EMISSION OF ULTRAFINE AND NANOPARTICLES FROM WASTE TO ENERGY PLANTS

Stefano CERNUSCHI, M. Giugliano, S. Ozgen, G. Ripamonti
Background

Ultrafine (UP) and nanoparticles (NP)

- Dimensions < 0.1 µm (UP) - 0.05 µm (NP)
- **Main environmental concerns** → nanotechnologies, nanomaterials, indoor exposures
- Recent attention to **combustion emissions**
  - most data available for vehicle exhaust
  - limited investigations for stationary sources
  - few studies for WTE plants
Background - concentration levels

PU concentrations in selected environments

- rural and coastal areas
- urban areas
- indoor domestic
- urban traffic sites
- kitchens
- smoking areas
- restaurants
- public buses

Particle number/cm³

10 100 1000 10000 100000 1000000
### Background - industrial levels

<table>
<thead>
<tr>
<th>Process</th>
<th>Concentration within 14 - 673 nm size range (particles/cm³)</th>
<th>Typical size range (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background, indoor</td>
<td>≥ 10 000</td>
<td></td>
</tr>
<tr>
<td>Silica fusion</td>
<td>≥ 100 000</td>
<td>280-520</td>
</tr>
<tr>
<td>Metal grinding</td>
<td>≥ 130 000</td>
<td>17-170</td>
</tr>
<tr>
<td>Metal soldering</td>
<td>≥ 400 000</td>
<td>36-64</td>
</tr>
<tr>
<td>Plasma cutting</td>
<td>≥ 500 000</td>
<td>120-180</td>
</tr>
<tr>
<td>Bread baking oven</td>
<td>≥ 640 000</td>
<td>32-109</td>
</tr>
<tr>
<td>Airport landing runway</td>
<td>≥ 700 000</td>
<td>&lt; 45</td>
</tr>
<tr>
<td>Electrode welding</td>
<td>54 000 - 3 500 000</td>
<td>33-126</td>
</tr>
<tr>
<td>Steel welding</td>
<td>100 000 - 40 000 000</td>
<td>40-600</td>
</tr>
</tbody>
</table>
Background - domestic levels

Home indoor

Particle number concentration (n/cm³)

Indoor microenvironments

Number concentration (cm⁻³)

Café  Hairdresser  Supermarket  Church service
Background - personal exposures

Weekday

Saturday

S. Cernuschi - Ultrafine and nanoparticle emissions from WTE plants
Background

UP/NP emissions from combustion

Zone 1. Fuel
- Atomized oil droplets
- Coal particles with metal/mineral inclusions

Zone 2. Flame
- Pyrolysis/oxidation
- Oxidative pyrolysis/metal suboxides
- Vaporization
- Heterogeneous condensation
- Char fragmentation
- Char burnout
- Fly ash (1–2 μm)

Zone 3. Postflame
- Organic vapors
- Oxidation/metal oxides
- Condensation
- Metal seed nuclei (1–10 nm)
- Metal catalyzed reaction
- Particulate metal-organic complexes (10–1,000 nm)
- Soot (10–1,000 nm)
- Pollutant vapors

Primary particles

Condensable particles
(semivolatiles nucleation driven by atmospheric gas dilution)

Cormier et al., Env. Health Persp. 2006
Research contents

ULTRAPART project

- Characterization of ultrafine and nanoparticle emissions from stationary combustion sources
  - waste to energy plants
  - residential boilers fuelled with biomass, light fuel oil and natural gas
- Particle number concentration and size distribution
- Evaluation of the condensation effects by diluting and cooling the exhaust gas prior to measurements
- Measurement issues
  - no standard protocol
  - significance in terms of number rather than mass
  - contribution of condensable fraction from semivolatiles driven by atmospheric gas dilution
1. Hot sampling + FP capture (≥ 2,5 µm)

2. Controlled dilution with conditioned air

3. Particle counting (0.007 µm - 10 µm in 12 classes)
   Inertial impactor ELPI™
Sources investigated

- Urban and commercial waste
- 4 plants, capacity 600 - 1200 tpd
- BAT design for flue gas treatment
  - dry removal + SCR (2 plants)
  - dry/wet removal + SCR (1 plant)
  - dry/wet removal + SNCR (1 plant)

Measurement campaigns

- Hot sampling
- Dilution sampling
  - low: DR = 15 → 20
  - medium: DR = 25 → 35
  - high: DR = 40 → 60
- Ambient air
WTE 1 - Dry, FF at 170°C

Number concentration (particles cm\(^{-3}\))

<table>
<thead>
<tr>
<th>Condition</th>
<th>Particle Number Concentration (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient Air</td>
<td>Average = $1.3 \times 10^4$</td>
</tr>
<tr>
<td>Hot Sampling</td>
<td>$4.9 \times 10^3$</td>
</tr>
<tr>
<td>Low Dilution</td>
<td>$1.1 \times 10^4$</td>
</tr>
<tr>
<td>Medium Dilution</td>
<td>$1.1 \times 10^4$</td>
</tr>
<tr>
<td>High Dilution</td>
<td>$1.7 \times 10^4$</td>
</tr>
</tbody>
</table>

