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PREDICTION OF NUCLEATION AND COAGULATION MODES IN THE FORMATION OF DIESEL PARTICULATE MATTER

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Additional Details Available From the Following Papers

1. "On the Prediction of Concentration Variations in a Dispersing Heavy-duty Truck Exhaust Plume Using k-e Turbulent Closure", **Atmospheric Environment,** Vol. 35(31), pp. 5267-75 (2001)
2. "Modeling Nucleation and Coagulation Modes in the Formation of Particulate Matter Inside a Turbulent Exhaust Plume of a Diesel Engines", **Journal of Colloid and Interface Science,** Vol. 249(1), pp. 96-103 (2002)
3. "Effect of Ambient Dilution on Coagulation of Particulate Matter in a Turbulent Dispersing Plume", *Air Emissions From Mobile Sources- Recent Data and Trends (Session Code: ENV4) at SAE Congress 2002,* Cobo Center, Detroit, MI, March 4-7, 2002, **SAE Paper Number 2002-01-0652**
4. "Prediction of Pollutant Concentration Variation Inside a Turbulent Dispersing Plume Using PDF and Gaussian Models", *Air Emissions From Mobile Sources- Recent Data and Trends (Session Code: ENV4) at SAE Congress 2002*, Cobo Center, Detroit, MI, March 4-7, 2002, **SAE Paper Number 2002-01-0654**
5. "Effect of Soot on Nox in Industrial Furnaces", AFRC Fall Symposium, San Francisco, CA, October 4, 1999

Particulate Matter Formation

- Particulate Matter in Diesel Exhaust

  Continuous Transformation: Nucleation, Coagulation,

  Condensation and Evaporation of Organics

  and Inorganics

- Fate of Condensable Organics and Inorganics
  - Affected by Atmospheric Aging and Dilution of the Exhaust Stream
  - Process of Changing Size Distribution-Nucleation, Coagulation

    and Condensation

Objectives

- To Predict the Nucleation, Coagulation, and Dynamics of Particulate Matter Emissions in the Plume of a Class-8 Diesel-fueled Tractor Operating at 55 miles/hour.

  To Predict the Structure of Plume, Including Variation of Temperature, Concentration and Dilution Ratio

Technical Approach

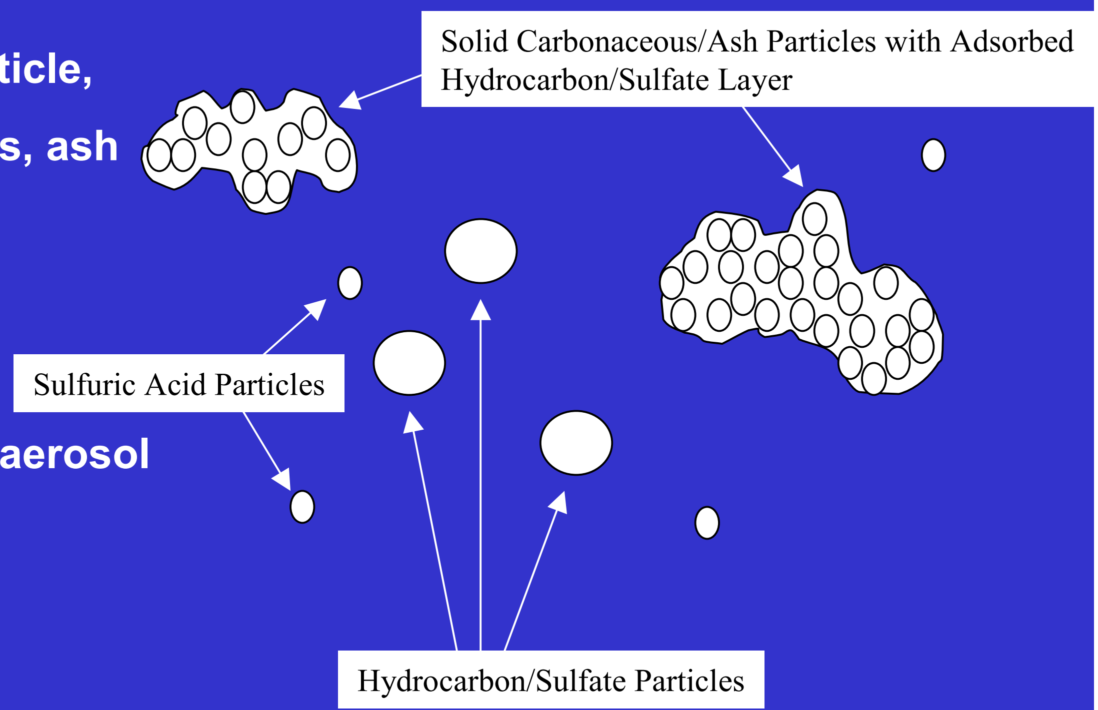
- Predicted CO_2 concentration, dilution ratio, and temperature variations inside the plume using CFD models
- Solved-using FLUENT Solver
  - k-ε turbulent closure, eddy dissipation species transport, energy equation
- Included effect of nucleation, condensation, and coagulation of particulate matter formation, simultaneously
- With this method, the data required to solve these equations was significantly reduced.
- Particle concentration predicted based on the sulfur content of fuel, F/A ratio and ambient conditions

Plume Models

- Empirical Gaussian Models (Kaharabata *et al*., 2000, Hanna, 1984)
- Similarity Models (Obasaju and Robins, 1998, Huai and Li, 1993)
- Probability Density Function Models (PDF) (Reynolds, 2000)
- k-ε Models (Sharan and Yadav, 1998, Hwang and Chiang 1988)
- Statistical Models (Heinz and vanDop, 1999, Sawford, 1983)
- Large Eddy Simulation Models (LES) (Sykes *et al.,* 1984)

Typical Structure of Engine Exhaust Particles

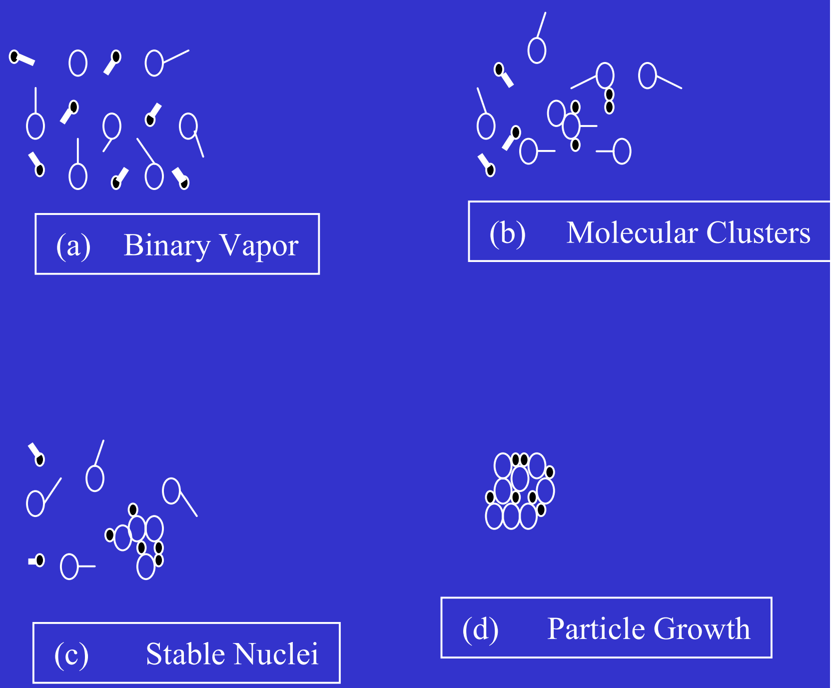
- Agglomerated solid carbonaceous particle,
  volatile organic, sulfur compounds, ash
- Most of sulfur in the fuel
  - oxidized to SO_2, then
  - oxidized to SO_3
  - leads to sulfuric acid and sulfate aerosol
- Metal compounds in fuel and lube oil
  - lead to inorganic ash



(Seinfeld and Pandis, 1997)

Nucleation Process

- Homogeneous nucleation (Springer, 1978)
  - In the absence of condensation nuclei
  - Require large saturation ratio (S>1)
- Heterogeneous nucleation
  - Occurs on a foreign substance or surface, such as an ion or a solid particle
- Binary homogeneous nucleation
  - Two or more vapor species



