Environment Ultrafine Particles: From Tailpipes to Ambient Background

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From Tailpipe to Ambient Background

- **Tailpipe** (600 K) → **Curbside** (300 K) → ~100 m from roadway → **Ambient Background** (~km)

  **Plume Processing**
  - Spatial: ~ meters
  - Temporal: ~ minutes

  **“Tailpipe-to-Road”** → **“Road-to-Ambient”**
  - 1000:1 in ~1 s
  - 10:1 in ~2 min

  **Ambient Processing**
  - Spatial: ~ km
  - Temporal: ~ hours to days

* Summarized in Zhang and Wexler, Atmos. Env. 38(38): 6643-6653 2004
From Tailpipe to Ambient Background

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“Tailpipe-to-Road”
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Ambient Processing
- Spatial: ~ km
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59 to 75 °F in 24 hours

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From Tailpipe to Ambient Background

- Steep temperature gradient triggers **New Particle Formation** and **Gas/Particle Partition**.

  **Temporal:** ~ minutes
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  **Spatial:** ~ meters
  **Temporal:** ~ minutes to hours

- “Tailpipe-to-Road” ~1 m from roadway
- “Road-to-Ambient” ~ km

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Ambient Processing

- **Spatial:** ~ km
- **Temporal:** ~ hours to days

59 to 75 °F in 24 hours
“Tailpipe-to-Road”: 0 – 1 second

Hot exhaust is rapidly diluted by Vehicle-generated Turbulence

High Saturation Ratios for gas phase compounds

H₂SO₄-H₂O

Organic Vapors

condense on pre-existing soot particles

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Hot exhaust is rapidly diluted by Vehicle-generated Turbulence.

**High Saturation Ratios** for gas phase compounds

H$_2$SO$_4$-H$_2$O

Organic Vapors

condense on pre-existing soot particles

nucleate to form nm-sized nuclei

grow fresh nuclei

condense on pre-existing soot particles

Tailpipe Curbside

600 K

300 K

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“Tailpipe-to-Road”: 0 – 1 second

- Sulfur makes particles and organics grow particles
- There is a competition between Condensation and New Particle Formation.

* Summarized in Zhang and Wexler, Atmos. Env. 38(38): 6643-6653 2004
“Road-to-Ambient”: the next 2 minutes

No New Particle Formation
Dilution + Gas/Particle Partition

Vapor Saturation Ratio (VSR)

τ_Dilution << τ_Equilibrium

Condensation
Evaporation

τ_Dilution ~ τ_Equilibrium

Exhaust Particles

“Road-to-Ambient”: the next 2 minutes

Tailpipe

Curbside

~ 100 m from roadway

Ambient Background ~ km

Vapor Saturation Ratio (VSR)

Exhaust Particles

Condensation

Evaporation

Kelvin effect

\[ \tau_{\text{Dilution}} \ll \tau_{\text{Equilibrium}} \]

\[ \tau_{\text{Dilution}} \sim \tau_{\text{Equilibrium}} \]

VSR=1 Equilibrium

“Road-to-Ambient”: the next 2 minutes

- Ultrafine Particles are volatile: They don’t maintain their original size or composition.
- Small particles tend to evaporate.

Vapor Saturation Ratio (VSR)

Dilution + Gas/Particle Partition

No New Particle Formation

Condensation

Evaporation

1 s

2 min

Condensation

Evaporation

Kelvin effect

Ambient Background

~ km

VSR=1
Equilibrium

Emission is dynamic

- Ultrafine Particles are volatile: They don’t maintain their original size or composition.
- Small particles tend to evaporate.

Receptor-dependent Emission Factors (EF)

Tailpipe-level Emission:
The emission profiles near the exit of the tailpipe

* Summarized in Zhang et al., Atmos. Env. 39 (22): 4155-4166 2005
Receptor-dependent Emission Factors (EF)

Road-level Emission: The emission profiles on or near the roadway curb

* Summarized in Zhang et al., Atmos. Env. 39 (22): 4155-4166 2005
Receptor-dependent Emission Factors (EF)

**Grid-level Emission**: The emission profiles near the end of plume processing (particle dynamics slows down significantly at this point)

* Summarized in Zhang et al., Atmos. Env. 39 (22): 4155-4166 2005
“Emission is in the eyes of the beholder”

* Summarized in Zhang et al., Atmos. Env. 39 (22): 4155-4166 2005
Deriving Ultrafine Particle Emission Factors

* Summarized in Zhu et al., JAWMA 52: 1032-1042 and Zhang et al., Atmos. Env. 39 (22): 4155-4166 2005
Deriving Ultrafine Particle Emission Factors

- Measured at gradually increasing downwind distances (17/30m to 300m)
- Particle size distribution → Particle Emission Factor distribution

* Summarized in Zhu et al., JAWMA 52: 1032-1042 and Zhang et al., Atmos. Env. 39 (22): 4155-4166 2005
Road-Level vs. Grid-Level: I-405 (L) and I-710(R)
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Plume Processing
Road-Level vs. Grid-Level: I-405 (L) and I-710 (R)

- Road-level: multi-modal
- Grid-level: mono-modal
- Living near the roadways → Higher ultrafine particle exposure.
Summer vs. Winter: I-405(R) and I-710(L)
Summer vs. Winter: I-405(R) and I-710(L)

• The **seasonal** effects are **significant**.
• Mode shifts from **60** nm in summer to **10** nm in winter.
• Higher ultrafine particle exposure in the winter even living further away from freeways!
I-405 (5% diesel) vs. I-710 (25% diesel) : Grid-Level

Grid-Level

- 405s (5% diesel)
- 710s (25% diesel)
I-405 (5% diesel) vs. I-710 (25% diesel) : Grid-Level

- The effect of diesel fraction effect on grid-level emissions is limited (due to evaporation of ultrafine particles) according to this study.
- More studies needed.
Number vs. Mass: I-405(R) and I-710(L)
The mass emission factor distributions (<220 nm) have no appreciable size shift from road to grid-level emissions.