Dilution sampling
WTE 1 - Dry, FF at 170°C

Size fractions

- 0.007<dp<0.05
- 0.05<dp<0.1
- 0.1<dp<10µm

<table>
<thead>
<tr>
<th>Dilution ratio</th>
<th>Size fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot sampling</td>
<td>74%</td>
</tr>
<tr>
<td>Low</td>
<td>79%</td>
</tr>
<tr>
<td>Medium</td>
<td>84%</td>
</tr>
<tr>
<td>High</td>
<td>93%</td>
</tr>
</tbody>
</table>

- 0.007<dp<0.05
- 0.05<dp<0.1
- 0.1<dp<10µm

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Size distributions

WTE 1 - Dry, FF at 170°C

Hot sampling
TN: $4.9 \times 10^3$ cm$^{-3}$

Dilution sampling
TN: $1.4 \times 10^4$ cm$^{-3}$
Number concentration (particles cm$^{-3}$)

<table>
<thead>
<tr>
<th>Dilution sampling</th>
<th>ambient air</th>
<th>low dilution</th>
<th>medium dilution</th>
<th>high dilution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number concentration (cm$^{-3}$)</td>
<td>1.3·10$^4$</td>
<td>5.0·10$^3$</td>
<td>4.8·10$^3$</td>
<td>7.9·10$^3$</td>
</tr>
<tr>
<td>Average</td>
<td>5·10$^3$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Size fractions

- 0.007 < dp < 0.05
- 0.05 < dp < 0.1
- 0.1 < dp < 10 µm

Dilution ratio

Low: 74% 19% 7%
Medium: 71% 20% 9%
High: 82% 13% 5%
Size distribution

Dilution sampling
TN: $4.8 \cdot 10^3 \text{ cm}^{-3}$

$dN/dDp \left[ 10^6 \text{ cm}^{-3} \mu m^{-1} \right]$

$Dp [\mu m]$

$0$ $0.01$ $0.1$ $1$ $10$

$0$ $0.05$ $0.1$ $0.15$
WTE 3 - Wet/ dry

Number concentration (particles cm\(^{-3}\))

Average = \(5.4 \times 10^4\)

Particle number concentration (cm\(^{-3}\))

- Ambient air: \(2.0 \times 10^4\)
- Hot sampling: \(2.7 \times 10^4\)
- Low dilution: \(4.7 \times 10^4\)
- Medium dilution: \(5.6 \times 10^4\)
- High dilution: \(7.8 \times 10^4\)

Dilution sampling
Size fractions

- 0.007<dp<0.05
- 0.05<dp<0.1
- 0.1<dp<10μm

<table>
<thead>
<tr>
<th>Dilution ratio</th>
<th>Size fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot sampling</td>
<td>78%</td>
</tr>
<tr>
<td>Low</td>
<td>82%</td>
</tr>
<tr>
<td>Medium</td>
<td>84%</td>
</tr>
<tr>
<td>High</td>
<td>86%</td>
</tr>
</tbody>
</table>

Legend:
- Light blue: 0.007<dp<0.05
- Red: 0.05<dp<0.1
- Yellow: 0.1<dp<10μm

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Size distribution

Hot sampling
TN: $2.7 \cdot 10^4 \text{ cm}^{-3}$

Dilution sampling
TN: $6.4 \cdot 10^4 \text{ cm}^{-3}$
Ultrafine and nanoparticle emissions from WTE plants

Number concentration (particles cm$^{-3}$)

- **WTE 4 - Wet/dry**

<table>
<thead>
<tr>
<th>Condition</th>
<th>Number Concentration (particles cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient air</td>
<td>4.6 · 10$^3$</td>
</tr>
<tr>
<td>Hot sampling</td>
<td>1.5 · 10$^5$</td>
</tr>
<tr>
<td>Low dilution</td>
<td>1.7 · 10$^5$</td>
</tr>
<tr>
<td>High dilution</td>
<td>5.7 · 10$^5$</td>
</tr>
<tr>
<td>High dilution*</td>
<td>5.4 · 10$^5$</td>
</tr>
<tr>
<td>Very high dilution*</td>
<td>1.1 · 10$^5$</td>
</tr>
</tbody>
</table>

Average = 2.8 · 10$^5$

*Reduced potential
Size fractions

<table>
<thead>
<tr>
<th>Dilution ratio</th>
<th>0.007&lt;dp&lt;0.05</th>
<th>0.05&lt;dp&lt;0.1</th>
<th>0.1&lt;dp&lt;10µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot sampling</td>
<td>83%</td>
<td>14%</td>
<td>3%</td>
</tr>
<tr>
<td>Low</td>
<td>83%</td>
<td>15%</td>
<td>2%</td>
</tr>
<tr>
<td>High</td>
<td>86%</td>
<td>13%</td>
<td>1%</td>
</tr>
<tr>
<td>Very high</td>
<td>72%</td>
<td>23%</td>
<td>5%</td>
</tr>
</tbody>
</table>
Ultrafine and nanoparticle emissions from WTE plants

