LABORATORY OF APPLIED THERMODYNAMICS

Transport-related airborne nanoparticles: Sources, different aerosol modes, and their toxicity

Ilias Vouitsis, Anastasios Kontses and Zissis Samaras

ARISTOTLE UNIVERSITY THESSALONIKI
SCHOOL OF ENGINEERING
DEPT. OF MECHANICAL ENGINEERING

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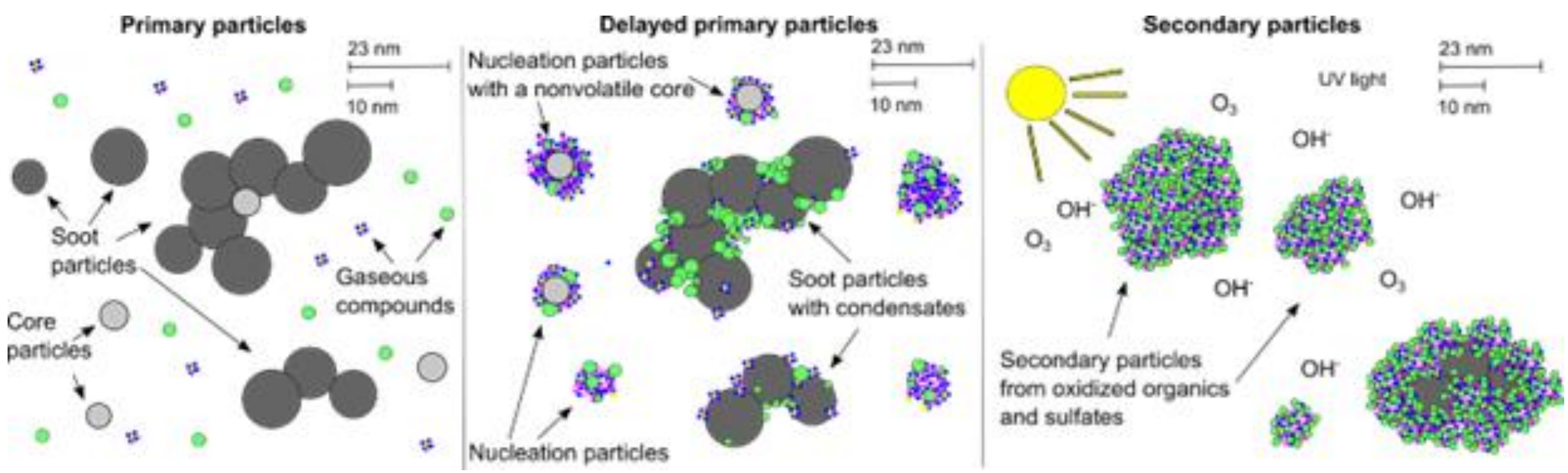
Nanoparticles (NPs) – Definition and background

- Most common NPs definition: particles **<100 nm** in size. These are also referred to as ultrafine particle (UFPs).
- Recent alternative NPs definitions:
  - Particles <200 nm (Ostro et al., Environ. Health Perspect. 123 (9), 2015)
  - Particles <500 nm (Kittelson et al., J. Aerosol Sci. 159, 2022).