(Baumgard and Johnson, 1996)

Nucleation Process (Cont'd)

- **Certain number of H_2O and H_2SO_4 molecules collide**

  For critical cluster- sufficient energy to be stable

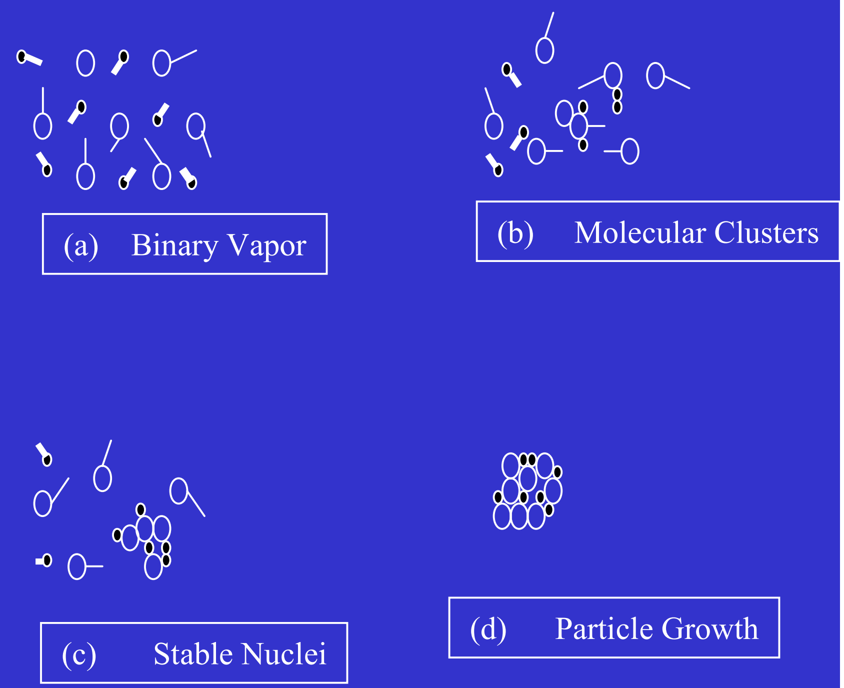
  - Greater than critical size, grow (less, shrink)

  - Rate of nucleation (H_2SO_4 hydrate (embryo) formation predicted by Reiss, 1950):

$$J = C \exp(-\Delta G^* / kT)$$

  (Grow past critical size)

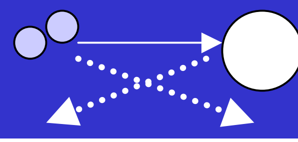
- **Higher nucleation rate occurs at higher relative humidity, and lower temperature**



C is the frequency factor, k is the Boltzmann's constant, T is the temperature and ΔG is the free energy required to form an embryo

Coagulation Model

- **Integro-Differential Equation**



$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{2}\int_{v^*}^{v} \beta(v-\tilde{v},\tilde{v})n(\tilde{v},t)n(v-\tilde{v},t)d\tilde{v} - \int_{0}^{\infty} \beta(v,\tilde{v})n(v,t)n(\tilde{v},t)d\tilde{v},$$

$$n(v,0) = n_0(v),$$

$$n(v,t) = 0$$

Augmentation Term **Depletion Term**

- **Simple Monodisperse Coagulation (Hinds, 1982)**

  - Particles are monodisperse, contact one another, grow slowly.

- **Polydisperse Coagulation**

  - Governed by diffusion of particles to the surfaces of other particles

Techniques For Solving Coagulation Equations

- J-space Transformation (Yom and Brock, 1984)
- Asymptotic solution (Pilinis and Seinfeld, 1987)
- Discrete method (Tambour and Seinfeld, 1980)
- Moment method (Williams and Loyalka, 1991; McGraw, 1997)
- Parametrized Representation (Whitby, 1985)
- Similarity solution (Friedlander and Wang, 1966)
- Direct simulation by Monte Carlo method (Kruis *et al*., 2000; Maisels *et al*., 1999)

- **Semi-implicit Finite-Difference Scheme (Jacobson *et al*., 1994)**
  - **Most Generic**

GOVERNING EQUATION

The evolution of PM size distribution due to coagulation, nucleation and condensation is represented by the discrete dynamical equation:

$$\frac{\partial C_k}{\partial t} = \underbrace{\frac{1}{2}\sum_{j=1}^{k-1}\beta_{k-j,j}C_{k-j}C_j - C_k\sum_{j=1}^{\infty}\beta_{k,j}C_j}_{\text{COAGULATION}} + \underbrace{J(t)\delta(k)}_{\text{NUCLEATION}} + \underbrace{\beta_{1,k-1}C_1C_{k-1} - \beta_{1,k}C_1C_k}_{\text{CONDENSATION}}$$

C_k= time dependent number concentration (No./cm^3) of particles of volume v_k (cm^3)

β= coagulation kernel (cm^3 No.$^{-1}$ s^{-1}) of two colliding particles

J(t) = Nucleation rate

δ = Kronecker delta with a value of 1 for the kth bin of volume v_k; and 0 otherwise

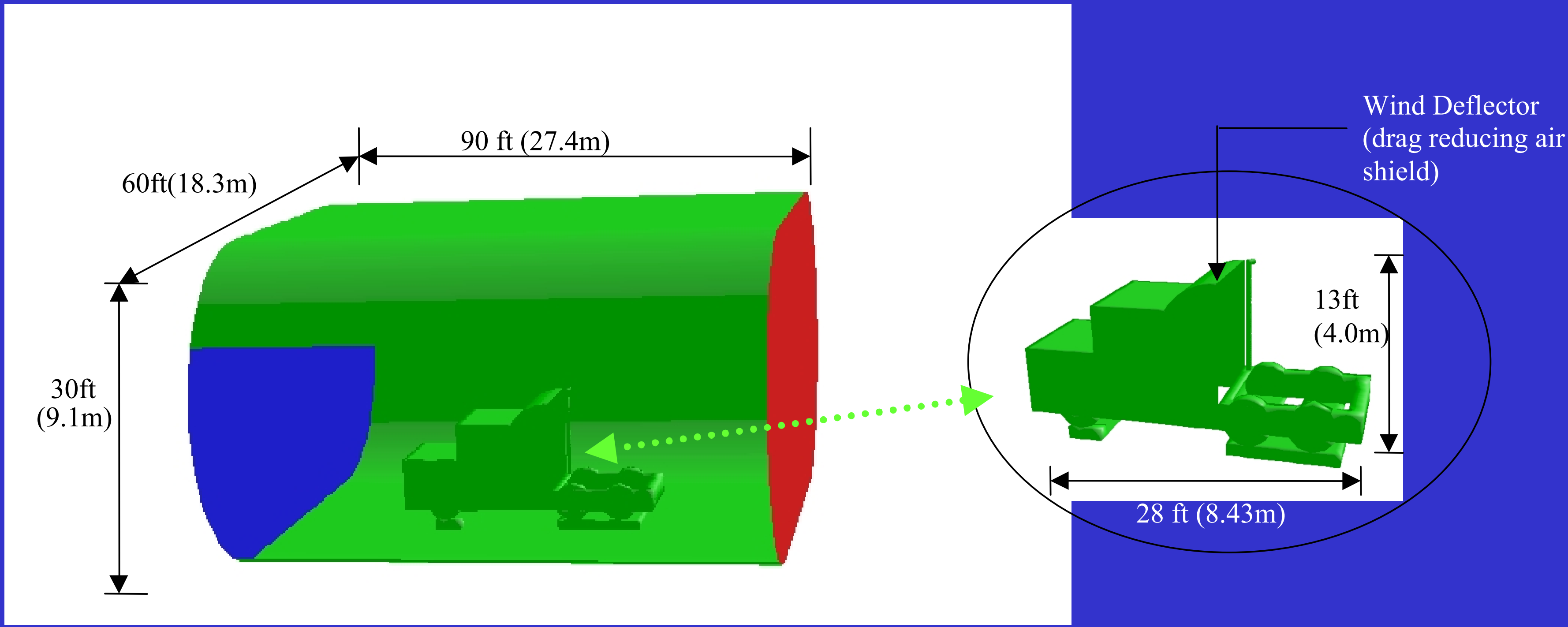
(Sienfeld and Pandis, 1997)