Size distribution

**WTE 4 - Wet/dry**

- **Hot sampling**
  - TN: $1.5 \cdot 10^5$ cm$^{-3}$

- **Dilution sampling**
  - TN: $3.8 \cdot 10^5$ cm$^{-3}$
**Total efficiency**
- UP+NP (< 100 nm) = 96.8%
- FP (100 nm - 1 µm) = 98.9% - >99.9%
Sampling techniques

- **Ultrafine (UP):** 100 nm
- **Nanoparticle (NP):** 50 nm

**Policarbonate filter**

**Aluminium foil**
UP/ NP chemical characterization

ANALYTICAL TECHNIQUES

- **IONS** (nitrates, sulphates, ammonium)
  - Anions → Ion chromatography
  - Ammonium → UV-Visible Spectrophotometry

- **METALLIC ELEMENTS** (Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Sb, Hg, Tl, Pb)
  - ICP-MS (inductively coupled plasma-mass spectroscopy)

- **TOTAL CARBON**
  - EGA (Evolved Gas Analysis) - 630°C in oxidising atmosphere with NDIR CO₂ detection

- **MASS**
  - Gravimetric (microbalance)
UP chemical characterization

WTE ultrafine size fraction chemical composition

- Fe 11.1%
- Zn 5.9%
- Ni 2.0%
- Al, Ti, V, Mn, Co, Cu, Cd 0.7%
- Pb 0.1%
- Cr 3.3%
- TC 17.6%
- ND 13.0%
- TC: total carbon; ND: unidentified

Cl⁻ 27.4%
NO₃⁻ 10.5%
NH₄⁺ 8.4%
UP chemical characterization

WTE ultrafine fraction chemical composition

- Al, Ti, V, Mn, Co, Cu, Cd: 0.7%
- Pb: 0.1%
- Zn: 5.9%
- Ni: 2.0%
- Fe: 11.1%
- Cr: 3.3%
- TC: 17.6%
- ND: 13.0%
- Cl⁻: 27.4%
- NO₃⁻: 10.5%
- NH₄⁺: 8.4%

TC: total carbon; ND: unidentified

Background air

Ultrafine fraction chemical composition

- NO₃⁻: 11.7%
- NH₄⁺: 4.6%
- SO₄²⁻: 3.0%
- Cl⁻: 0.7%
- Zn: 0.2%
- Pb: 0.1%
- Cu: 0.2%
- TC: 37.4%
- ND: 42.1%

TC: total carbon; ND: unidentified
NP chemical characterization

WTE nanoparticle size fraction chemical composition

- TC: total carbon; ND: unidentified

- Ti, V, Mn, Co: 0.2%
- Cl⁻: 14.7%
- ND: 20.6%
- Pb: 0.4%
- Zn: 7.8%
- Ni: 1.3%
- Fe: 6.2%
- Cr: 2.1%
- NO₃⁻: 13.0%
- NH₄⁺: 8.8%
- TC: 24.9%
NP chemical characterization

WTE nanoparticle fraction chemical composition

- TC: total carbon; ND: unidentified
- Ti, V, Mn, Co: 0.2%
- Zn: 7.8%
- Ni: 1.3%
- Fe: 6.2%
- Cr: 2.1%
- Pb: 0.4%
- ND: 14.7%
- Cl⁻: 20.6%
- NO₃⁻: 13.0%
- NH₄⁺: 8.8%
- SO₄²⁻: 3.6%
- Pb: 1.1%
- NO₃⁻: 9.9%
- NH₄⁺: 4.6%
- SO₄²⁻: 3.6%
- TC: 45.0%

Background air
Nanoparticle fraction chemical composition

TC: total carbon; ND: unidentified

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Conclusions

- Measured number concentrations
  - influence of flue gas treatment process configuration (scrubber, T baghouse)
  - generally comparable or slightly higher than ambient air
  - very high capture efficiency for FF: \(~97\%\) for NP+UP, 98-99,9\%\) for FP (0,1 - 1 \(\mu m\)), both for primary than for condensible particles

- Effects on concentration levels arising from fractions of condensable origin
  - UP and NP fractions largely prevailing in size distributions for all sampling conditions

- Chemical characterization
  - in accordance with waste composition and combustion process influence (presence of chlorides, Fe, Zn, Cr)
Conclusions

Comparative assessment

Particles cm⁻³ (log scale)

Ambient air
Wood pellet boiler
Closed fireplace
Light fuel oil boiler
Natural gas boiler
WTE 1
WTE 2
WTE 3
WTE 4
Diesel w/o DPF
Diesel w DPF
Gasoline conv
Gasoline DI

*DPF = diesel particulate filter

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