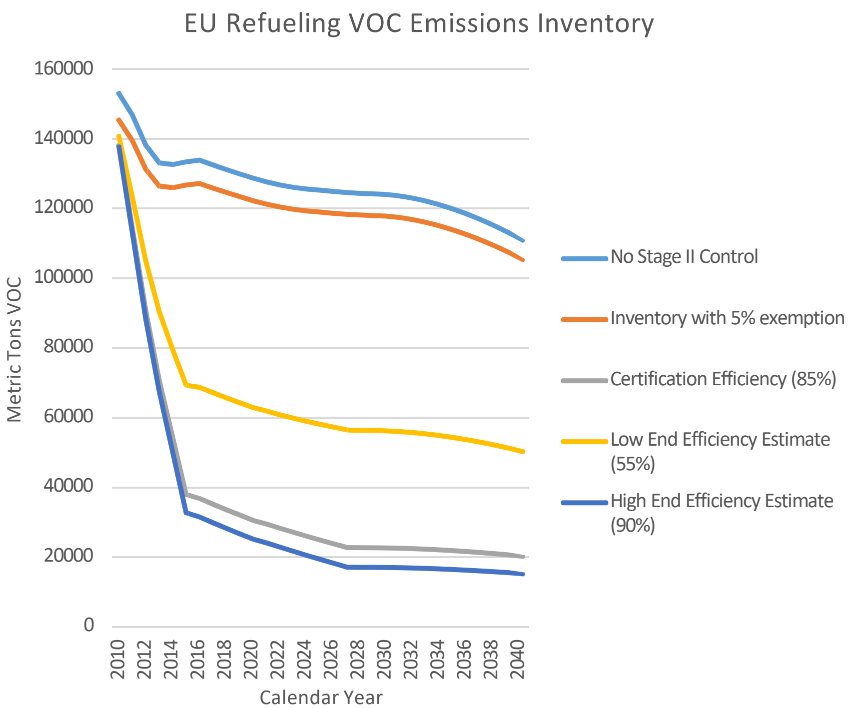
Case 2:China (benzene control and ORVR for 2020)

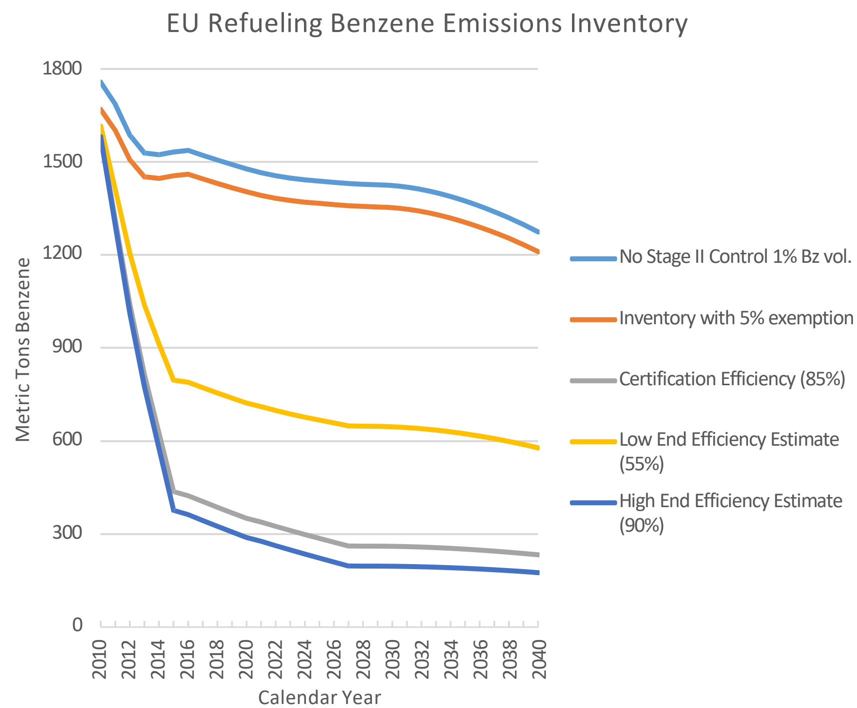




China has Stage II in several major cities, but the implementation rate and efficiency are unknown.