Exhaust Emissions

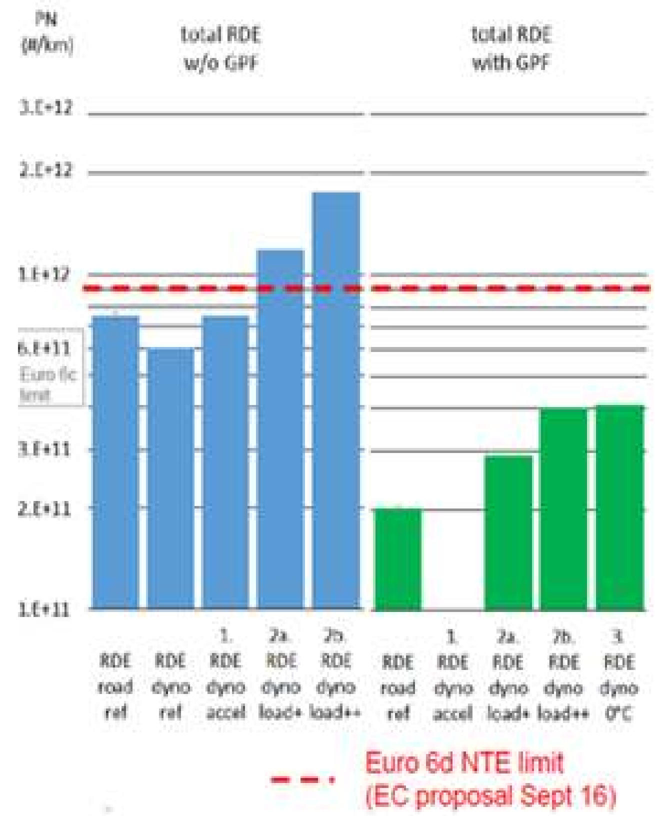
Road traffic

- Until recently, older non-DPF diesels dominated particle emissions
- The introduction of GDI engines increased gasoline contribution in particle emissions – GPF solves this issue

Primary particles

- Heterogeneously and homogeneously nucleated and agglomerated soot, ash, and solid sub-10-nm core particles.
- Core of EC (particles that survive agglomeration), adsorbed SVOCs (n-PAHs, hopanes, steranes, etc), and small amounts of sulfate, nitrate, metals, and other trace elements.
- Emission depends upon vehicle technology, fuel and lubricant properties, and driving conditions

GDI PN on RDE tests, without and with GPF



Source: Demuynck, 2016

Road traffic (2)

Delayed primary particles

- In gaseous phase under tailpipe conditions -condense or nucleate immediately when the exhaust is cooled and diluted
- Limited understanding of the nucleation processes but atmospheric nucleation studies suggest multicomponent processes involving clusters containing organic compounds
- DPPs also include contributions from sulfate (due to sulphur in fuel) and metals (e.g., Zn, Ca) that are used as fuel and oil additives.
- DPPs formation is dependent on technological parameters of vehicles (fuel and lubricant oil sulphur, exhaust aftertreatment devices)
- However, ambient T, RH and existing ambient aerosol may also affect their formation. Colder (winter) conditions seem to favor the formation of nucleation particles
- Increased primary and DPPs number concentrations may be observed during regeneration of the PFs

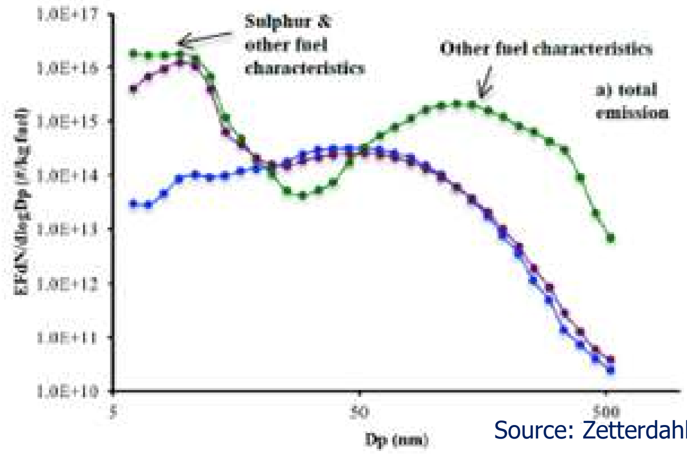
Secondary particles

- Formed from gaseous precursors via atmospheric photochemistry
- Vehicle technologies and driving conditions affect the SP precursor emissions
- In general, diesel fuel has the strongest formation potential because it is the least volatile fuel
- However, studies on latest technology vehicles indicate that gasoline emissions dominate over diesel ones