GOVERNING EQUATION

To account for the simultaneous effects of nucleation, coagulation, and condensation the general formula for volume-conserving, semi-implicit equation can be solved (Jacobson et al. , 1994; Kim et al., 2001) to predict the concentration variation of PM in the exhaust plume of a diesel truck traveling at highway speeds:

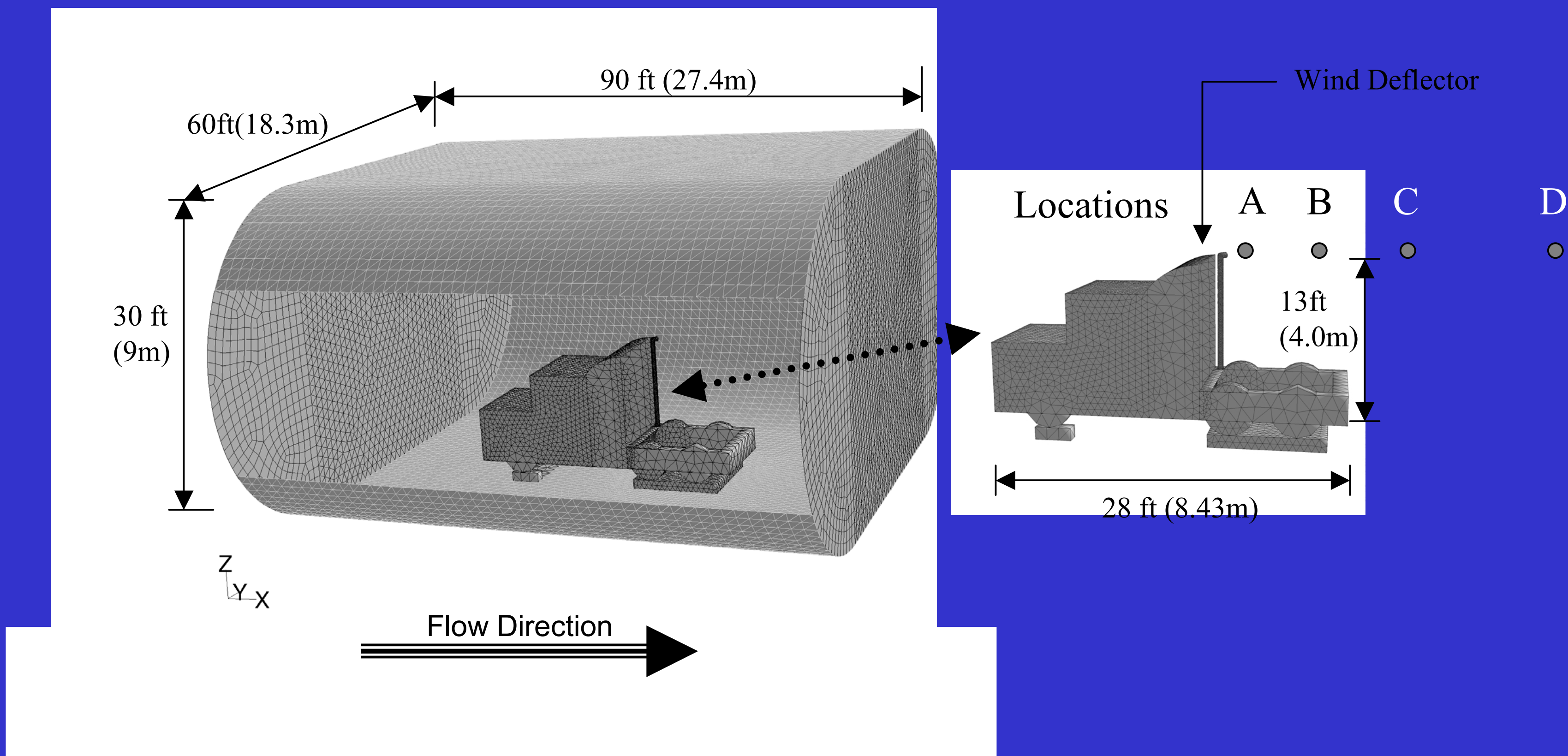
$$v_k C_k^{t+1} = \left(\frac{v_k C_k^t + \Delta t \sum_{j=1}^{k} \left\{ \sum_{i=1}^{k-1} f_{i,j,k} \beta_{i,j} v_i C_i^{t+1} C_j^t \right\} + \Delta t v_k J(t) \delta((k) + \Delta t v_k \beta_{1,k-1} C_1^{t+1} C_{k-1}^{t+1}}{1 + \Delta t \sum_{j=1}^{N_B} \left(1 - f_{i,j,k}\right) \beta_{k,j} C_j^t + \Delta t \beta_{k,j} Ct_1} \right) \frac{1}{Dilution\ Ratio}$$

SIMULATION CONDITIONS

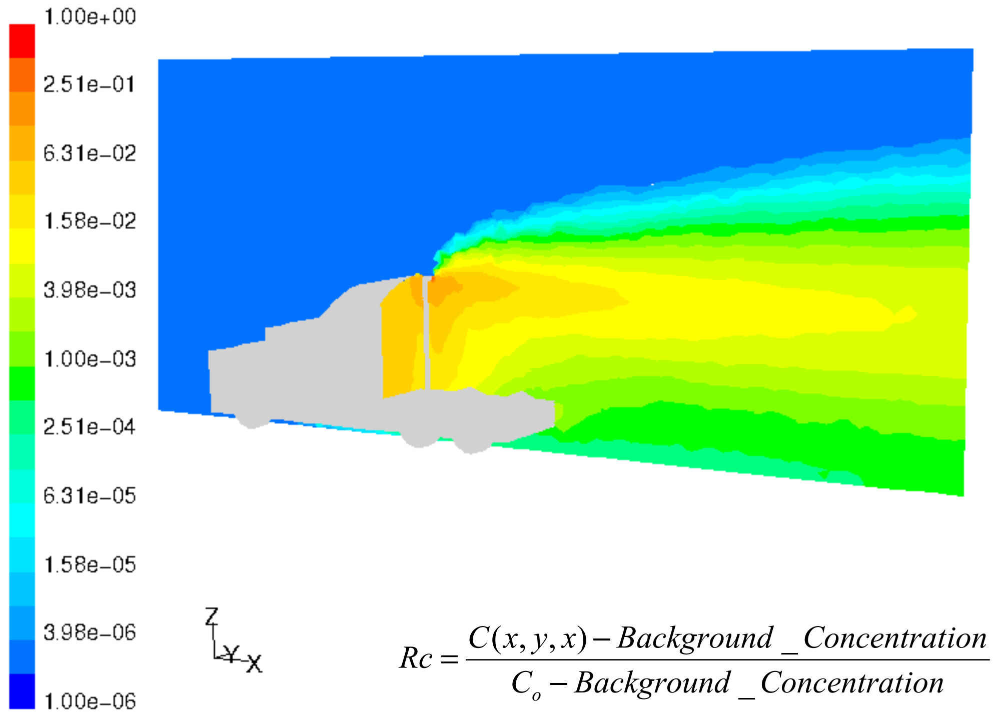


- Class-8 tractor heavy-duty diesel truck (330 hp) in a wind tunnel discretized using approx. 500,000 hexahedral and tetrahedral control volumes (cells).
- Steady state operation at 55 mph
- Exhaust exit velocity 29.8 m/s, Wind velocity 24.6 m/s
- Standard k-ε turbulence closure and finite rate chemistry/eddy dissipation
- Background concentration of CO_2 (640 ppm), raw exhaust (60,000ppm)