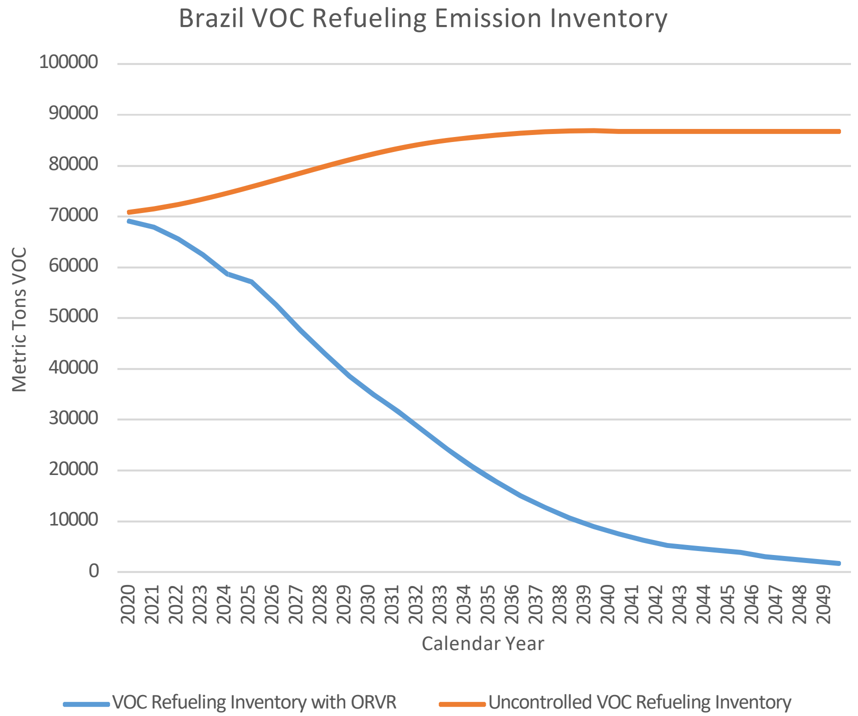
Case 3: EU 28 member states (widespread Stage II, but still phasing-in)