Shipping

Primary particle and DPPs

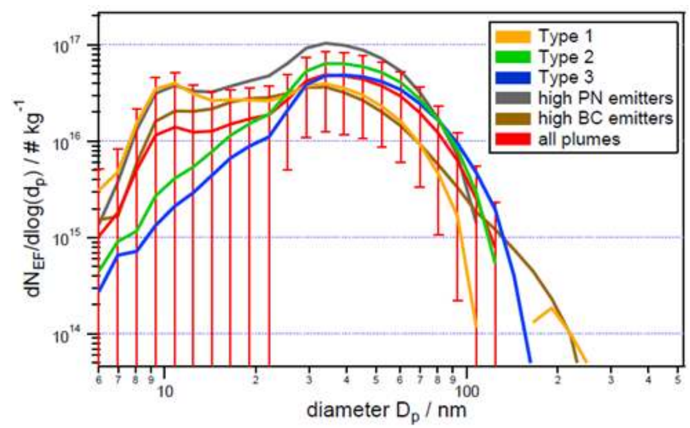
- Primary particles are formed from the thermal decomposition of large hydrocarbon molecules in the fuel and lube oil.
- After sufficient surface growth, aggregation/coagulation results in chains and clusters of the primary particles and an increase in size (to 10-100 nm)
- Depending on the conditions in the exhaust gas channel, the volatile compounds in the emission may undergo transformation and form new particles (DPPs), through nucleation, adsorption or condensation



Source: Zetterdahl, 2016

Secondary particles

- Depending on the plume age and the measurement context, plume PNSDs may be bimodal with peaks at 10–20 nm and 35 -100 nm or unimodal with a peak at 40 nm
- Marine ports PNSDs are bimodal with peaks at 20-40 nm and 80-100 nm

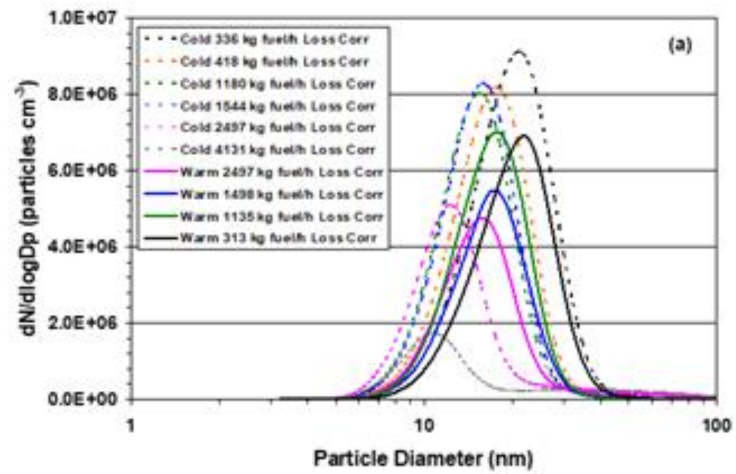


Source: Diesch et al., 20

Aviation

Non-volatile (primary particles) and volatile particles (DPPs)

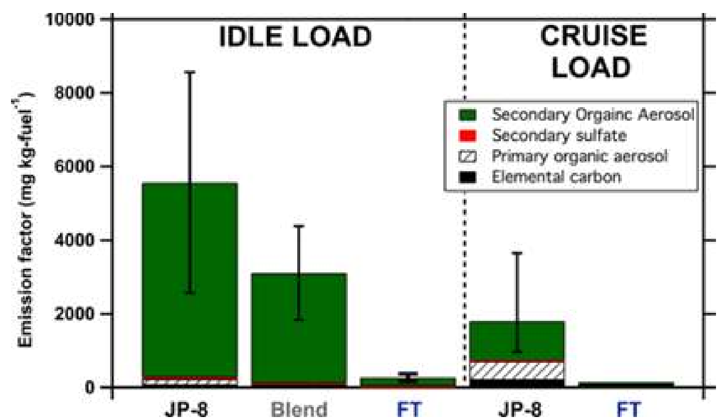
- Non-volatile primary particles are directly emitted by engines (graphitic/ elemental/black carbon with traces of metals
- Their PNSDs exhibit a unimodal distribution (in the range of 20-80 nm)
- Volatile particle components are partitioned into the gas- and particulate-phases and their behavior is sensitive on the changes in the environmental conditions with respect to the near-plume.
- Volatile particle diameters are ranging from 5 to 120 nm with a dominant mode at 18-20 nm