Computational Grid of the Truck Inside the Wind Tunnel



Filled Contours of Relative Concentration of CO_2 Inside the Wind Tunnel

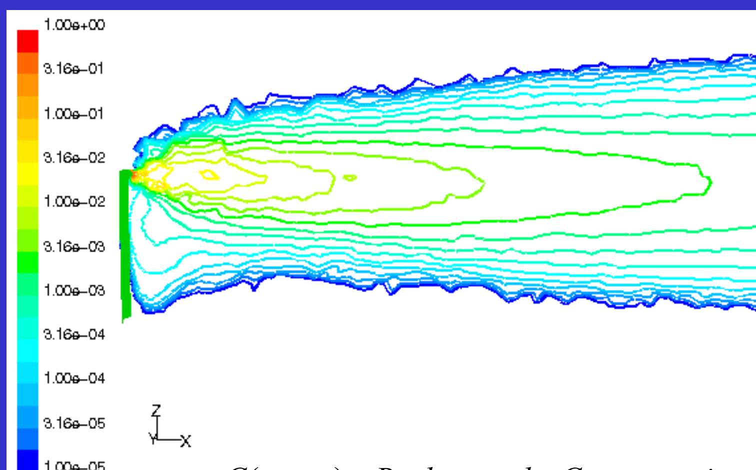


$$Rc = \frac{C(x, y, x) - Background\_Concentration}{C_o - Background\_Concentration}$$

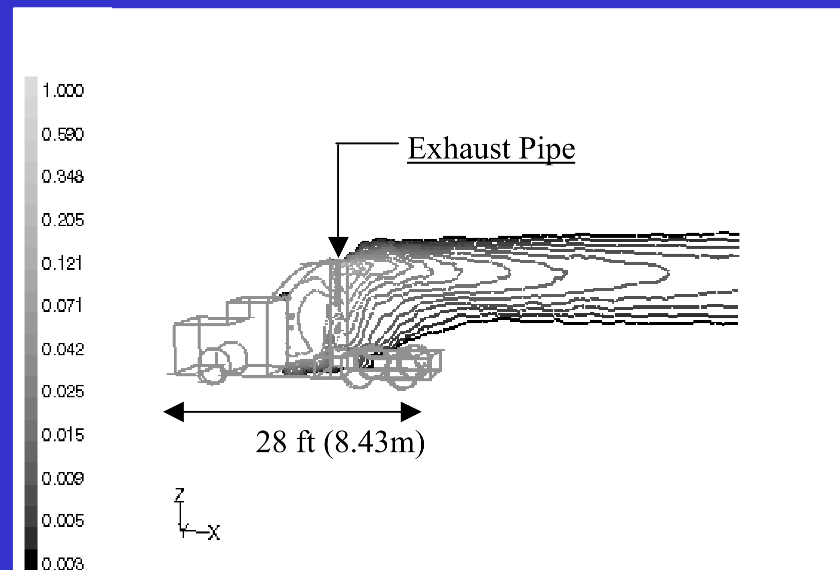
- **Re-circulation region below wind deflector**

Relative Concentration (R_c) is defined as the ratio of the CO_2 concentration at a given location (x,y,z) to the raw exhaust CO_2 concentration (C_0)

Contours of Relative Concentration of CO_2 Inside the Tunnel on a Plane Passing Through Exhaust Pipe



$$Rc = \frac{C(x, y, x) - Background\_Concentration}{C_o - Background\_Concentration}$$

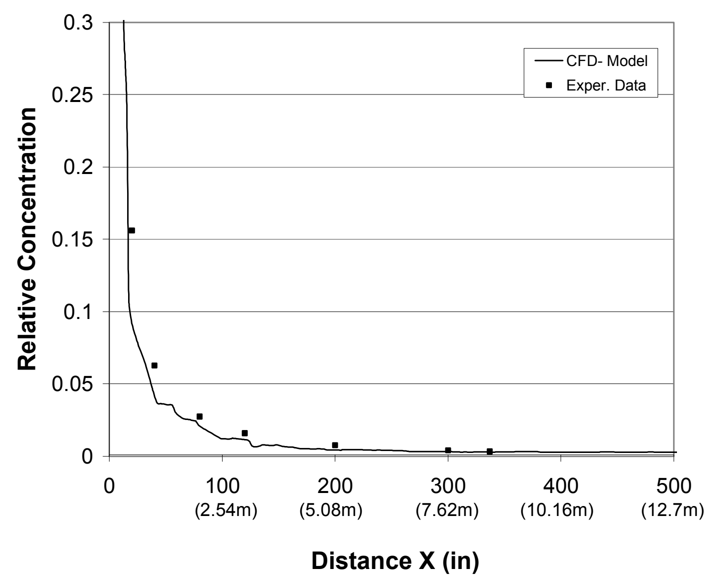


- Center of plume downward
  - wake effect

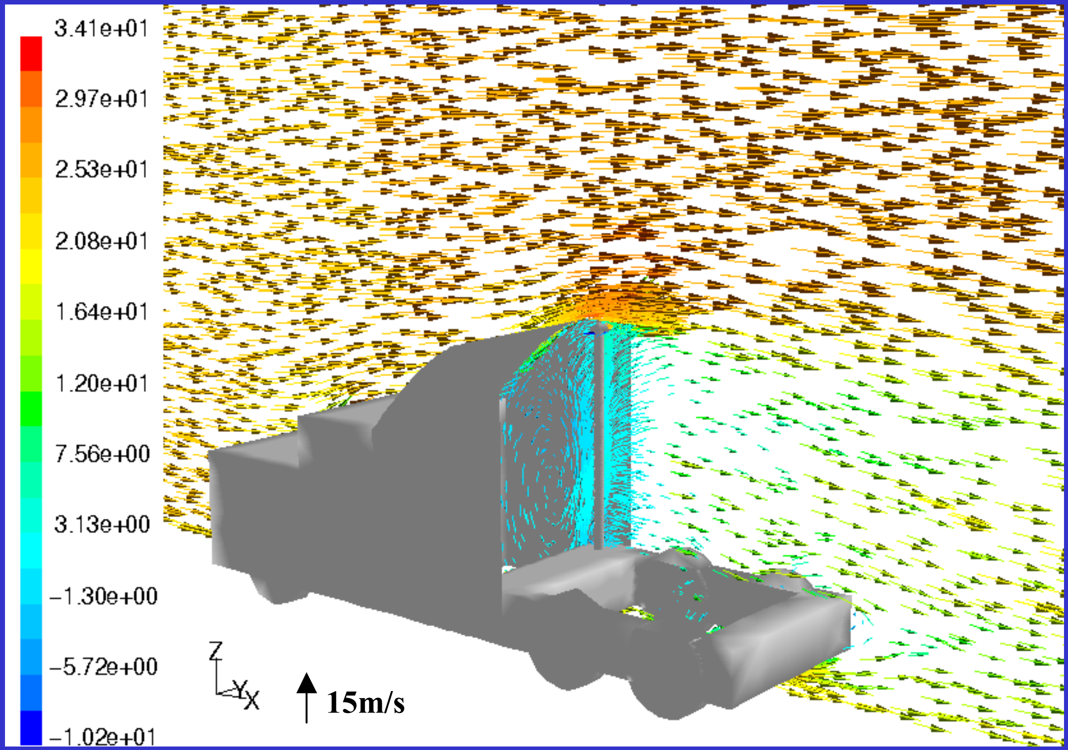
Relative Concentration of CO_2 Along the Centerline of Plume

- R_c of CO_2 dropped rapidly in 100"
  - -small flow rate of exhaust

$$R_c = \frac{C(x, y, x) - Background\ Concentration}{C_o - Background\ Concentration}$$