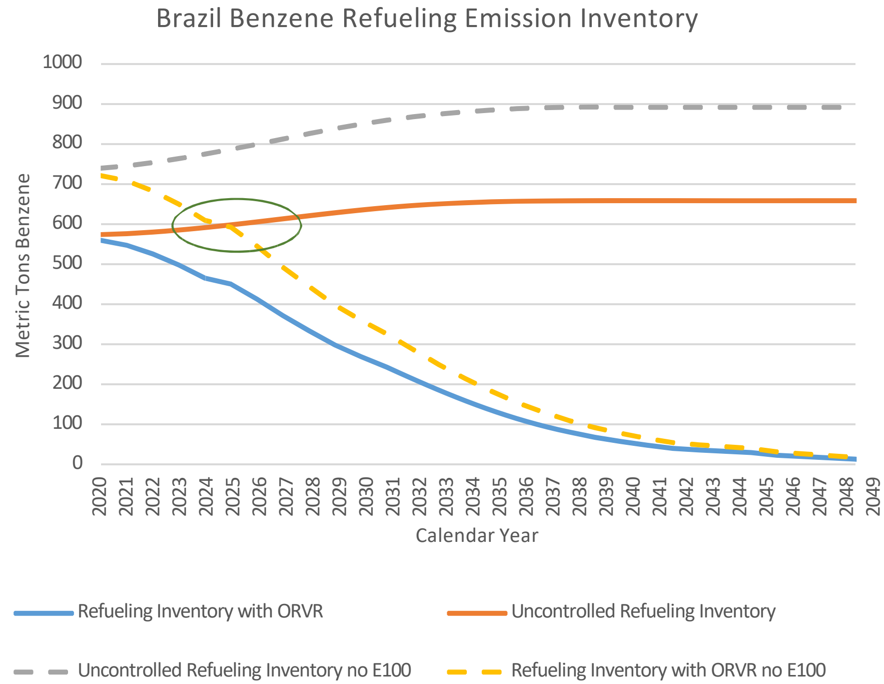




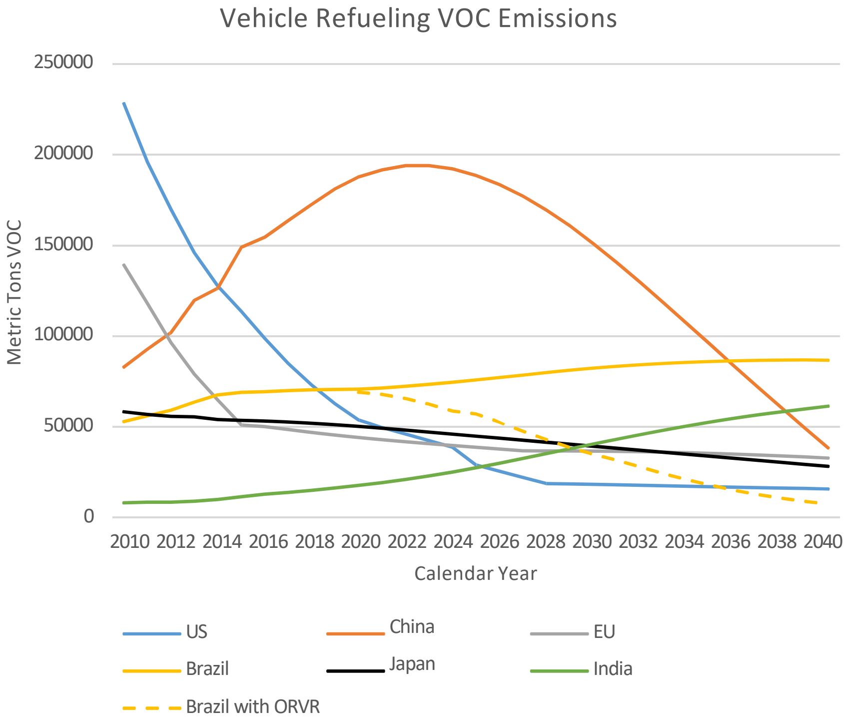
European Commission: Evaluation of Directive 1994/63/EC on VOC Emissions from Petrol Storage & Distribution and Directive 2009/126/EC on Petrol Vapor Recovery: Final Evaluation Report - December, 2015.

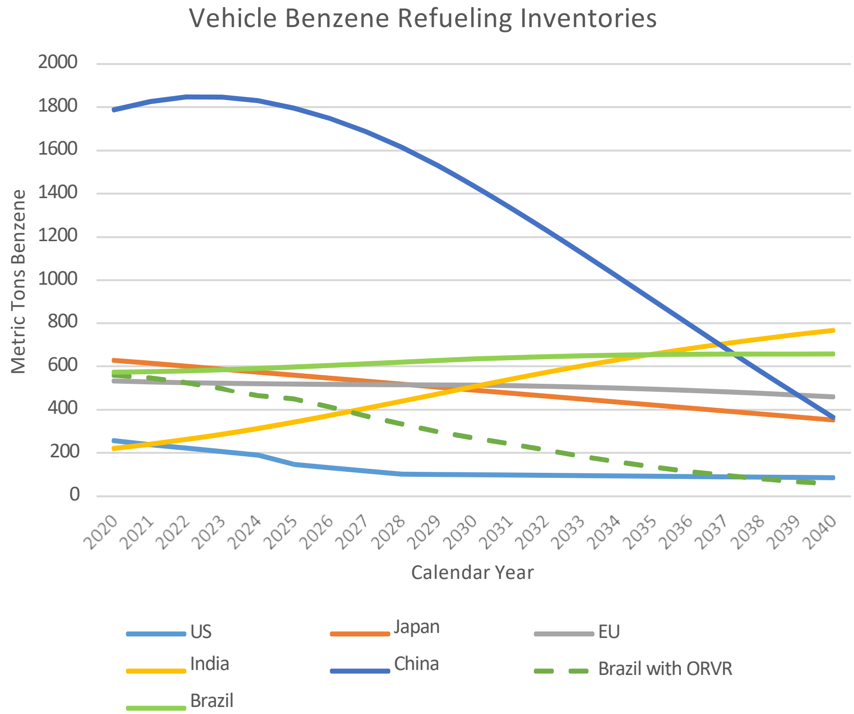
Brazil (uses gasoline C blend (E25) and E100 fuel)





Six Areas Refueling Emission Inventory Trends





Conclusions

- Refueling emissions are significant sources of VOCs and air toxics
  - Control provides reductions in ozone, SoA ($PM_{2.5}$), and air toxics
  - Inventories depend directly on gasoline and gasoline-blend consumption
    - Trends are definitely for reduced use of volatile fuels based on improved fuel economy requirements and powertrain electrification
- There are well established control techniques available.
  - Vehicle control: 98% efficient
  - Stage II: 70-75%

  Significant implementation, cost, and cost-effectiveness differences

  - Fuel quality: RVP limits, benzene limits and use of oxygenate and gasoline-oxygenate blends
- Analysis indicates significant inventory implications for Brazil and India which have no controls and project fuel large demand increase.

Thank you for your kind attention.

