16. Farinotti, D., Huss, M., Bauder, A., Funk, M. and Truffer, M., A method to estimate ice volume and ice-thickness distribution of alpine glaciers. *J. Glaciol.*, 2009, **55**, 422–430.
17. Haeberli, W. and Hoelzole, M., Application of inventory data for estimating characteristics of regional climate-change effects on mountain glaciers: a pilot study with European Alps. *Ann. Glaciol.*, 1995, **21**, 206–212.
18. Hutchinson, M. F., ANUDEM version 5.3. User's guide, Australian National University Fenner School of Environment and Society, Canberra, Australia, 2011.
19. Linsbauer, A., Paul, F. and Haeberli, W., Modeling glacier thickness distribution and bed topography over entire mountain ranges with GlabTop: application of a fast and robust approach. *J. Geophys. Res.*, 2012, **117**, F03007.
20. Fischer, A., Calculation of glacier volume from sparse ice-thickness data, applied to Schaufelferner, Austria. *J. Glaciol.*, 2009, **55**, 453–460.
21. Lee, D., Storey, J., Choate, M. and Hayes, R., Four years of Landsat-7 on-orbit geometric calibration and performance. *IEEE Trans Geosci. Remote Sensing*, 2004, **42**, 2786–2795.
22. Leprince, S., Barbot, S., Ayoub, F. and Avouac, J. P., Automatic and precise orthorectification, coregistration, and subpixel correlation of satellite images, application to ground deformation measurements. *IEEE Trans. Geosci. Remote Sensing*, 2007, **45**, 1529–1558.
23. Fujita, K., Suzuki, R., Nuimura, T. and Sakai, A., Performance of ASTER and SRTM DEMs and their potential for assessing glacial lakes in the Lunand region, Bhutan Himalaya. *J. Glaciol.*, 2008, **54**, 220–228.
24. Nye, J. F., The flow of a glacier in a channel of rectangular, elliptic or parabolic cross-section. *J. Glaciol.*, 1965, **5**(41), 661–690.
25. Kulkarni, A. V., Dhar, S., Rathore, B. P., Raj, B. and Kalia, R., Recession of Samudra Tapu Glacier, Chandra River Basin, Himachal Pradesh. *J. Indian Soc. Remote Sensing*, 2006, **34**(2), 39–46.

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Characterization of hazardous solid waste (soot) accumulated in tailpipe of typical Indian share autos

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In this communication, accumulated soot from typical Indian share autos and buses has been characterized using FE-SEM coupled with EDS and FTIR spectroscopy for its toxicity level. Analysis reveals the size of spherical-shaped primary particles to be less than 40 nm, which agglomerate to form fractal-like structures. In share autos, average weight percentage of heavy metals such as Cr, Fe, Cu and Pt (except Zn) is higher than that in buses; trace elements include non-carbon elements. FTIR results suggest that share autos contaminate soil of paved and unpaved roadways to a greater extent and at a faster rate compared to buses.

Keywords: Heavy metals, road soil contamination, share auto, soot particles, vehicular solid waste.

In developing countries, providing access to cheaper public road transport is a deciding factor for percentage share of vehicle types. Due to this reason share autos are now the leading public transport mode along with buses. This has resulted in exponential increase in their numbers over the past decade. Therefore, changes in the percentage share of vehicles plying on urban roads affect traffic and emission characteristics such as average traffic fleet speed, delay due to congestion and fuel consumption[1]. Share autos running with more than allotted capacity consume more fuel resulting in higher emissions[2–4]. Inadequate maintenance of vehicles enhances emission from them[5–9]. Besides, lack of controlling devices like catalytic converters and filters makes them even larger emitters of pollutants, especially soot particles. Therefore, it is important to study the chemical composition of soot particles emitted from share autos to understand their health and environmental impacts.