Source: Kinsey et al, 2010

Secondary particles

- Photo-oxidation processes plays a key role in forming of both inorganic (dominant at higher power) and organic (dominant at lower power) SPs.
- Total aerosol mass is dominated by SPs formation, approx. 2 orders of magnitude higher than the primary particles
- It is not clear if aircraft emissions can influence the amount of secondary aerosol on a large scale

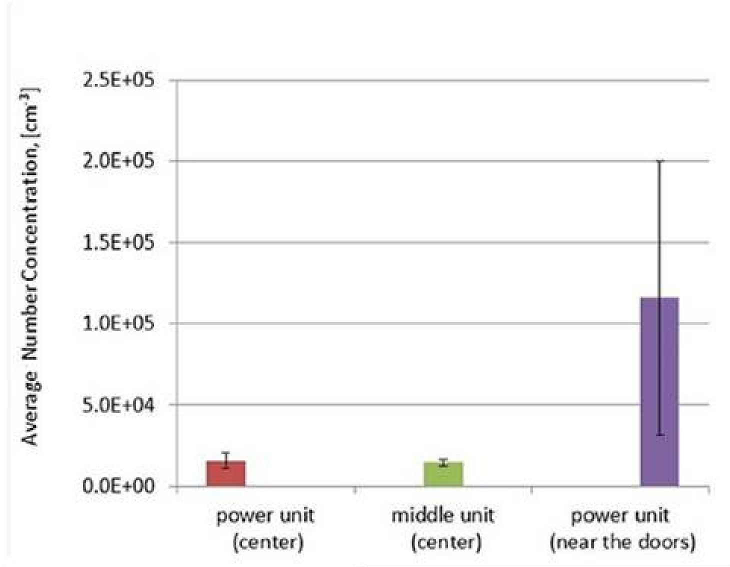


Source: Miracolo et al, 2011

Rail

- More than one-third of the EU rail network uses diesel-powered trains
- Exhaust particle emissions from diesel rail transport are not very well known and only few sources addressing actual emission rates are available
- Emissions depend on engine load, speed, and technology as well as on the type and elemental composition of the fuel, lubricant, engines, and after-treatment components
- NP levels in the indoor environment of diesel-propelled passenger trains are significant

Average NP number concentration inside passenger train carriages



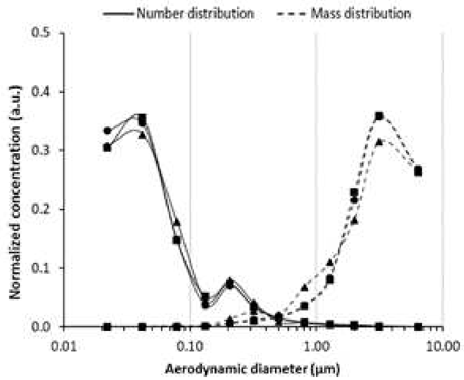
Source: Abramesko et al, 2019

Non exhaust emissions

Road emissions

➢ **Brake wear**

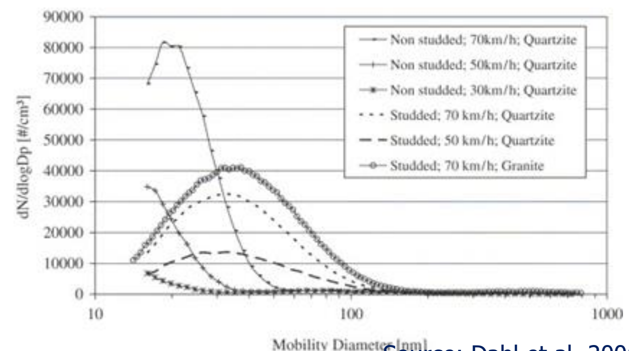
When considering measurements close to the sources NP number concentrations are dominant