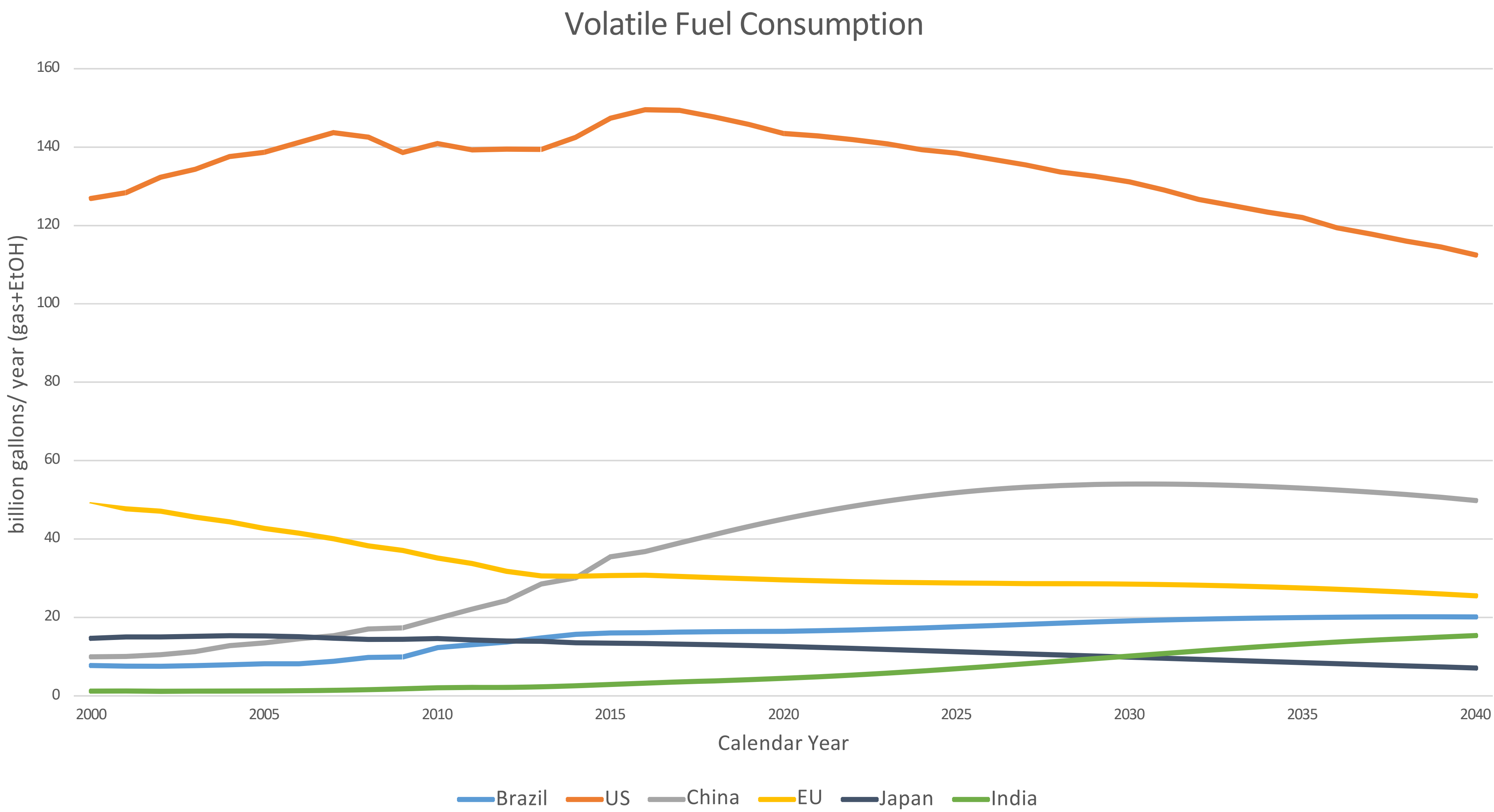
Glenn W. Passavant

[Ingevity Corporation](#)

