Chemical composition of the size-classified nanoparticle exhausted from gasoline vehicle

Kazumasa Okamura, Tetsuya Yamashita, Hiroyuki Kawase
TOYOTA MOTOR CORPORATION

As for the nanoparticle, there is the concern for the influence of cardiovascular system. In automobile emission, the relationship between chemical composition and the biological effect of nanoparticles are not clear yet.

Therefore, we investigated the chemical composition (metals, polycyclic aromatic hydrocarbons (PAHs) and other hydrocarbons) of the size-classified particles to clarify an actual property of the nanoparticles exhausted from gasoline DI engine.

We compared the chemical composition of 10 nm, 56 nm and 100 nm particles, sampled by reiteration of the NEDC mode driving (Cold start : Hot start = 1 : 12).

For metal compositions by ICP-MS analysis, Na, K, Ca, Zn and Fe were detected in 56 nm and 100 nm particles, and they were assumed oil and abrasion derivations. Na, K, Ca and Zn were detected in the 10 nm particles, but no unique metal compositions in this particle size were detected.

We analyzed US EPA's 16 priority pollutant PAHs by GC-MS. In 56 nm and 100 nm particles, Chrysene, Benz(a)anthracene, Benzo(k)fluoranthene, Benzo(a)pyrene and Indeno(1,2,3-cd)pyrene were detected in the common.

Furthermore, Naphthalene and Anthracene were detected only in the 56 nm particles, and Benzo(b)fluoranthene and Benzo(g,h,i)perylene were detected only in the 100 nm particles. PAHs of 5 rings or more in the 100 nm particles had tendency to be higher than that of 56 nm (The PAH concentrations of 56 nm vs. 100 nm were 0.28 ng/m3 to 0.85 ng/m3 at 5 rings or more, and 1.21 ng/m3 to 0.14 ng/m3 at 4 rings or less). On the other hand, PAHs in the 10 nm particles were less than lower limit of quantification.

For other hydrocarbons by thermal desorption GC-MS analysis, hydrocarbons of C8-C24, organic acids of C8-C18 and esters of C17-C28 were detected in each particle size. However, we could identify no specific hydrocarbon compositions in the 10 nm particles. In addition, it was confirmed that the surface of each particle size was more likely to be covered with hydrocarbons (especially organic acids) by FT-IR analysis.

In conclusion, it was confirmed that there was not so much difference of chemical compositions between each particle size.

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TOYOTA MOTOR CORPORATION
KAZUMASA OKAMURA

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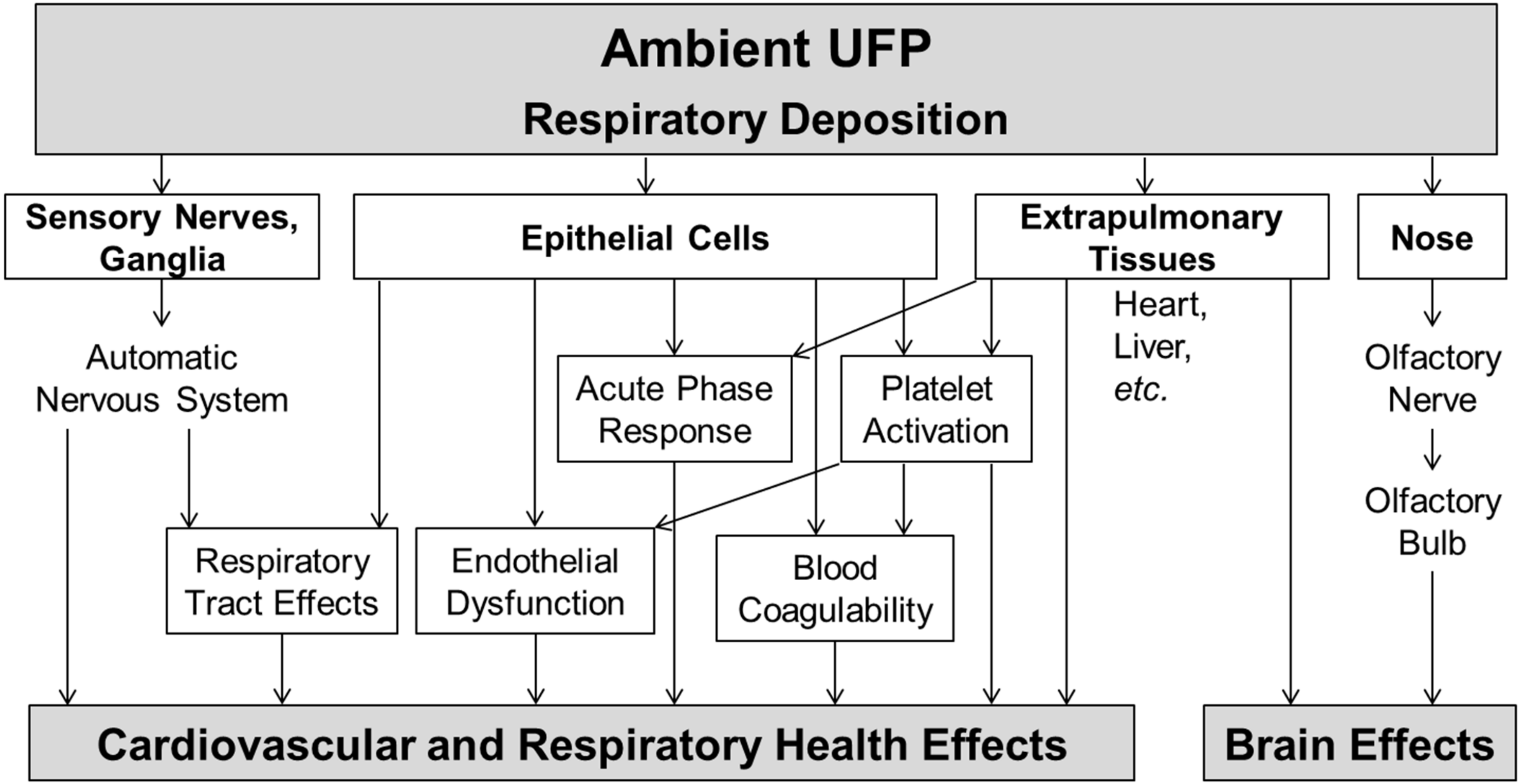
CONTENT