Source: Beji et al, 2020

➢ **Tyre wear**

Simulations suggest NP formation when studded tyres are used



Source: Dahl et al, 2006

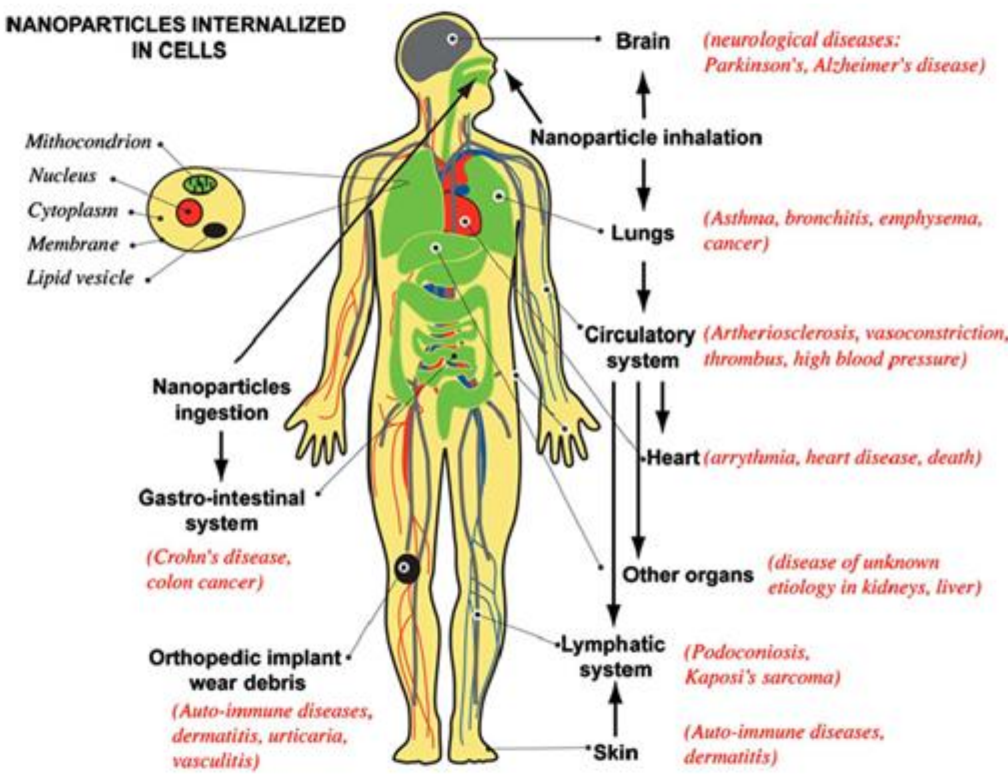
➢ **Road surface wear and resuspended road dust**-NPs have not been observed

- Non–exhaust NPs mainly composed of heavy metals (i.e., Zn, Cu, etc) and various organic compounds
- Electric vehicles emit particles from road, tyre and break wear (mainly PM10 and PM2.5)

Shipping, Aviation and Rail

- Sources of NPs in harbors (which specialise in vessel refit and repair activities): abrasive removal of filler and paint, spray painting with antifouling coatings, primers and topcoats.
- Types of harbor NPs:
  - highly regular (triangular, hexagonal) engineered nanoparticles (Ti-, Zr-, Fe-based), embedded as nano-additives in the coatings, and
  - Irregular, incidental particles emitted directly or formed during abrasion.
- Possible non-exhaust NP sources that may influence the air quality within an airport include emissions from auxiliary and ground power units, primary particles from tire erosion and brake wear, oil leaks and corrosion of aluminum alloys and topcoats.
- Very limited information for rail non-exhaust NPs. Some studies that analysed the chemical composition and morphology of rail NPs indicate similar metal-rich concentrations as in the coarse and fine fractions and a nonuniform granular shape