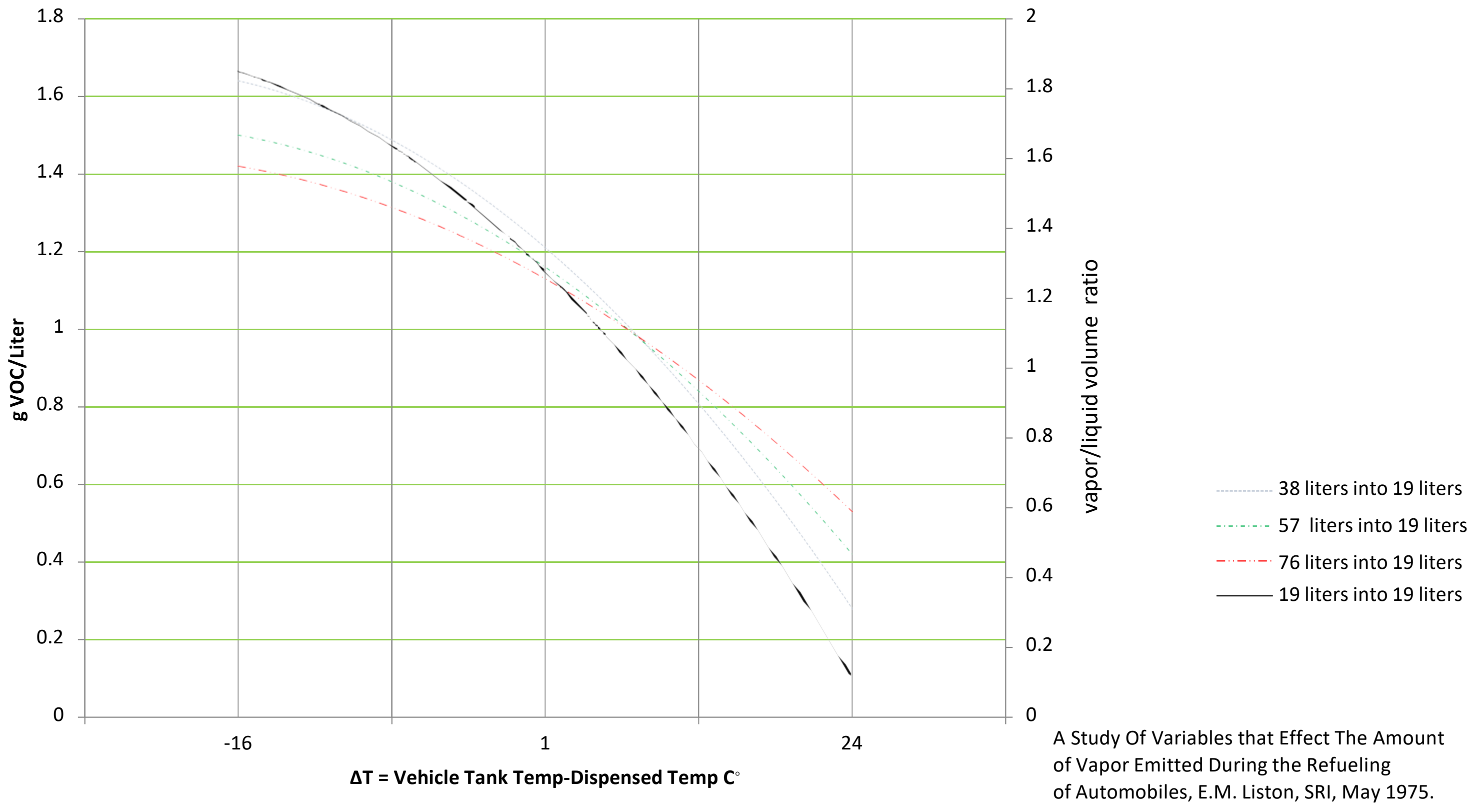
glenn.passavant@ingevity.com

517-759-9369

EXTRA SLIDES

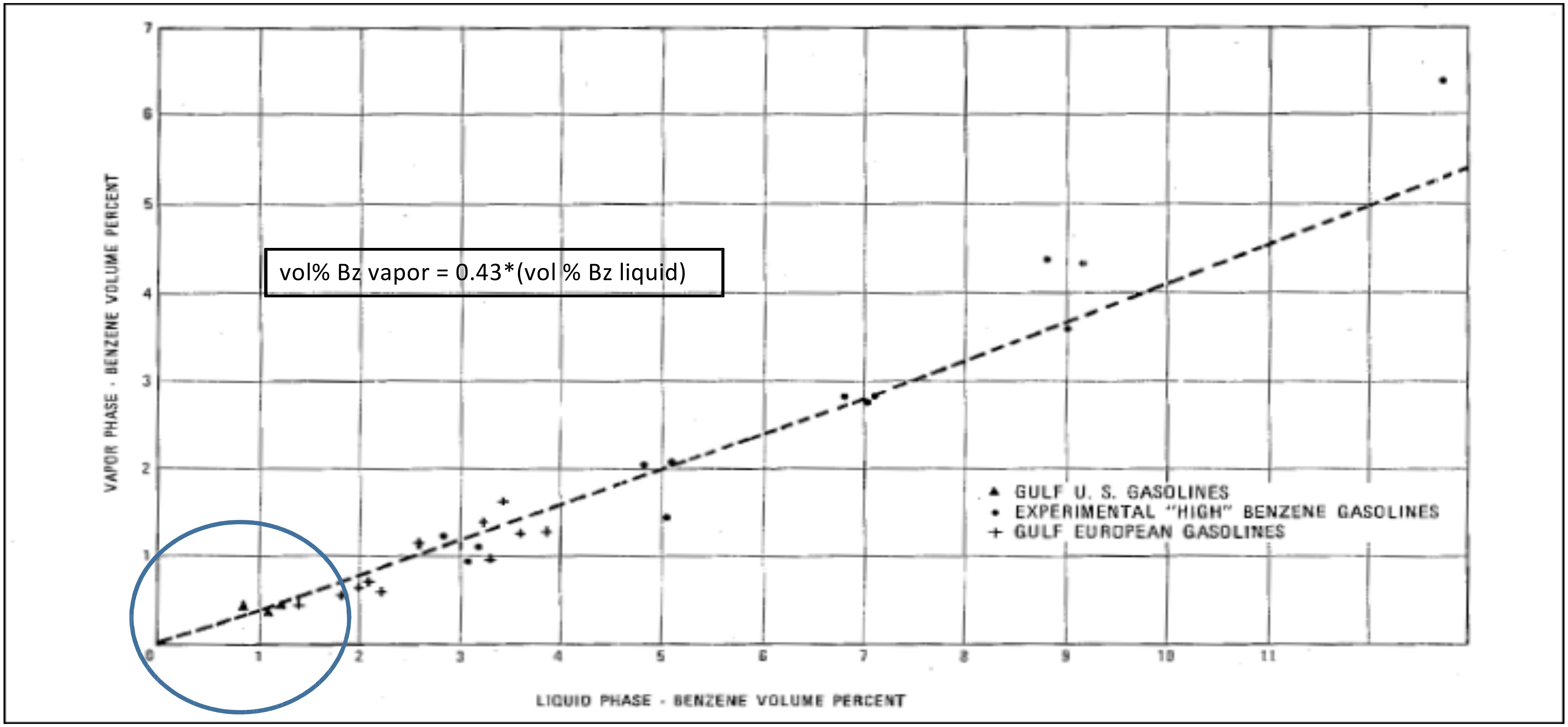

Volatile Fuel Consumption
160
140
120
100
80
60
40
20
0
billion gallons/ year (gas+EtOH)
2000
2005
2010
2015
2020
2025
2030