1. Background
2. Particle emissions from gasoline direct-injection vehicle
3. Chemical compositions of each particle size
4. Conclusion

Hypotheses for Health Effect of UFP

It is still uncertain that the health effect of ultra fine particles (UFP).



Reference: *HEI Perspectives 3* (2013)

Motivation

Is there the contribution of the nanoparticles exhausted from automobile to the health effect ?

Concern factor

- **Quantity**
  - **Number**
  - **Mass, Volume**
  - **Surface area**
- **Quality**
  - **Physically**
    - **Structure (Shape…)**
    - **State (Absorptive...)**
  - **Chemically**
    - **Component (Metal…)**
    - **Reactivity (Oxidative…)**

Objectives

To clarify the quantity and quality of the nanoparticles exhausted from automobile.

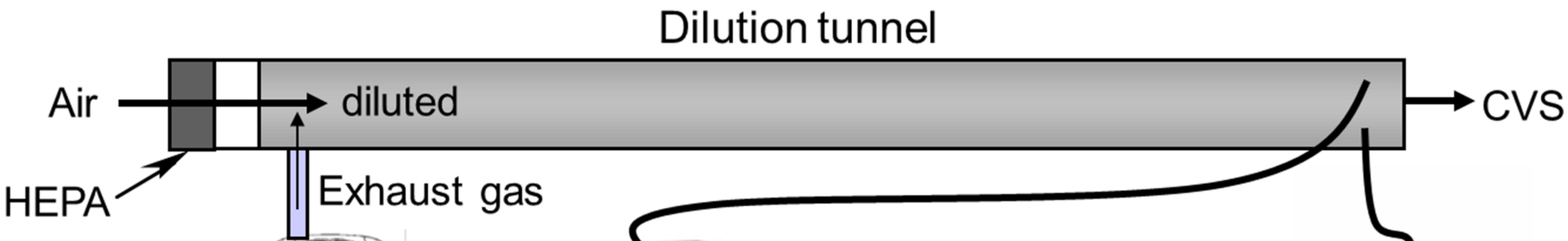
The following are investigated using the gasoline direct-injection (G-DI) vehicle.

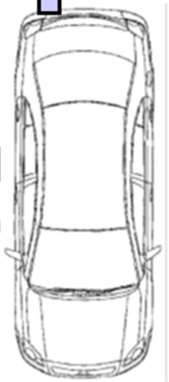
- Contribution of small nanoparticles* to each quantity of particle emission.
- Characterisation of chemical compositions in small nanoparticles.

*small nanoparticles; about 10-20 nm particles

Test Conditions

Several quantities of particle emission from G-DI vehicle are investigated.





- **G-DI engine**
  _4GR-FSE
  _2007 Model Year (Japan)
- **Driving**
  _NEDC
  (New European Driving Cycle)