Toxicity


NANOPARTICLES INTERNALIZED IN CELLS
Mithocondrion
Nucleus
Cytoplasm
Membrane
Lipid vesicle
Nanoparticles ingestion
Gastro-intestinal system
(Crohn's disease, colon cancer)
Orthopedic implant wear debris
(Auto-immune diseases, dermatitis, urticaria, vasculitis)
Brain
(neurological diseases: Parkinson's, Alzheimer's disease)
Nanoparticle inhalation
Lungs
(Asthma, bronchitis, emphysema, cancer)
Circulatory system
(Artheriosclerosis, vasoconstriction, thrombus, high blood pressure)
Heart
(arrythmia, heart disease, death)
Other organs
(disease of unknown etiology in kidneys, liver)
Lymphatic system
(Podoconiosis, Kaposi's sarcoma)
Skin
(Auto-immune diseases, dermatitis)

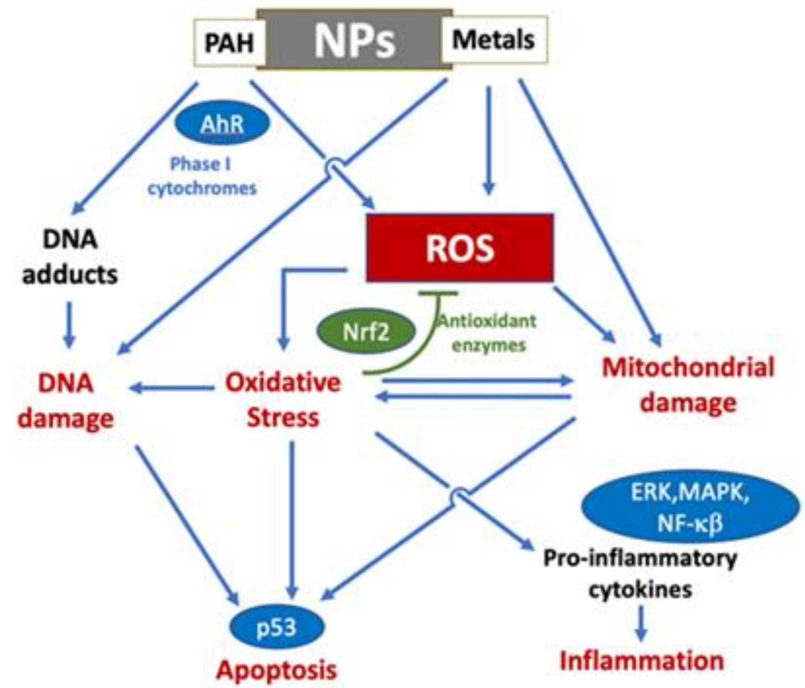
Toxicity

Assessment of toxic effects

- The analysis of their toxicity is hampered by their ability to aggregate or disintegrate during the processes of collection, storage, or/and analysis
- Limited number of methodologies. Three main groups: 1. epidemiological and clinical studies; 2. animal models, and 3. cellular models (fourth potential method, namely in silico toxicity assessment, is still in its infancy but it seems to be promising)

Mechanisms of toxicity

- A synergy between PAHs , the protein AhR (Aryl Hydrocarbon receptor), metals and ROS (Reactive oxidative species) leading to DNA damage and finally to apoptosis.
- In parallel, the ROS that formed from PAHs and metals induce oxidative stress contributing further to the apoptosis as well as to mitochondrial damage and inflammation
- Inflammation and oxidative stress are deemed to be the determinants of the systemic toxic effects. NPs may be translocated into the bloodstream and reach many organs (i.e., brain, liver, or kidneys)