Several researchers have studied the chemical constituents of vehicular soot particles for their toxicity or carcinogenicity[10–13], and health impacts of emissions from diesel-driven vehicles on school-going children, adult commuters, drivers and passengers[14–17]. However, there is a limited number of publications discussing the composition of condensed soot particles which accumulate on the inner surface of the tailpipe of share autos. A small fraction of the volatile or semi-volatile content of the exhaust could subsequently undergo gas-to-particle conversion once it gets cooled to form the accumulated particles on the surface of the tailpipe[18,19]. Upon saturation, accumulated coarser soot particles are prone to desorption while subjected to external forces such as velocity and temperature of exhaust gas and mechanical disturbances caused due to vehicular speed. Owing to larger size and weight, desorbed soot containing polyaromatic hydrocarbons (PAHs) deposits around nearby areas, i.e. road soil[20]. These contaminated soils can pose a threat to human beings by virtue of re-suspension generated by moving vehicles.

The emission of soot particles is a result of incomplete combustion of fuel in the engines. Diesel particulate emissions consist of carbonaceous material, generally 75% elemental carbon (EC) known as 'soot' and 20% organic carbon (OC)[21]. The elemental fractions are generated from diesel fuel droplet during pyrolysis, whereas

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the organic part has been reported to come from unburned diesel fuel, lubricating oil and combustion by-products[22]. The soot particles can condense quickly on different surfaces of graphite rods, quartz tubes, ceramic tubes, fire bricks and materials of Fe, Co and Ni[23]. A fraction of total particulates consists of metal oxides, heavy metals, PAHs and trace elements originating from incomplete diesel combustion, lubricating oils and engine material due to engine-wearing process[24–27].

Primary soot generated in the engines has been observed to increase in size along the exhaust path[28]. The other gaseous pollutants released in exhaust gas such as metals, organic components and trace elements have been reported to be adsorbed on soot[26,29,30]. The precise evaluation of the shape of diesel soot is difficult because of its composite morphology; yet many researchers have succeeded in doing so[29,31–36]. Depending on the location of their formation, the primary particles formed in the engines or tailpipes were differentiated from the secondary particles formed in the atmosphere after emission from the tailpipe[26].

To evaluate significant impact of share autos on the environment and to study the threat to health of the drivers and passengers, determination of characteristics of the accumulated soot in them is of utmost importance. This communication aims to examine the characteristics of toxic solid waste or accumulated soot in share autos. Characteristic features of soot in share autos need to be studied for their management and control.

Figure 1 shows the selection criteria for sample collection and instrumentation used for the characterization.

Collection of accumulated soot using scarp method from vehicles

Share autos
Buses

↓

Soot sample with respect to vehicle type and age

Auto (<1 yr): SA_1	Bus (<1 yr): B_1
Auto (1–5 yrs): $SA_{1–5}$	Bus (1–5 yrs): $B_{1–5}$
Auto (5–10 yrs): $SA_{5–10}$	Bus (5–10 yrs): $B_{5–10}$

↓

Physical and chemical characterization

Instrumentation	Outcome
SEM	Size and shape
EDS	Elemental composition
FTIR	Presence of functional group

Figure 1. Methodology which includes collection of accumulated soot from different share autos and buses with respect to their age and outcomes of the instruments used for characterization.

Accumulated soot particles were collected from the inner surface of the tailpipe of the vehicles and were considered to have similar characteristics as that those emitted into the atmosphere. Soot particles were collected by scrap using nickel spatula and were dried in hot-air oven at 80°C for 1 h. The collected samples were marked on the basis of vehicle type and age of the vehicle.

Soot particles were prepared for analysing them under field emission scanning electron microscope (FE-SEM) coupled with energy dispersive X-ray spectroscope (EDS) for the estimation of their morphology and elemental composition. Morphological and elemental analyses have been performed with high-resolution digital FE-SEM (SUPERA 55, ZEISS, Germany). The EDS was coupled with a circular high-performance in-lens SE detector. The acceleration voltage used in the study was 5.0 keV. Soot particles were coated with a conductive film of platinum (Pt), using an ion sputter coater. Fourier transform infrared (FTIR) spectroscope was used for analysis of functional groups present in the sample of accumulated soot. FTIR spectroscopy (Frontier™ IR systems) has been used to characterize the functional group composition of potassium bromide (KBr) pellets of accumulated soot samples. FTIR analysis measures the range of wavelengths in the infrared (IR) that are absorbed by a material and hence the presence of functional group. Outputs of the characterization of soot particles will be further used to study the management and control of in-engine emissions by share autos to regulate soil and air quality in urban roadways.