2035
2040
Calendar Year
Brazil
US
China
EU
Japan
India

Vapor Generation During Refueling



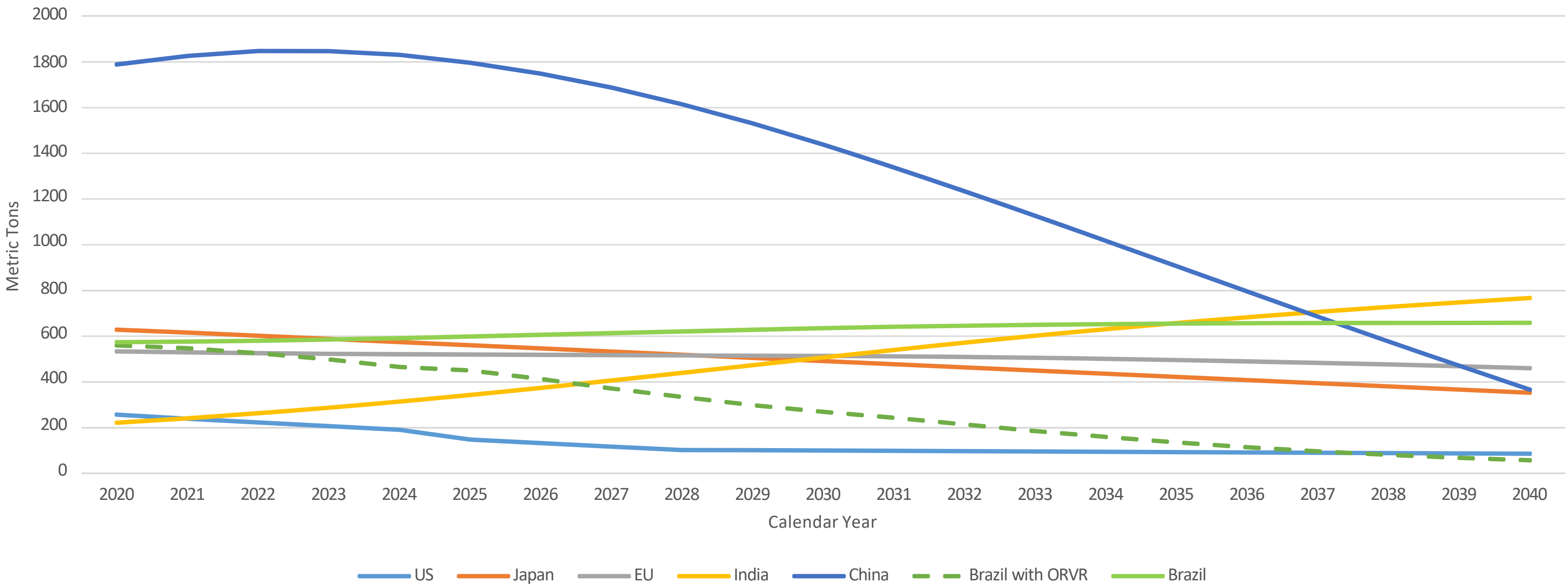
A Study Of Variables that Effect The Amount of Vapor Emitted During the Refueling of Automobiles, E.M. Liston, SRI, May 1975.