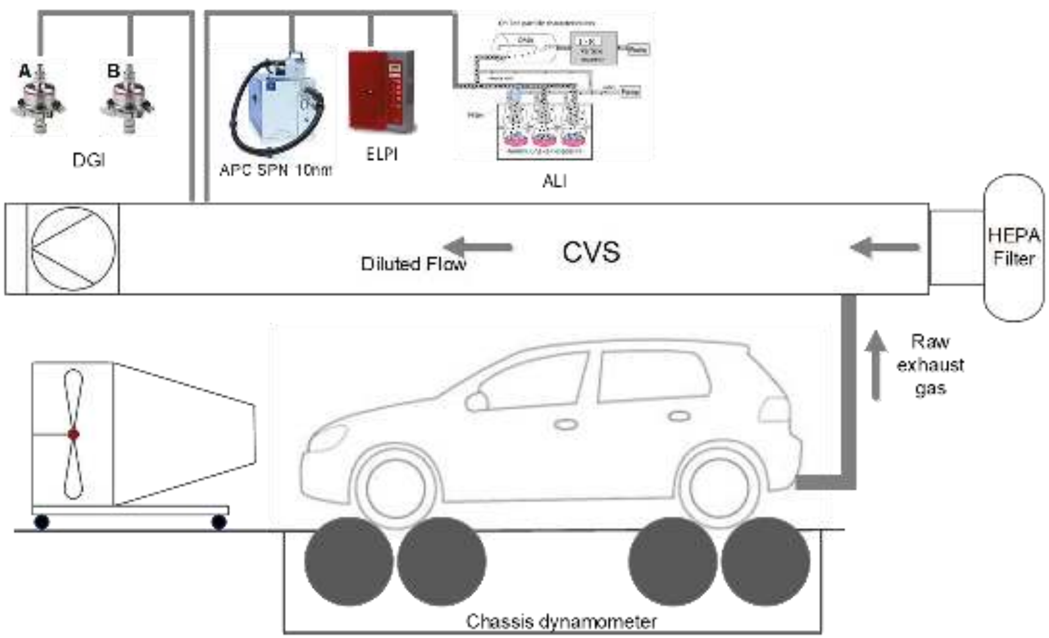


Toxic effects of exhaust & non-exhaust NPs

- It is still **unknown whether the effects of diesel NPs are more severe than those of PM2.5** on the systemic organs because NPs concentrations have rarely been measured in epidemiological studies.
- The toxicity effects of **gasoline NPs** emissions, especially from GDI engines, are not yet well understood.
  - Increasing evidence suggests that transition **metals present in particles, as well as certain organic species, generate ROS** that may be involved in the production of undesirable respiratory symptoms
  - Primary particles cause a change in the breathing patterns of male Sprague-Dawley
  - GDI NPs contribute to the upregulation of genes associated with the metabolism of PAHs and oxidative stress
- **Shipping** NPs have not been sufficiently studied - epidemiological studies indicate that can trigger biological effects, such as oxidative stress and cytotoxicity.
- **Aviation** NPs have not been sufficiently studied also. The current data suggests similar to diesel exhaust particles pulmonary toxicity.
- Exposure to airborne Fe-bearing road **non exhaust** NPs may be particularly hazardous to human health due to their high bioreactivity and potential toxicity.
- **Subway** non exhaust NPs appeared to be eight times more genotoxic and four times more effective at causing oxidative stress than above-ground particles, because they can form intracellular ROS.

Toxicity assessment in the nPETS project

- nPETS aims at **studying the life of the sub-100 nm emissions from its creation to its potential path to human beings and animals.**
- Interdisciplinarity: aerosol science, toxicology, chemistry, transport policy studies
- Indicative example of **set-up for vehicle exhaust NPs evaluation (chassis dyno)**:
  - **Physicochemical** characterization (on-line and filter collection)
  - **Toxicity** analysis:
    - PM collection on filters for **off-line tox analysis** and
    - **On-line cell exposure (air-liquid interface, ALI)** to exhaust gas and off-line tox characterization



Conclusions

- The **size** of nanoparticles determines (in a probabilistic sense) their fate in the air and their potential of toxicity.
- **New technology** road vehicles have much lower particle mass emissions, but **higher nanoparticles number** emissions.
- Particle size distribution within the plume of **ships** may cover a size range from nanoparticles (5 nm) to coarse particles (3 μm).
- **Aircraft**-related NPs concentration and size distribution at airports demonstrate a clear dependence on aircraft operations – ground level activities are more important.
- Rail (diesel) exhaust particle emissions are not very well known.
- **Aviation**, **rail** and **road transport** are significant/ sources of **non-exhaust** particle emissions associated with the **tyre, brake, and road surface wear and tear.**
- **NPs toxicity** should be further evaluated
- The **toxicity of exhaust nanoparticles** seems to be critical in the physiology of pulmonary pathologies

Thank you for your attention

Ilias Vouitsis

vouitsis@auth.gr