EEPS@TSI
↓
Particle size distribution

MEXA-2000SPCS@HORIBA
↓
Transient emission

Particle number (PN) | **Surface area (PS)** | **Particle mass (PM)** | **PN**

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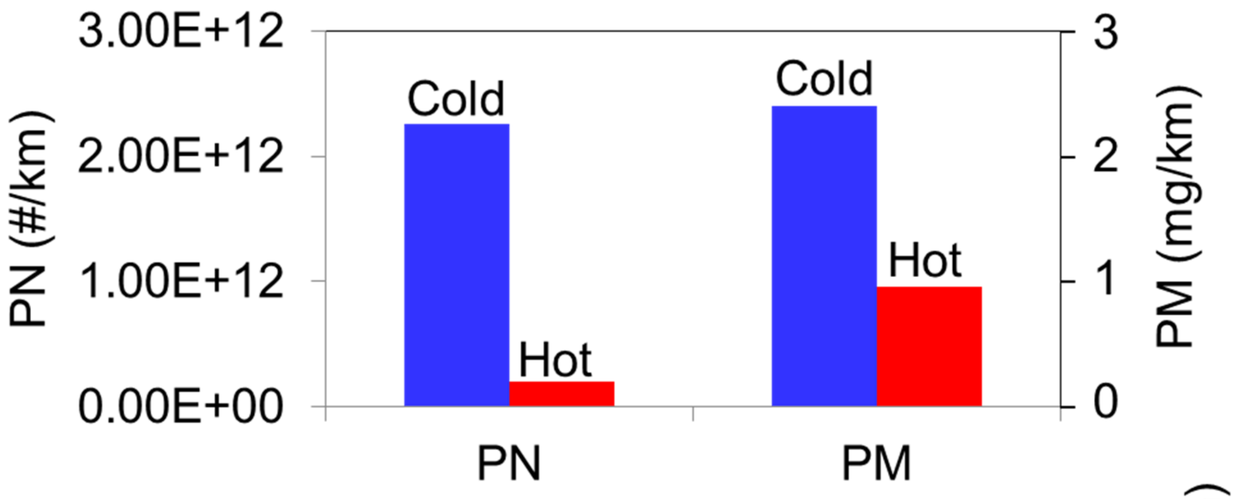
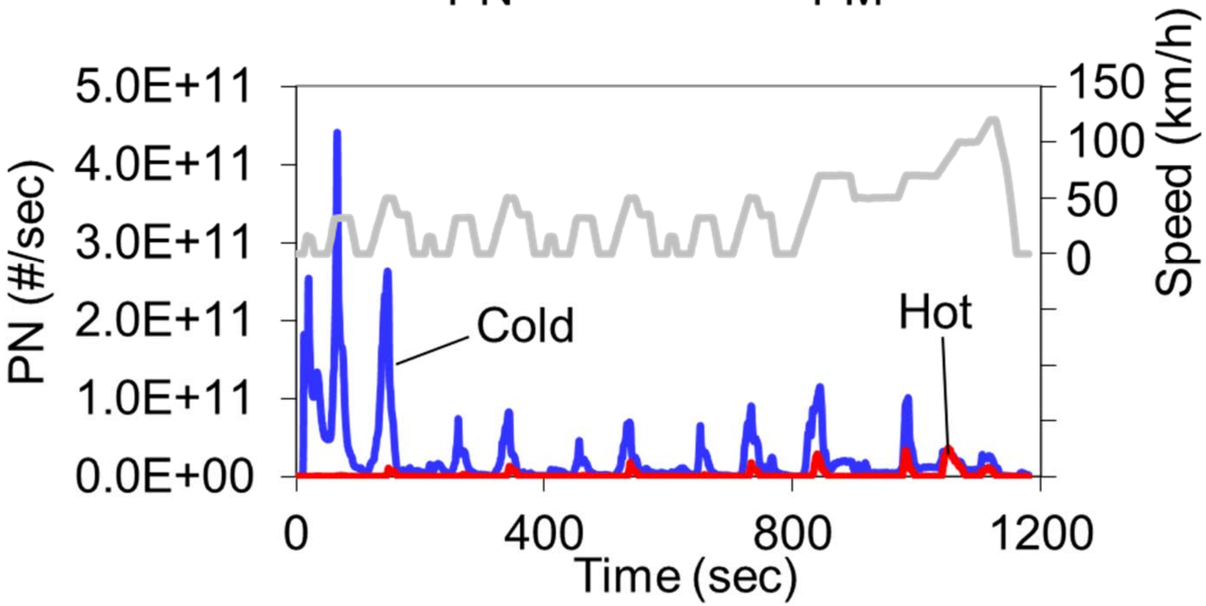