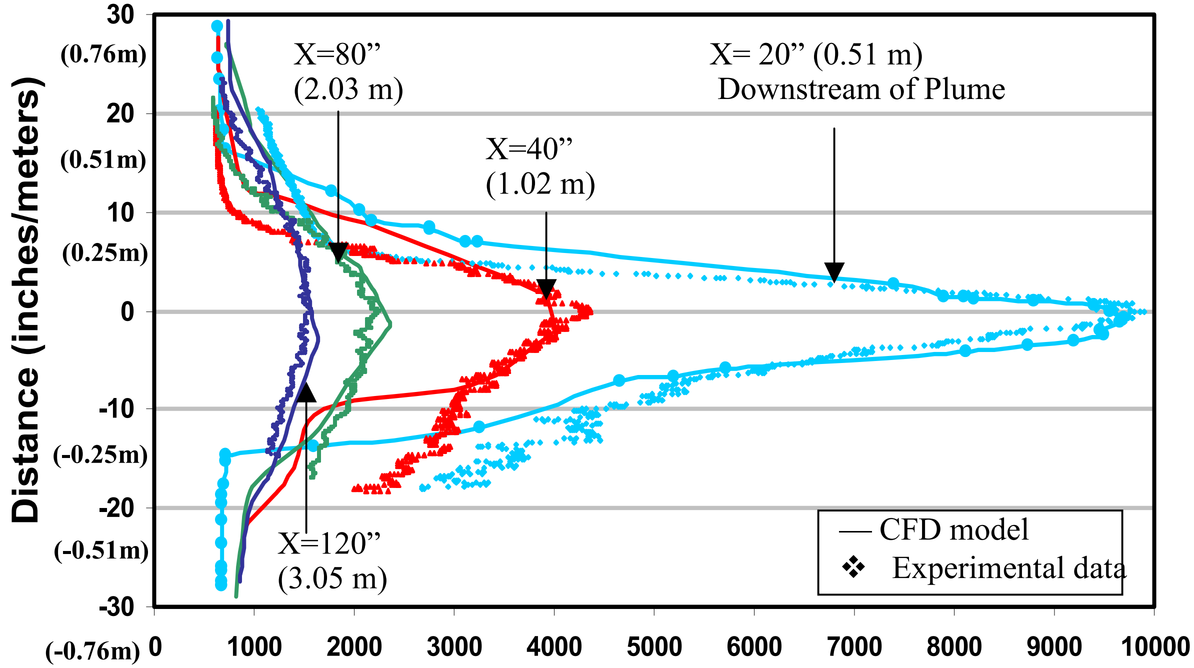


Velocity Vectors Showing Recirculation Near the Exhaust Pipe of the Tunnel



- Significant recirculation of the flow below wind deflector
- Dispersion coefficient not constant

CO_2 Concentration Inside the Plume Perpendicular to the Centerline

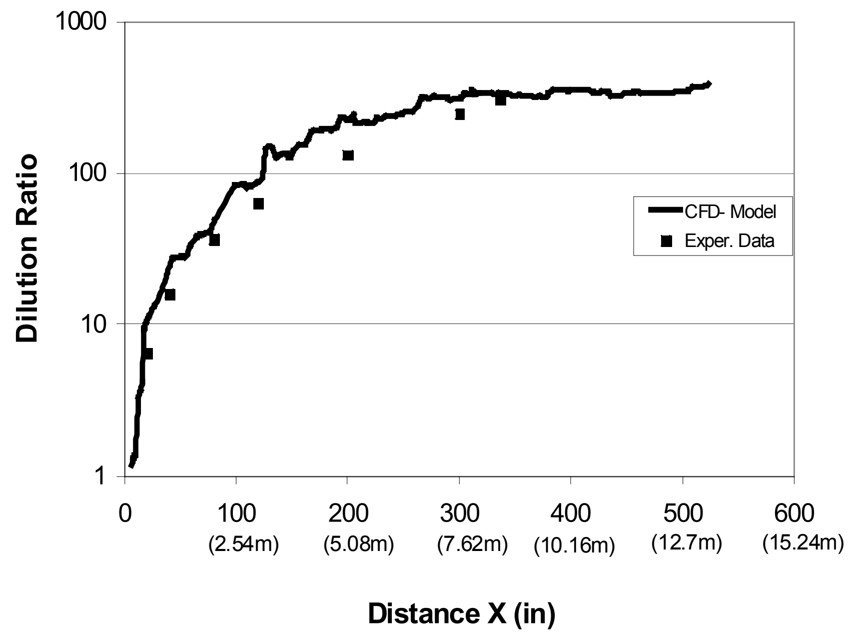


CO_2 Concentration (ppm)

- Asymmetry of plume - presence of wall
- Re-circulation region (undercarriage of flow)
- Symmetry of the plume- at large distances downstream

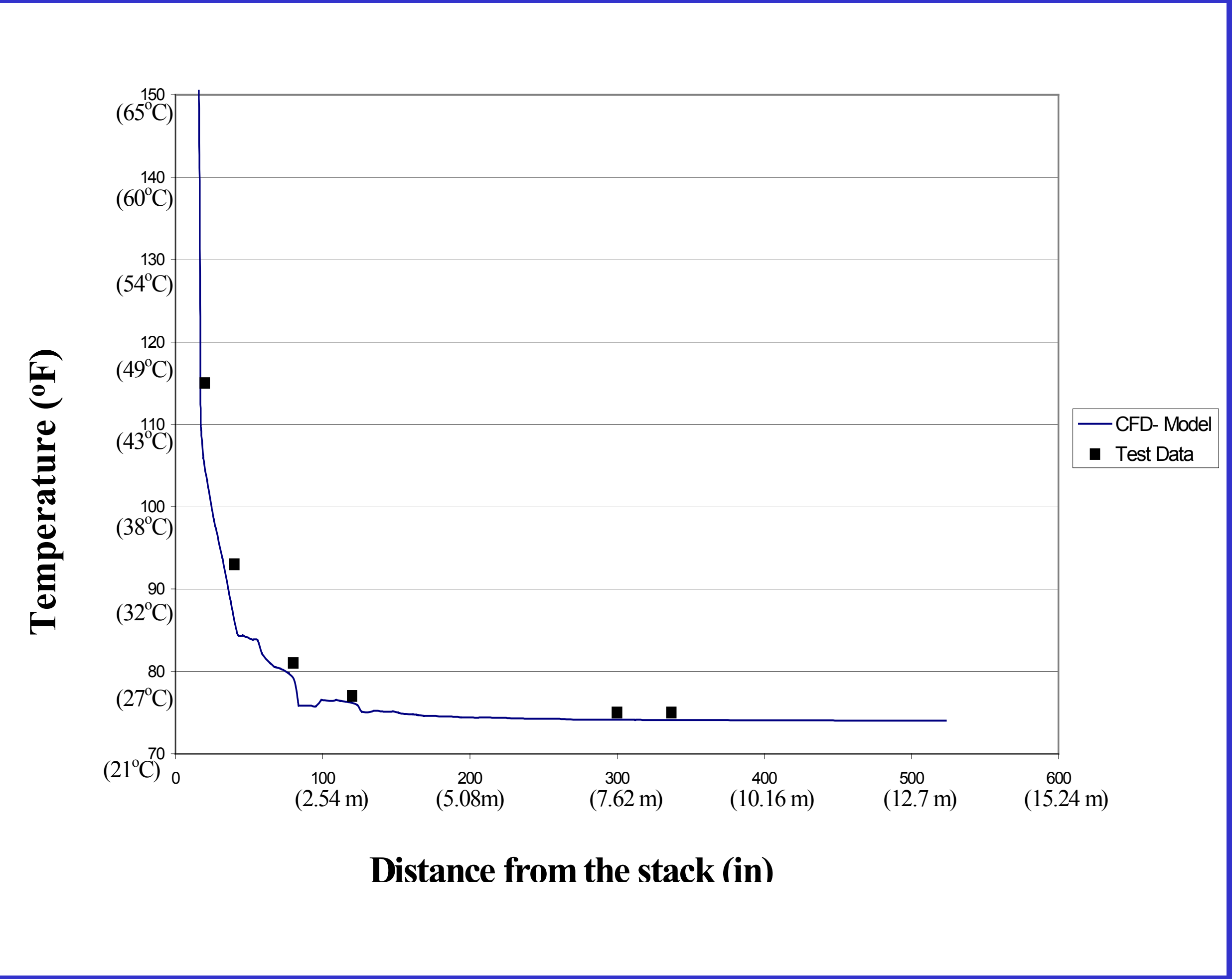
Dilution Ratio of CO_2 along the Centerline of Plume