The effects of plume processing on particle number are much more profound than on particle mass.
How to Control Ultrafine Particles?

- Hot exhaust is rapidly diluted by **Vehicle-generated Turbulence**
- **High Saturation Ratios** for gas phase compounds
- Condense on pre-existing soot particles
- **H₂SO₄-H₂O** nucleate to form nm-sized nuclei
- Grow fresh nuclei
- **Organic Vapors**
- Condense on pre-existing soot particles

600 K to 300 K
How to Control Ultrafine Particles?

- Controlling precursor vapors is most effective.
- Control Sulfur? Control Organics?
- Developed a mechanistic model to identify the precursor vapors.

**H$_2$SO$_4$-H$_2$O**

Condense on pre-existing soot particles

Nucleate to form nm-sized nuclei

Grow fresh nuclei

Condense on pre-existing soot particles

Hot exhaust is rapidly diluted by Vehicle-generated Turbulence

Tailpipe Curbside

300 K

600 K

Tailpipe Curbside

High Saturation Ratios for gas phase compounds

Hot exhaust is rapidly diluted by Vehicle-generated Turbulence

Organic Vapors

How to Control Ultrafine Particles?
A Mechanistic Aerosol Dynamics Model for “Road-to-Ambient” Process

Road-level Emission Profiles (30 m)

Compositions

Emission Profiles at Each Distances (60, 90 m …)

**Dilution**

- Particle / Gas:
  \[ N_{i,j}^{k}(x) = \frac{f(x)}{f(x - \Delta x)} \cdot N_{i,j}^{k}(x - \Delta x) \]
  
  \( f \) was determined by measured CO profile.

**Gas/Particle Partition**

- Particle (Gibbs-Thompson effect and Raoult’s Law):
  \[
  \frac{dm_{i,k}^{j}}{dt} = 2\pi D_k D_{p,i}^{j} \left[ C_k^{\infty} - y_{i,k}^{j} C_k^{0} Ke \right] 
  \]

  \[ 1 + \frac{8\lambda}{\alpha D_{p,i}^{j}} \]

- Gas:
  \[
  \frac{dC_{k}^{\infty}}{dt} = N_{i,j}^{k} \frac{dm_{i,k}^{j}}{dt} 
  \]

 Particle / Gas:

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  \]
A Mechanistic Aerosol Dynamics Model for “Road-to-Ambient” Process

**Dilution**

Particle / Gas:

\[ N_{i,j}^r(x) = \frac{f(x)}{f(x-\Delta x)} \cdot N_{i,j}^r(x-\Delta x) \]

\( f \) was determined by measured CO profile.

**Gas/Particle Partition**

Particle (Gibbs-Thompson effect and Raoult’s Law):

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\frac{dm_{i,k}^j}{dt} = \frac{2\pi D_k D_{p,i}^j}{\alpha D_{p,i}^j} \left[ C_k^{\infty} - y_{i,k}^j C_k^0 Ke \right] \left( 1 + \frac{8\lambda}{\alpha D_{p,i}^j} \right)
\]

Gas:

\[
\frac{dC_k^{\infty}}{dt} = N_{i,j}^r \frac{dm_{i,k}^j}{dt}
\]
Simulation Results: I-405 Summer

(a) 60 m / 405S
- tail effect: -91.5%
- measured
- predicted

(b) 90m / 405S
- tail effect: -88.2%
- measured
- predicted

(c) 150 m / 405S
- tail effect: -15.8%
- measured
- predicted

(d) 300m / 405S
- tail effect: -43.0%
- measured
- predicted
Simulation Results: I-405 Winter

(a) 60 m / 405W
-28.3%
-19.9%
6.2%    13.5%
22.5%  2.2%  2.9%  2.1% -9.3%

(b) 90 m / 405W
5.8%    6.2%  13.5% -3.8%
6.7%  5.3% -8.7%

(c) 150 m / 405W
0.0%    -30.2% -9.9%
22.5%  6.5% -7.3% -30.5%

(d) 300 m / 405W
1.1%    -5.9% -11.5% -12.9%
-9.1% -17.5% -39.6%
We identified that the precursor organic vapors have carbon number between 20 to 24. It is in the range where the largest fuel molecules and smallest lubrication oil molecules reside. Fuel or Oil or Both contribute to the ultrafine particle dynamics.
Conclusions

- Steep temperature gradient triggers New Particle Formation and Gas/Particle Partition.
- There is a competition between Condensation and New Particle Formation.
- Ultrafine Particles are volatile and their emission profiles are dynamics.
- People living near freeways have much higher ultrafine particles exposure.
- Meteorological conditions significantly affect ultrafine particle emissions.
I-405 (5% diesel) vs. I-710 (25% diesel) : Road-Level

Road-Level
- 405s (5% diesel)
- 710s (25% diesel)