PN/PM Emission in Cold/Hot Start

There are few PN emissions in hot-start operation.





- **G-DI engine _4GR-FSE _07MY(JPN)**
- **Driving _NEDC**

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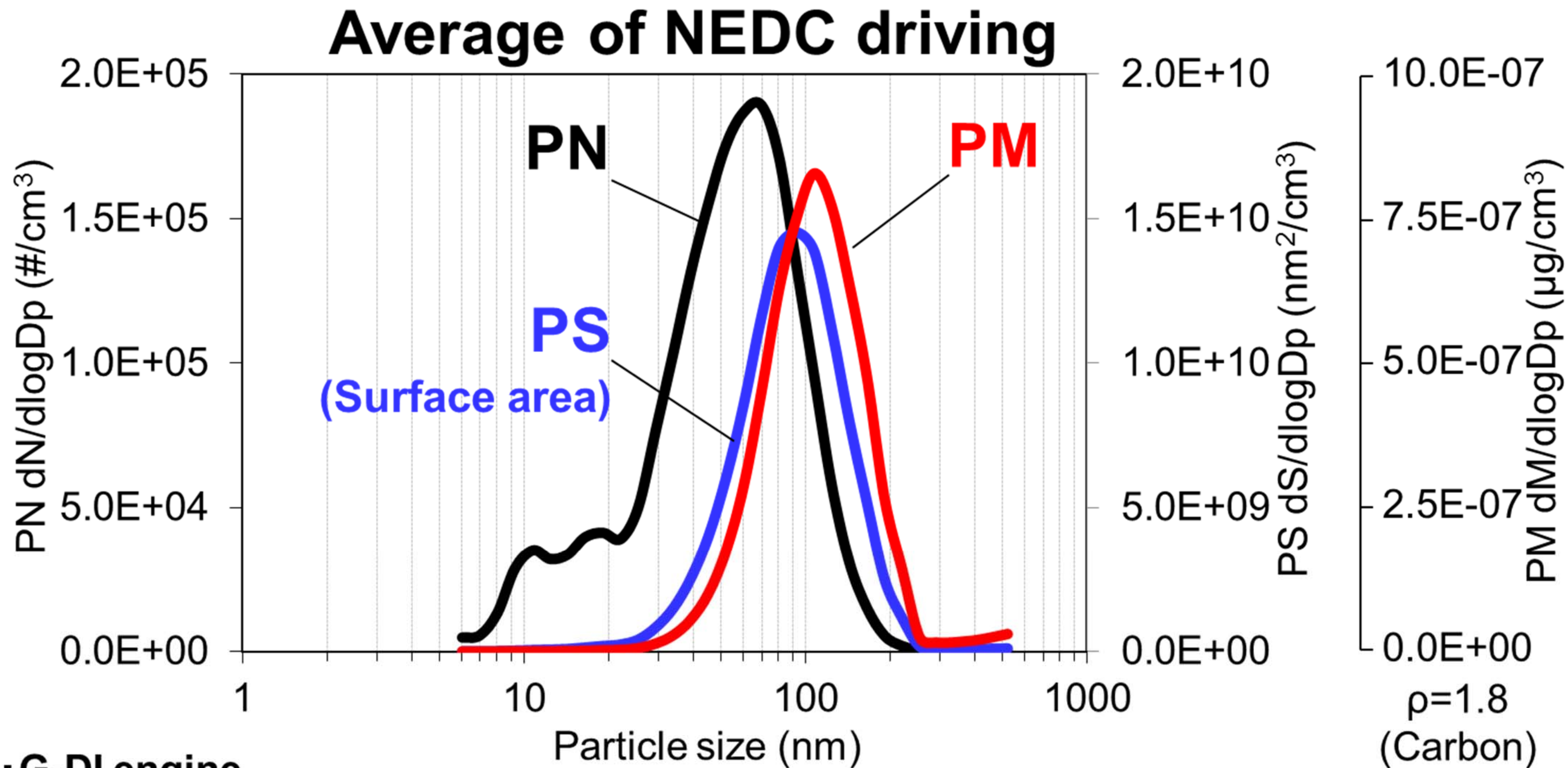
Size Distribution of PM/Surface Area