- Increased rapidly
  - higher flow rate of air

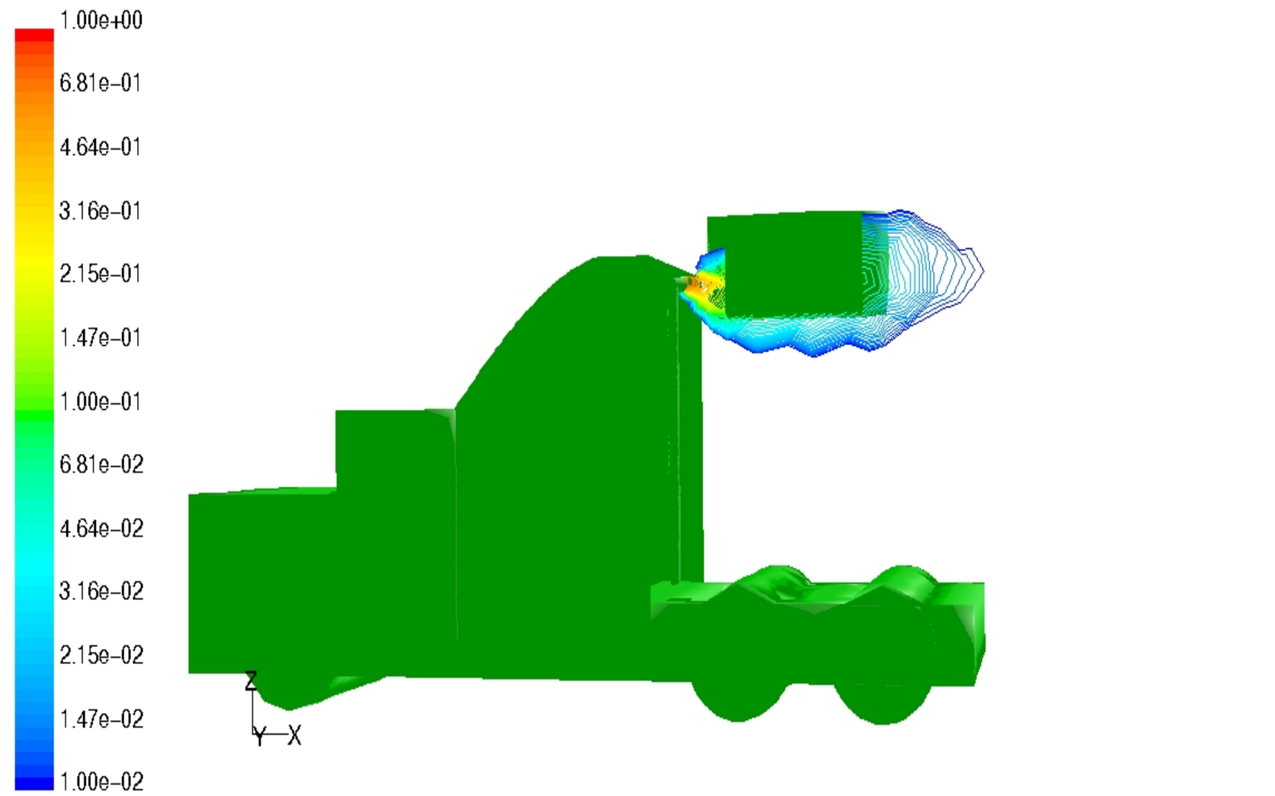


Temperature Along the Centerline of Plume

- Rapidly decreased
  - -dilution increased
  - - 100 inches (75 ºF)

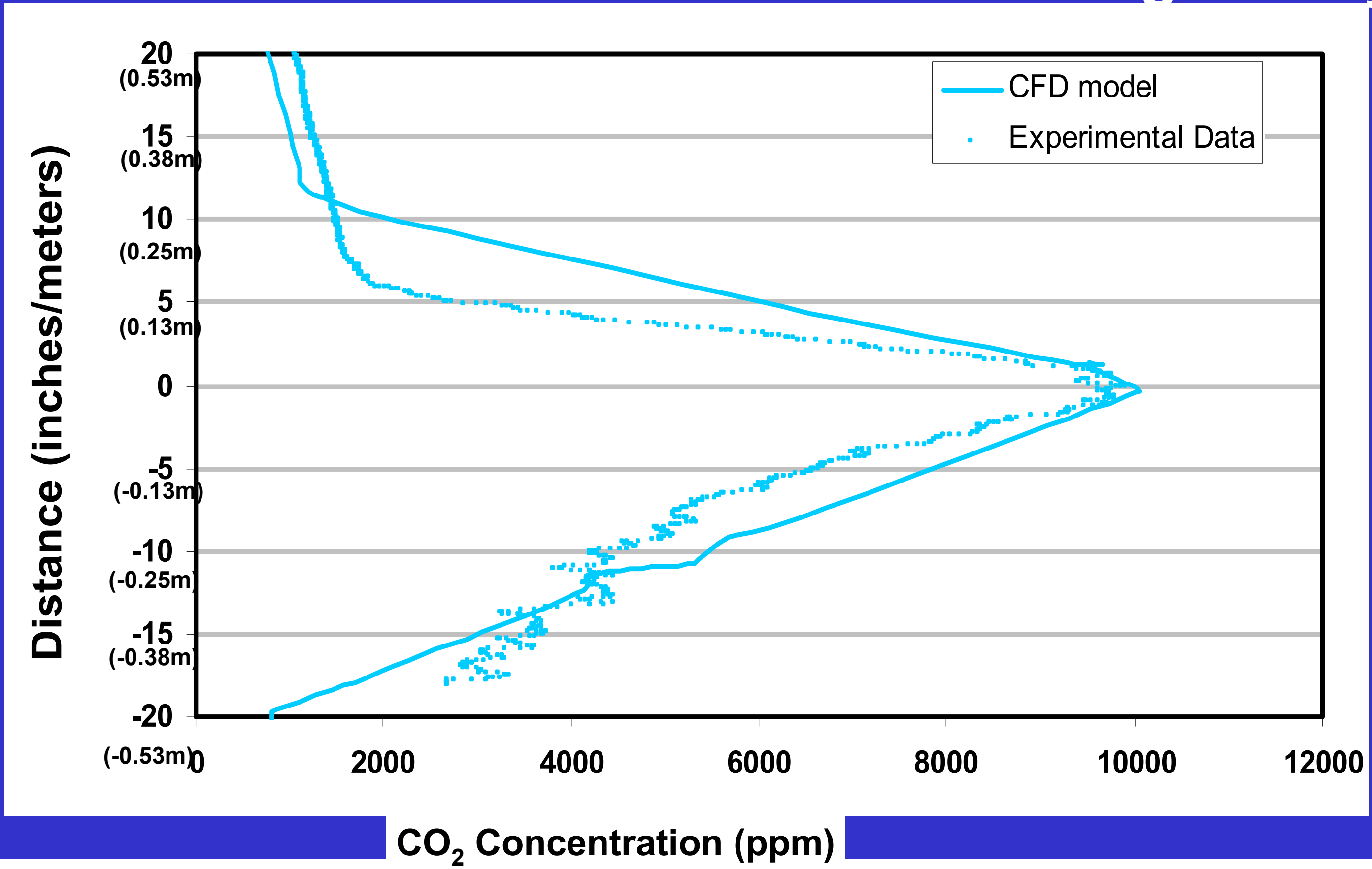


Relative Concentration of CO_2 near the Moving Gantry inside Wind Tunnel



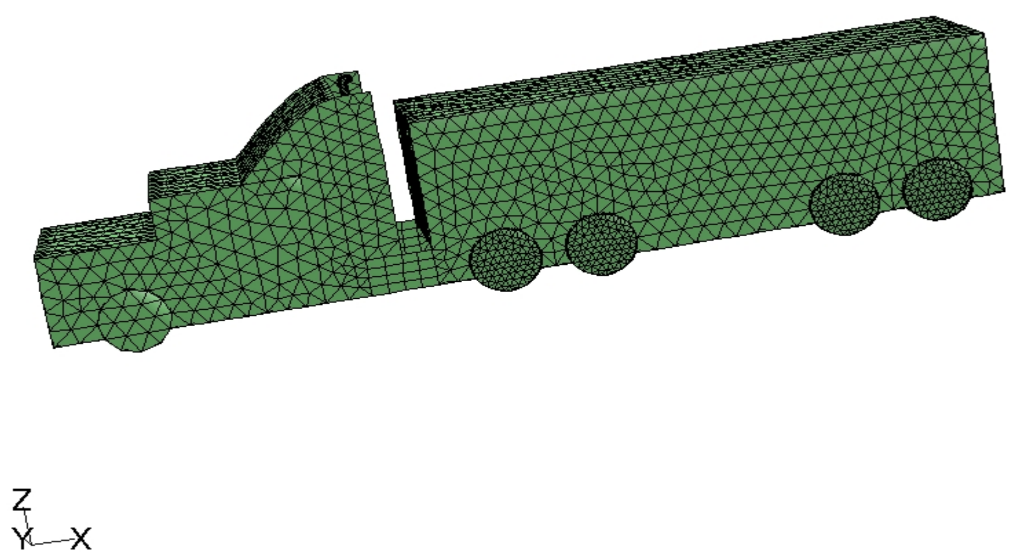
- **Geometry was re-discretized to account for the effect of gantry**