The microscopic images of soot particles (Figure 2) reveal the similarity in both types of vehicle mode in terms of their morphological features. The primary soot particles were found to be spherical in shape and having the tendency to agglomerate to form open, branched and fractal-like structures and finally get accumulated on the tailpipes. The size of the individual particles was found to be less than 40 nm making them dangerous when inhaled, as they can reach deep inside the respiratory tract and get incorporated into the blood stream causing further damage to other viscera.

Figure 3 shows spectra of average elemental composition in wt% for carbon (C) and non-carbonaceous elements. Soot particles are highly carbonaceous in nature; buses were found to have an average of 14.5% more C in comparison to share autos. The age of vehicles also had a slight impact on wt% of C. The different combustion conditions and engine capacity of share autos resulted in higher percentage of non-carbonaceous elements compared to buses. Among the non-carbonaceous elements, Na, Mg and K were mostly absent in case of buses due to lack of use of lubricating oils. The average wt% of heavy metals (Fe, Cu, Zn, Pt and Cr) in share autos was observed to be 9.4 against 4.8 for buses. This suggests exhaust gas in share autos contains more wearing of engine moving parts than buses. Except Zn, other heavy

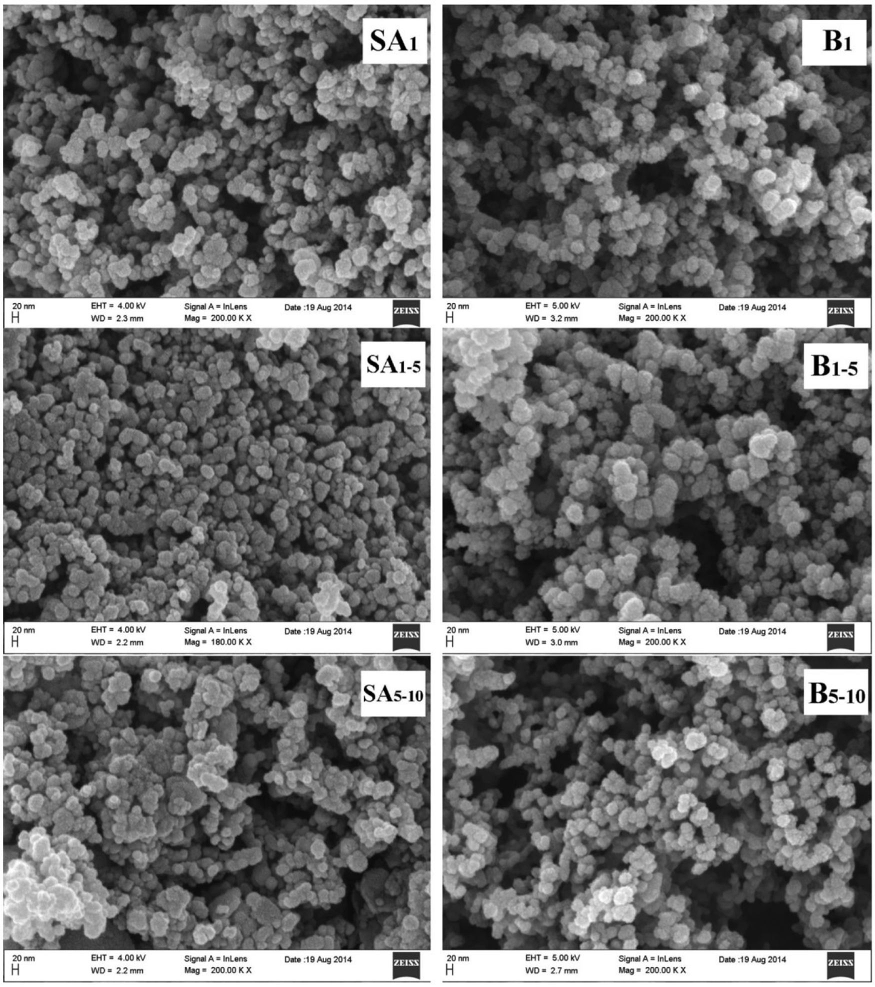

Figure 2. Scanning electron photomicrographs of soot deposited on the inner surface of the tailpipe of share autos (SA_1, $SA_{1–5}$ and $SA_{5–10}$) and buses (B_1, $B_{1–5}$ and $B_{5–10}$).

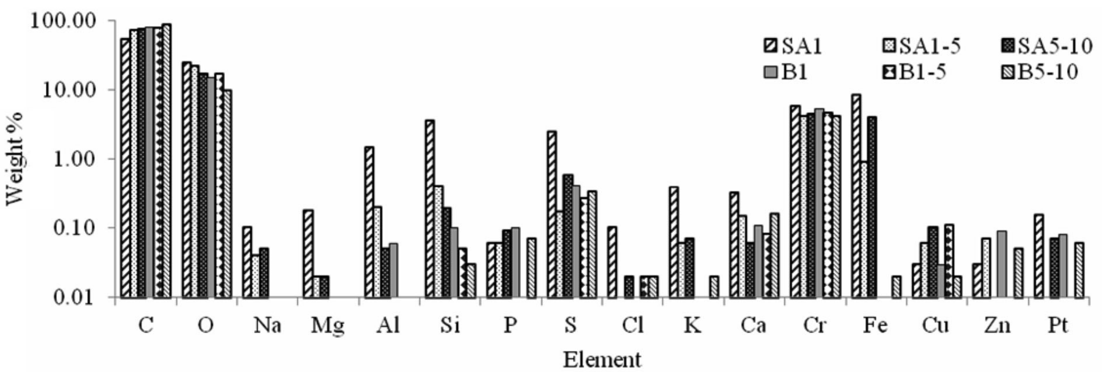

Figure 3. Graphical representation of elemental composition of accumulated soot in the tailpipe of share autos (SA_1, $SA_{1–5}$ and $SA_{5–10}$) and buses (B_1, $B_{1–5}$ and $B_{5–10}$) obtained by energy-dispersive X-ray spectroscopy.

metals were observed to be higher in case of share autos. The reason for higher average wt% of Zn in buses is the higher amount of tyre wear in comparison to share autos due to larger dimension and higher pressure being applied on the tyres. Average wt% of Si in share autos was much higher (>20 fold) compared to buses. The increased Si contamination in soot is due to the lower height of the tailpipes in share autos. It might have originated from the re-suspended dust settled inside the tailpipes of share autos. Most of the non-carbonaceous elements from soot