The peak diameter are shift to about 100 nm in PM and PS exhausted from a G-DI engine.



・G-DI engine
_4GR-FSE

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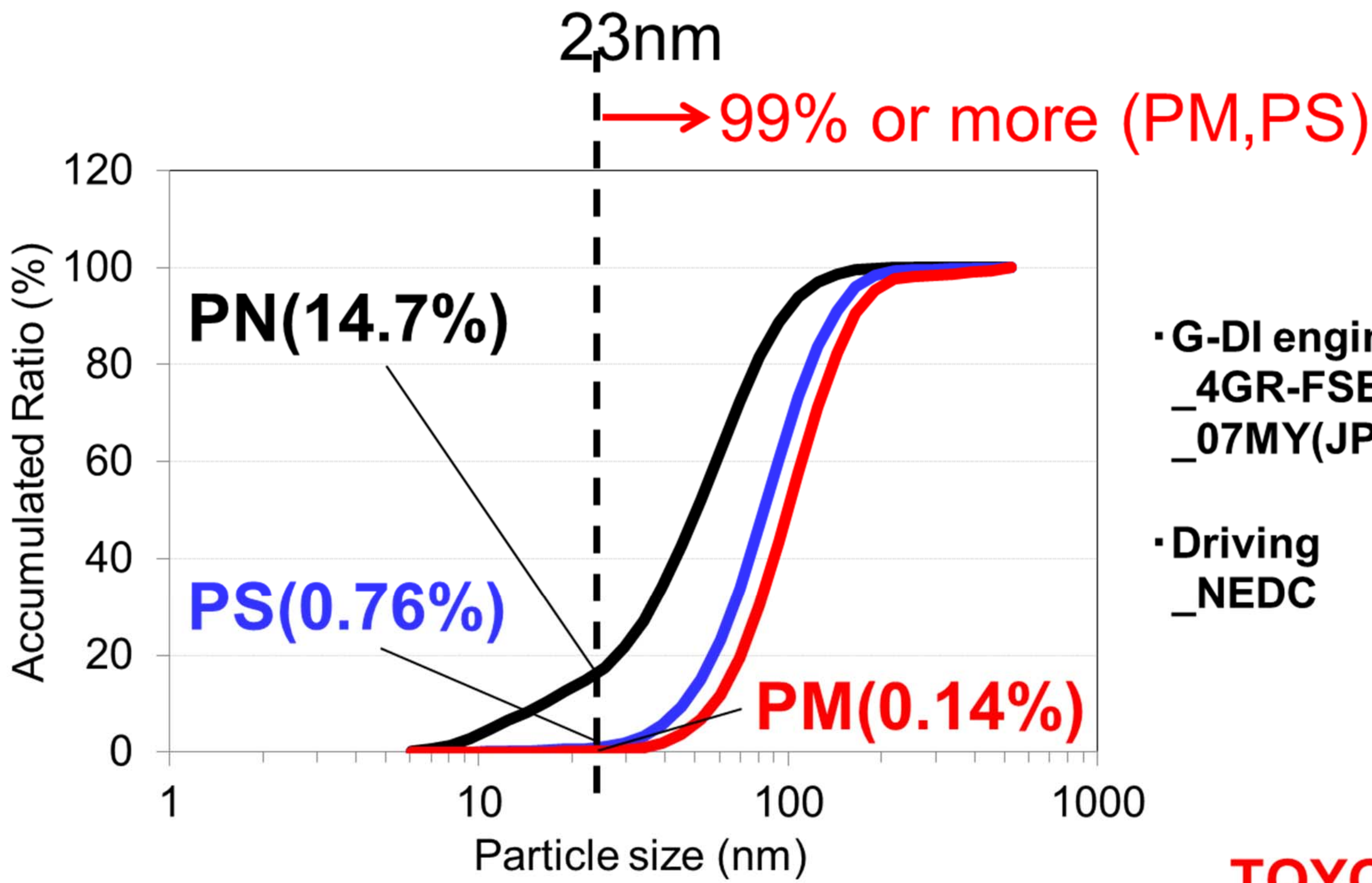
Accumulated Ratio of Each Quantity