Variation of CO_2 Concentration inside the Plume Perpendicular to the Centerline near Moving Gantry



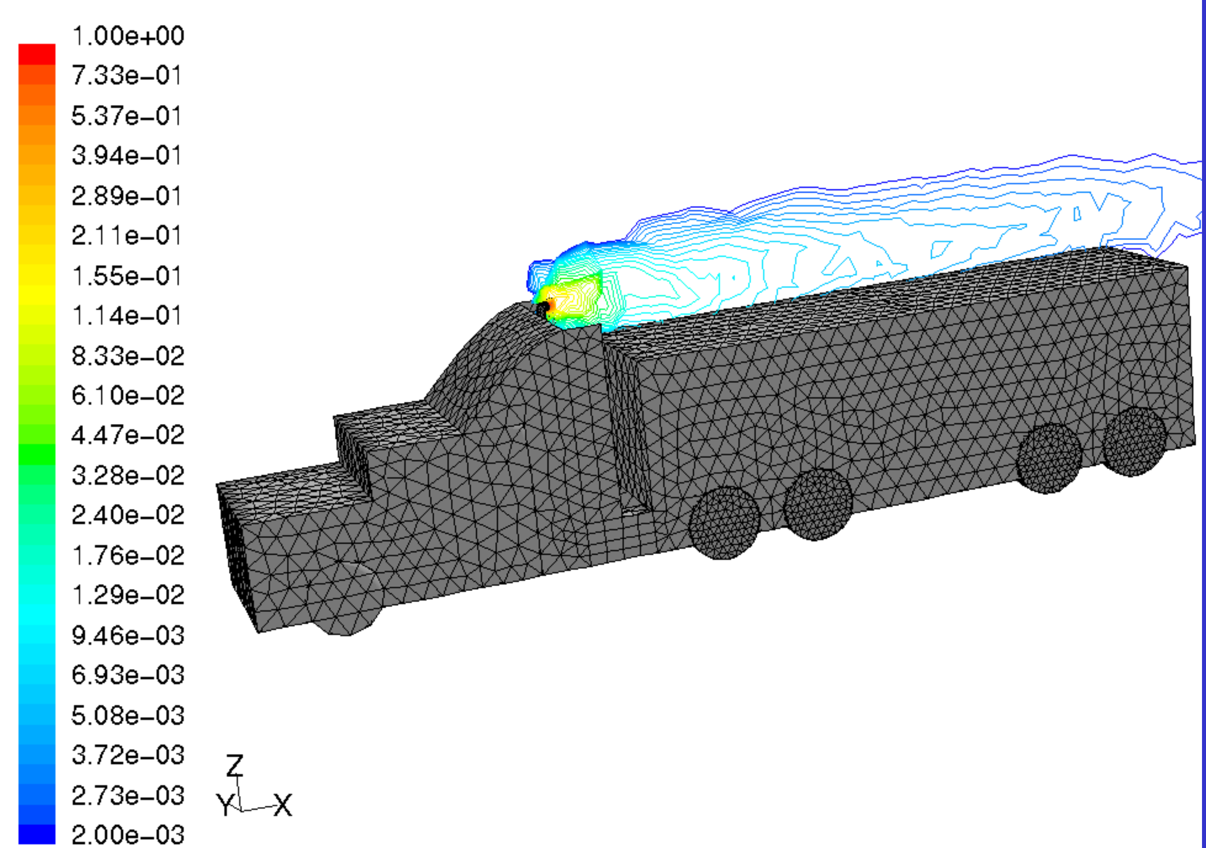
- **Better agreement with experimental data than simulation without the gantry at 20 inches downstream from stack**
- **Will not affect significantly far away due to high dilution ratio**

COMPUTATIONAL GRID OF TRACTOR-TRAILER



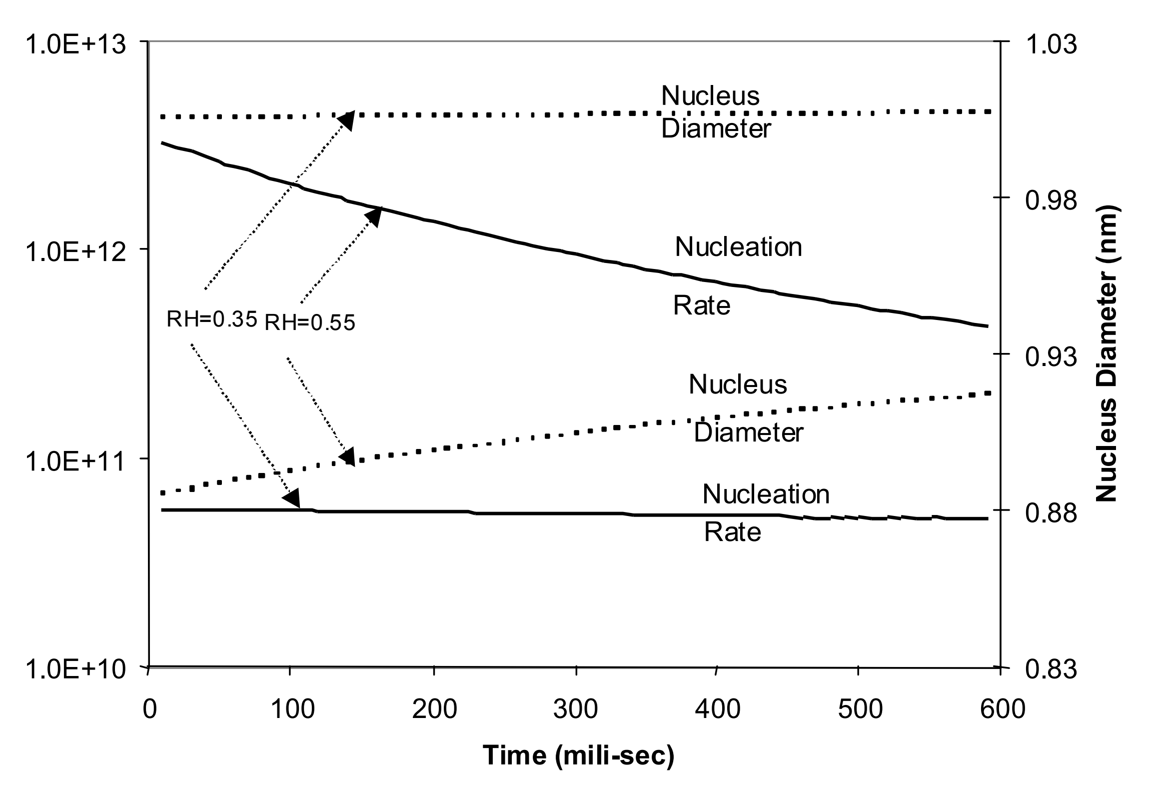
- Traditionally, the trucks are accompanied by the trailers.
- Tractor-trailer recreated using FLUENT software.
- Same velocity and temperature boundary conditions.