Benzene concentration in refueling vapor varies with fuel benzene content (mass % = 0.85 vol %)

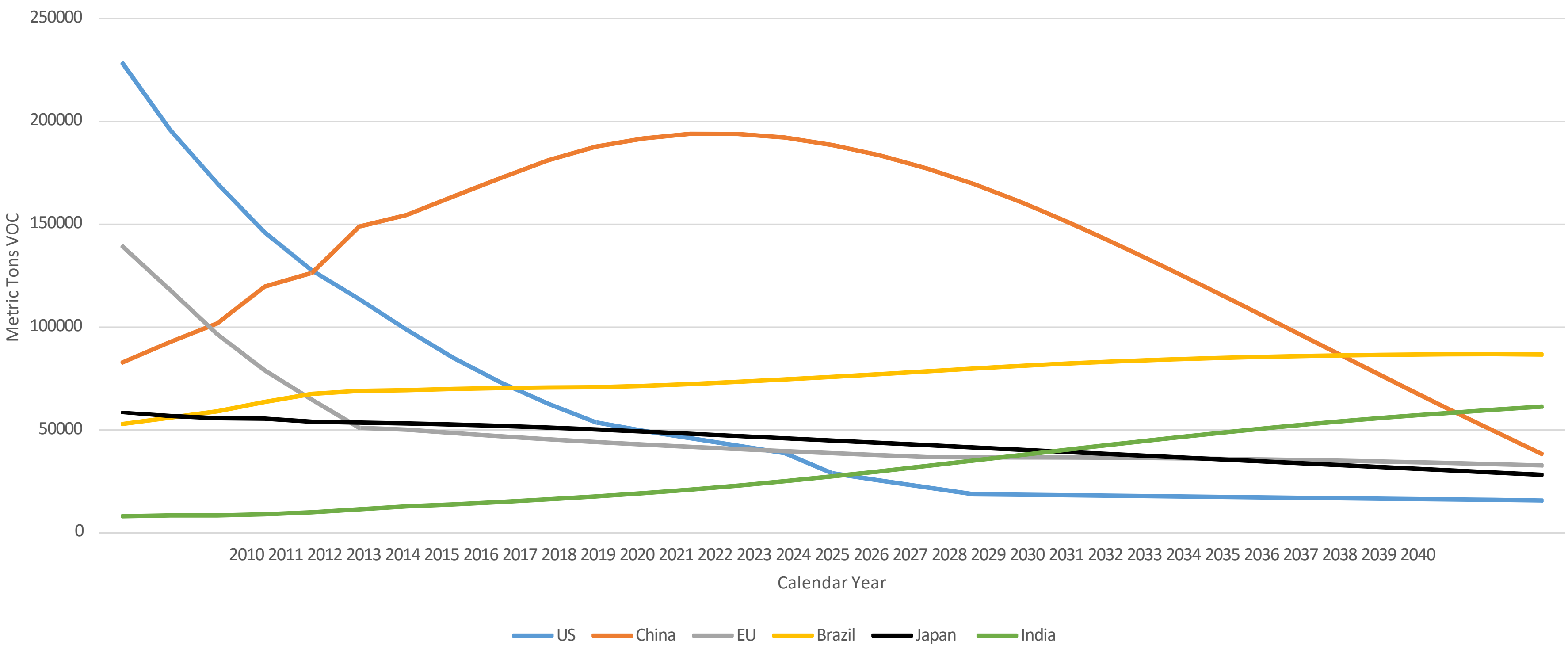


HOWARD E. RUNION (1975) Benzene in Gasoline, American Industrial Hygiene Association Journal, 36:5, 338-350