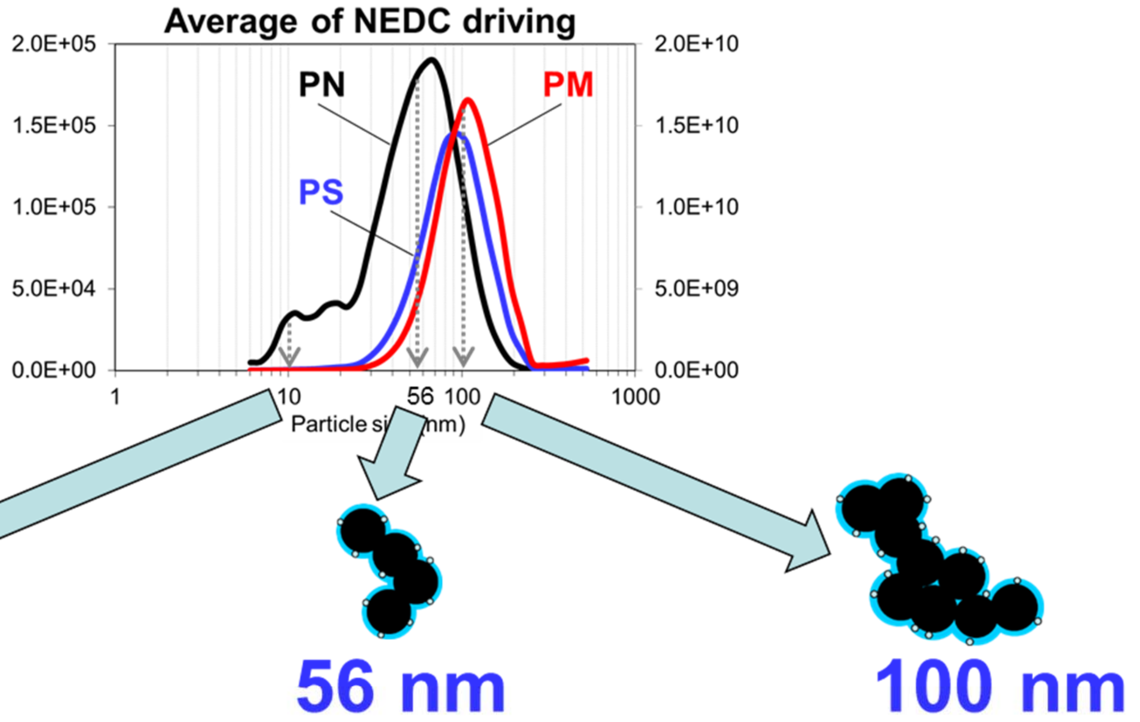
More than 99% of PM and PS are occupied in current PN regulation.



- G-DI engine _4GR-FSE _07MY(JPN)
- Driving _NEDC

Comparison of Chemical Compositions

To clarify the chemical compositions of 10 nm, 56 nm and 100 nm particles.



Main Target (Concerned chemical composition)

_**Metals**

_**Polycyclic aromatic hydrocarbons (PAHs)**

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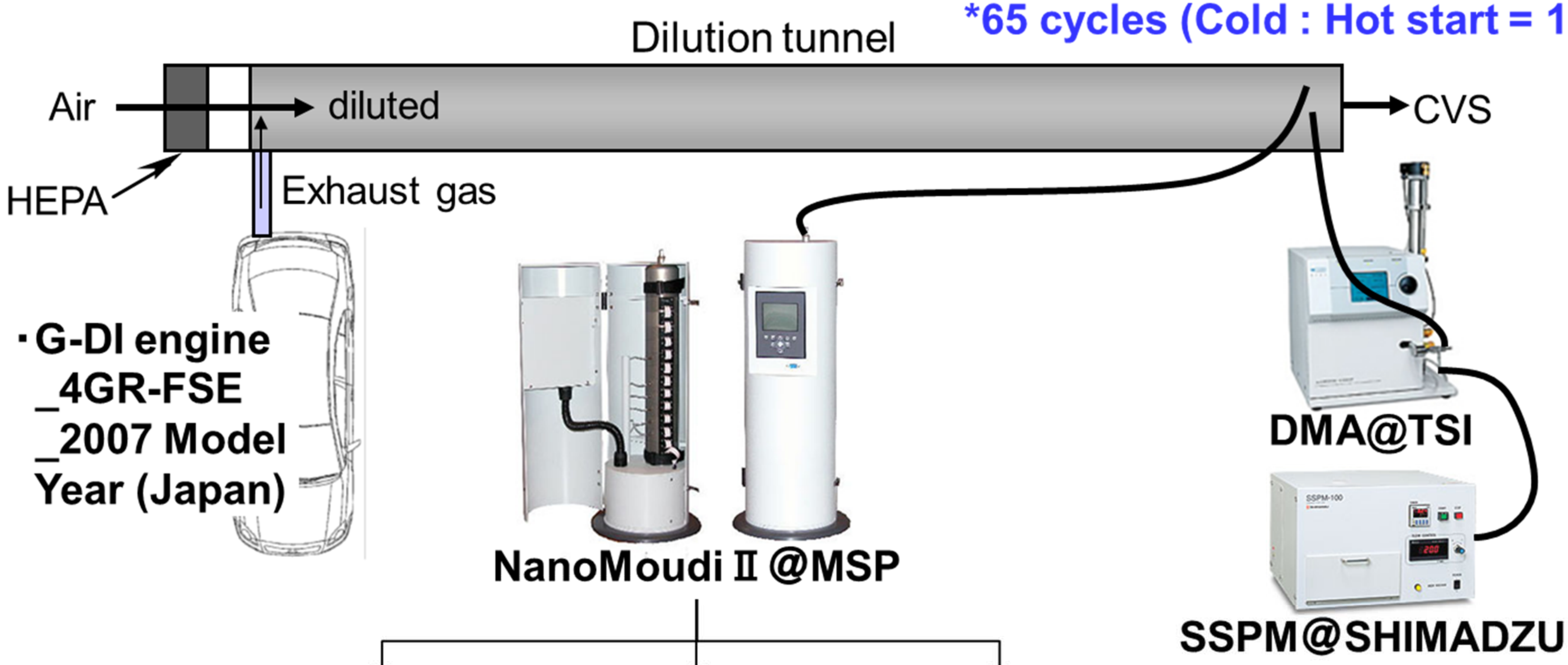
Test Conditions (2)

PM with cut-off at 10 nm, 56 nm and 100 nm are sampled by reiteration* of the NEDC driving.