Contours of Relative Concentration of CO_2 on Tractor-Trailer



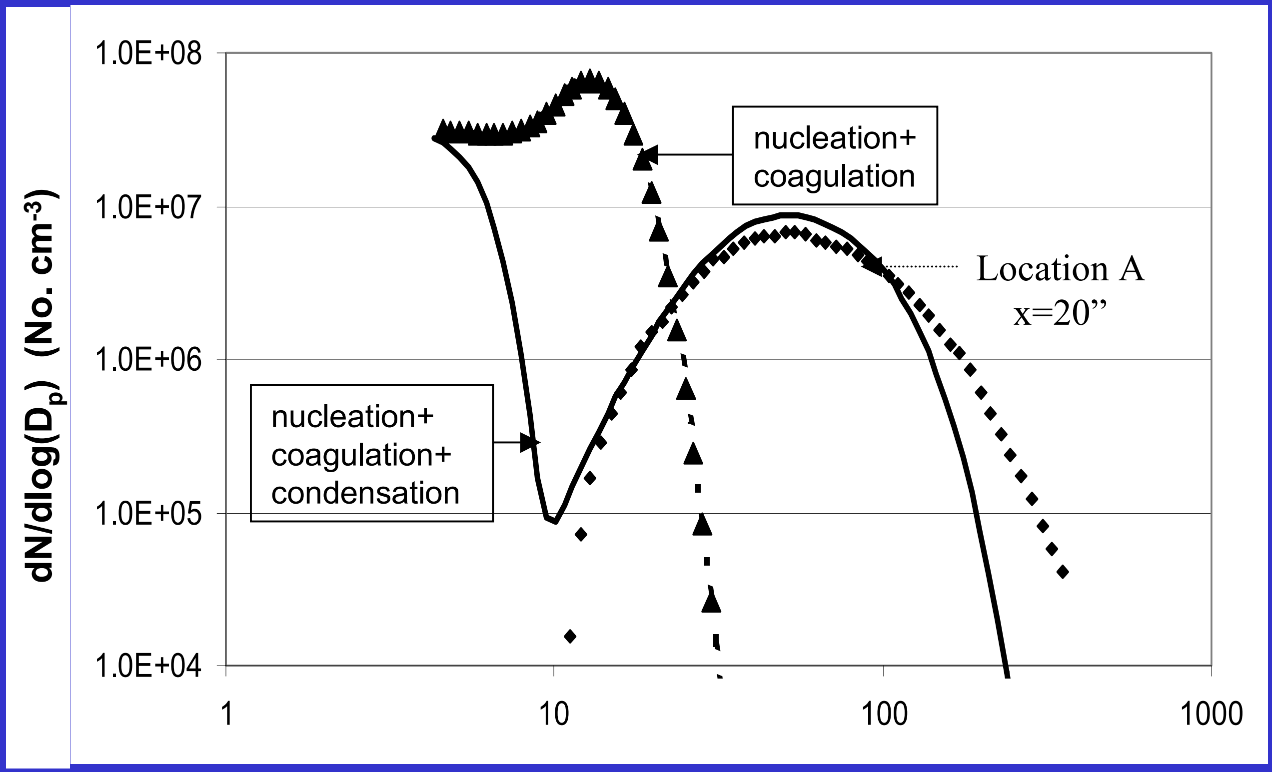
- **Longer plume for the trailer configuration**
- **Plume remained attached to the body.**
  (mix with ambient slowly)
- **Plume decayed slowly in the presence of trailer.**

Effect of Relative Humidity on Nucleation and Nucleus Size



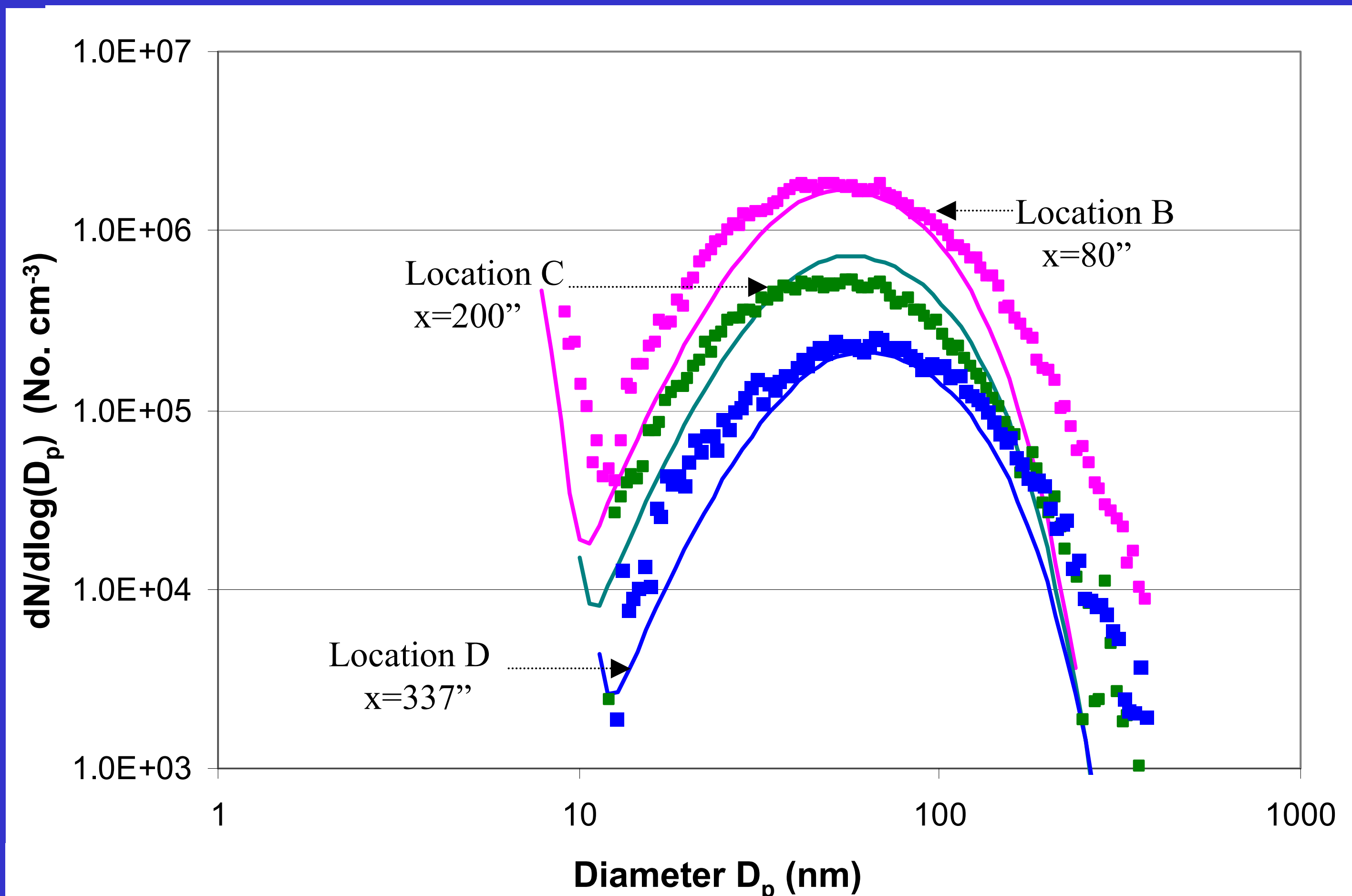
- Nucleus diameter decreased with increasing relative humidity
- Nucleation rate increased with increasing relative humidity
- At lower relative humidity, more molecules required for particle to be stable. (tendency for particles to evaporate)

Particle Concentration Variation With Particle Diameter at a Location 20”



- CMD shifted to the right from about 10 nm to 60 nm with condensation effects.
- Condensation essentially increased the nucleus radius.
- Particles with high diffusion coefficients diffused to large particles.
- Condensation effects are important near the stack (rapid dilution taking place).

Particle Concentration Variation with Diameter at Different Locations



CONCLUSIONS

- FLUENT k-ε model
  - Predicted the plume dispersion that included the effects of turbulent mixing, convection, diffusion, and temperature variations, and species transport
  - Agreed well with the concentration of CO_2 experimental data
  - Relative concentration CO_2 dropped rapidly from 1 to 100 within a distance of 100 inches (due to small exhaust flow rate mixed with ambient)
  - Center of the plume pointing downward (due to wake effects)
  - Numerical model showed a significant recirculation (Dispersion coefficients are not constant in CFD model)
  - CFD models could be used to predict the dispersion of pollutant, and to evaluate the impact of emission of pollutant.

CONCLUSIONS (continued)

- Nucleation rates in the formation of PM were calculated from the fuel sulfur content, F/A Ratio, and exhaust flow rate
- Nucleus diameter decreased by 30% from 10% to 90% relative humidity
- Number rate increased by a factor of 6 from 10% to 90% relative humidity
- Condensation effects were very important near the exhaust stack where rapid dilution is taking place.
- PM count median diameter increased from 10 to 60 nm with condensation effects.
- A good agreement was seen between the model predictions and the experimental data at four different locations.