Vehicle Benzene Refueling Inventories

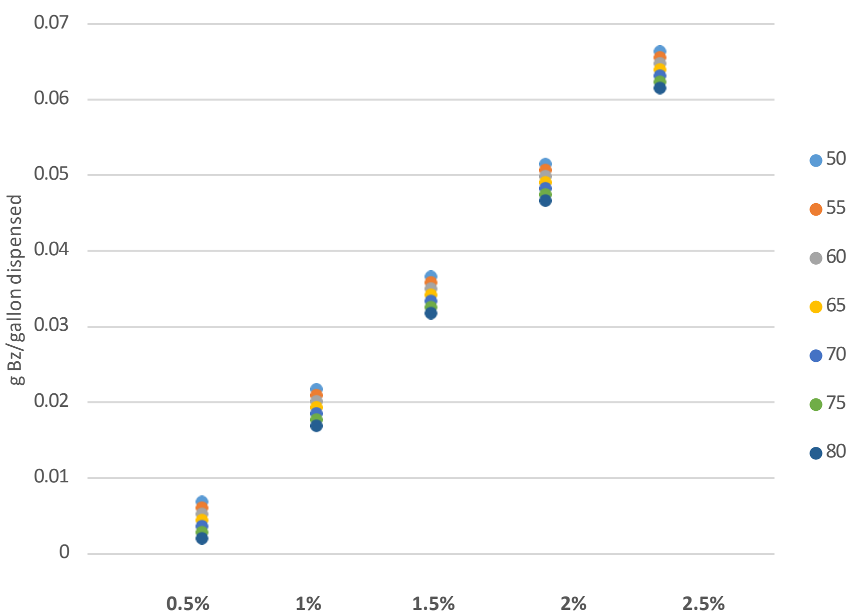


Time-series Comparison of Refueling VOC Emission Inventories – 6 areas

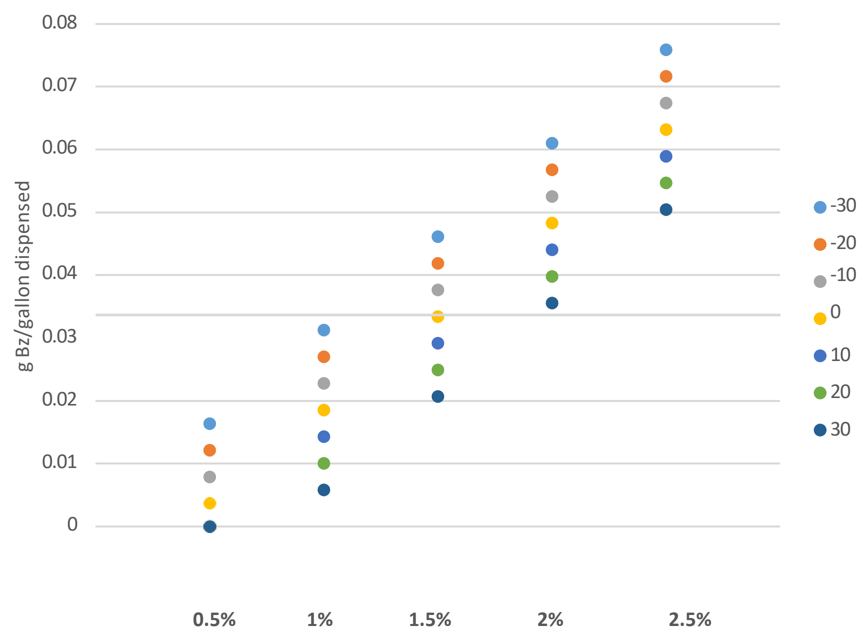


Benzene refueling emission rate is impacted by dispensed (T_d) and fuel tank temperature (T_t)

Benzene Refueling Emissions: % vol vs. T_d; ΔT= 0



Benzene Refueling Emissions: % vol vs. ΔT where $\Delta T=(T_t-T_d)$; T_d=70F



Bz (g/gal) = $0.038*(\% Bz_m)-(1.60 E\text{-}4 *T_d)-(4.24 E\text{-}4*\Delta T)$: Equation from: SAE Paper 861559: Factors Influencing Benzene Emissions from Passenger Cart Refueling, October 1986.