*65 cycles (Cold : Hot start = 1 : 12)



Target	Metals	PAHs, Hydrocarbons(HC)	Sulfate	Property on PM surface
	↓	↓	↓	↓
Analyses	ICP-MS	GC-MS	Ion Chromato.	FT-IR

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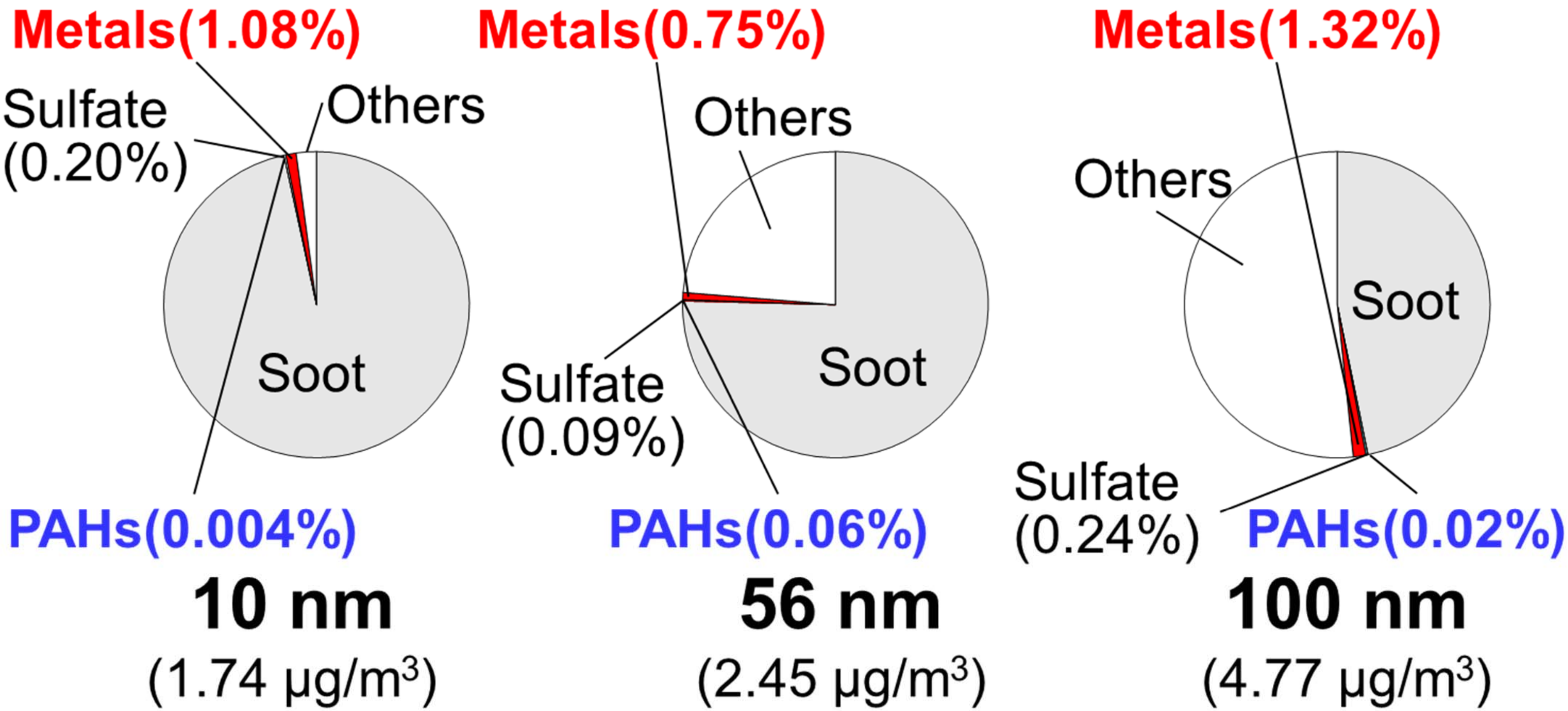
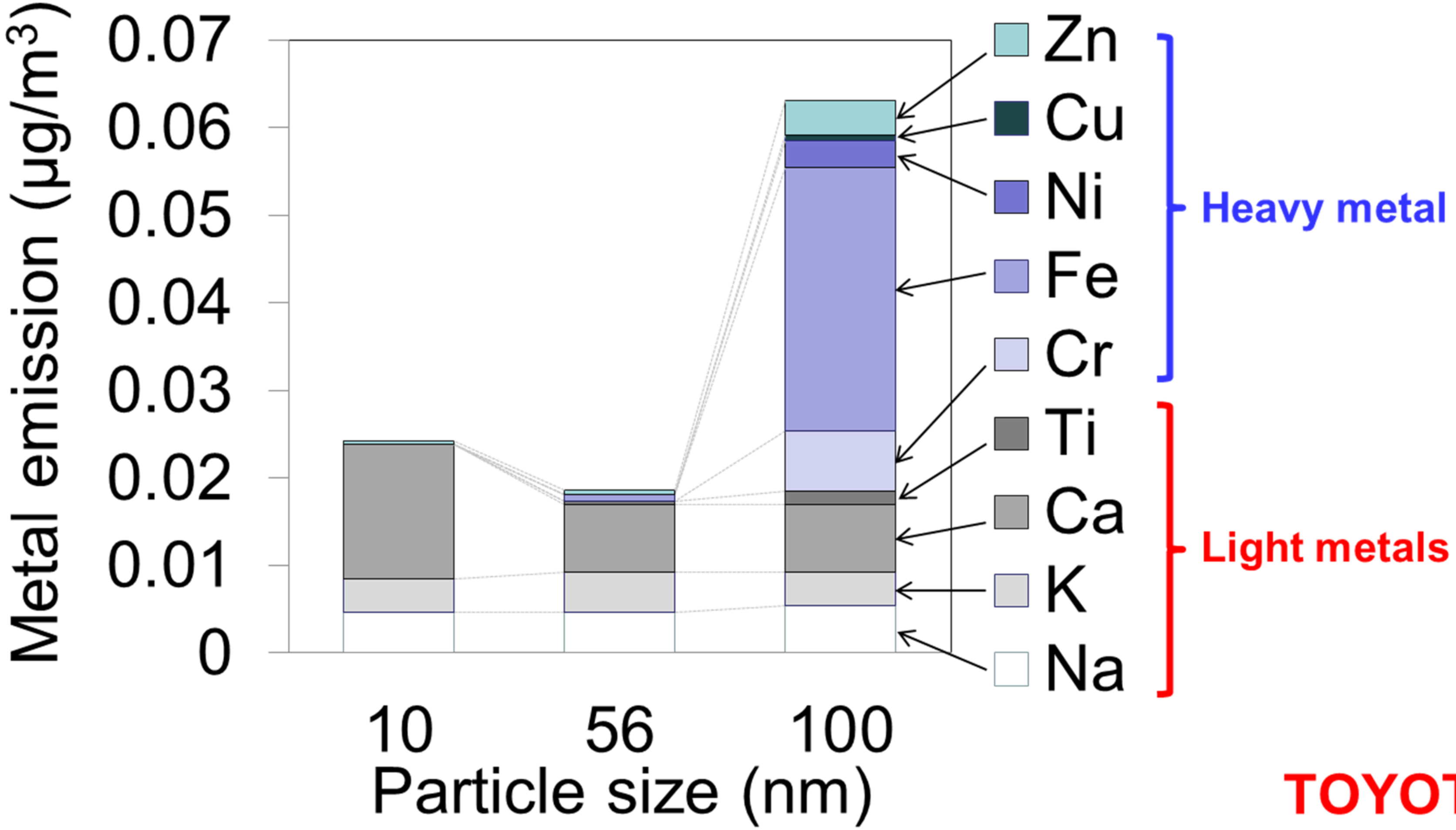
Ratio of Chemical Compositions

Metals and PAHs are less than 1.5% in each particle size.



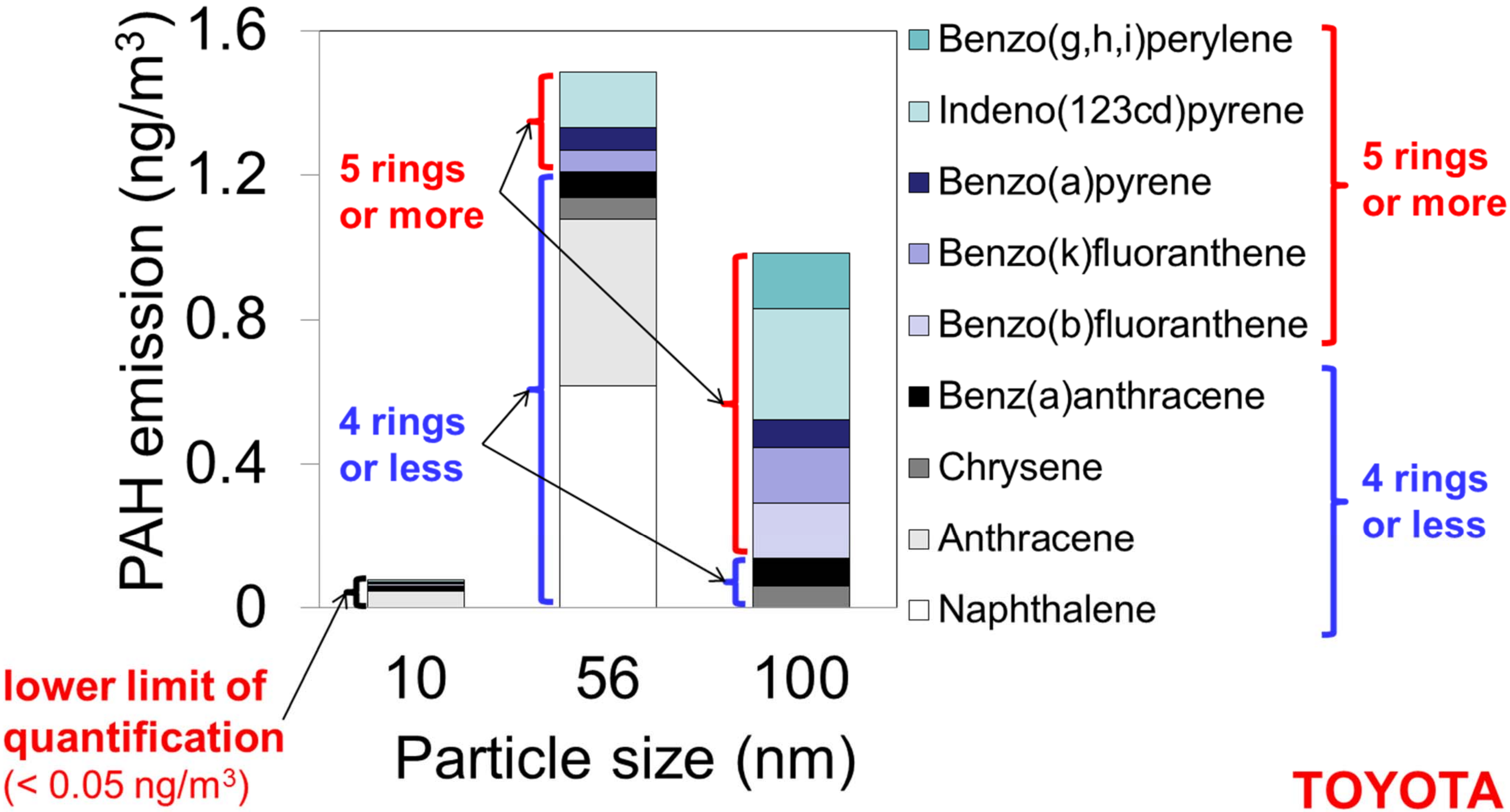
Metal Compositions

- No unique metal compositions in the 10 nm particles are detected.
- There are mainly light metals in the 10 nm particles.



Polycyclic Aromatic Hydrocarbons

Most of PAHs in the 10 nm particles are less than lower limit of quantification.



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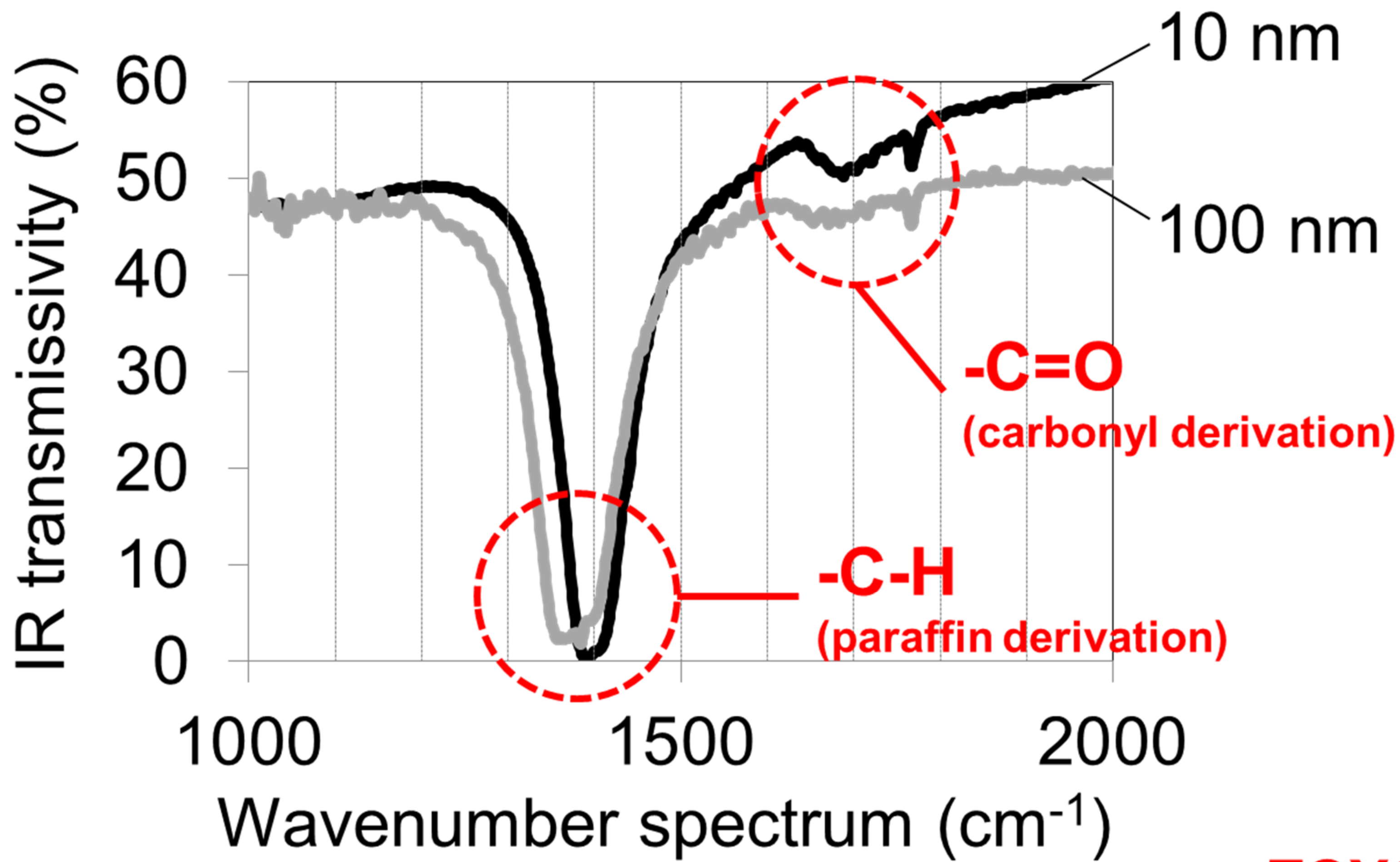
Property on PM Surface

There is not so much difference of surface property between the 10 nm and the 100 nm particles.



CONCLUSIONS

- There was a little contribution of the small (10 nm) particles to PM and Surface area.

- There was no unique chemical compositions in the 10 nm particles.

Future

- **Remaining concern factors are investigated.**
  _Physical Structure (Shape…)
  _Physical State (Adsorptivity...)
  _Chemical Reactivity (Oxidative potential…)

- **The chemical compositions of various engine PM are continuously investigated.**
  →There are some still problems in the sampling method of PM.
  ex.) A large amount of PM are necessary to control the effect of filter background.

Thank you for your attention