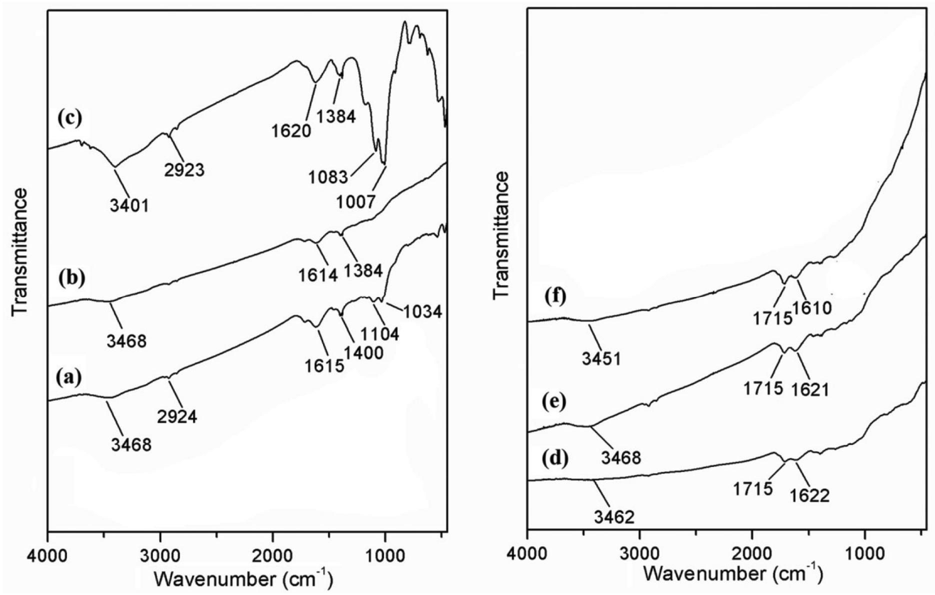

Figure 4. FTIR spectra of collected soot in share autos (*a*–*c*) and buses (*d*–*f*) depicting the presence of functional groups in the respective vehicle type.

of share autos are due to use of lubrication oil, engine wear-out and entering of re-suspended dust back into the lower tailpipes.

Analyses of FTIR spectra (Figure 4) of soot in shared autos revealed that most of peaks are at similar positions as in buses. However, the peaks are sharper in share autos, suggesting the presence of functional groups in higher quantity than in buses. Spectra also confirm soot particles are composed of incomplete combustion and combustion by-products of hydrocarbon fuel with some unburned part as well. The assigning of different frequencies to their functional groups was approved by comparison with those reported by different authors[37–39]. Peaks observed between band position range 3400–3500 cm^{-1} correspond to N–H group stretching vibration. Peak at 2920 ± 10 cm^{-1} is attributed to CH_2 asymmetric stretching vibration. The presence of C–H stretching in aliphatic groups suggests methyl, methylene and methane groups bonded to aromatic rings. The IR spectrum also reveals other characteristic signals in the region 1700–1000 cm^{-1}, where the most important one corresponds to C=O stretching of carboxylic acids. C=C stretching of aromatic or alkene groups and aliphatic C–H plane deformation of CH_2/CH_3 groups were found between 1550 and 1380 cm^{-1}. Stretching frequency –C–O–C– is observed between 1000 and 1100 cm^{-1}. Broadening in the region 1000–1300 cm^{-1} in share autos is observed in the spectrum where aromatic C–C and C–H plane deformation structures appear.

The physical and chemical characterization of soot emitted by typical Indian share autos consists of hazardous constituents such as heavy metals, organic groups and carcinogens. Share autos discharge significant amount of soot to nearby road soil, which in turn can pose a threat to human beings and the environment. The share autos emit a higher percentage of non-carbonaceous elements compared to buses. Most of the non-carbonaceous elements from soot particles of share autos are due to the use of lubrication oil, engine wear-out and entering of re-suspended dust back into the lower tailpipes. Among the non-carbonaceous elements, Na, Mg and K are mostly absent in the case of buses due to variation in use of lubricating oils. The study suggests that exhaust gas in share autos contains more wearing of engine moving parts than buses. The average wt% of Zn in buses is due to higher amount of tyre wear in comparison to share autos, which is due to the larger dimension and higher pressure being applied on the tyres. Average wt% of Si in share autos is much higher (>20 fold) compared to buses. Thus the Indian share autos contribute more to soil contamination in comparison to buses. Further research is needed for detailed information on the quantitative analysis of soot accumulation in the tailpipes of share autos. Detailed study is also necessary on the adsorption of soot particles on the tailpipe metal surfaces and discharge mechanism to nearby soil, their fate and impact on human health.

1. Pandian, S., Gokhale, S. and Ghoshal, A. K., Evaluating effects of traffic and vehicle characteristics on vehicular emissions near traffic intersections. *Transport. Res. D*, 2009, **14**, 180–196.
2. Wenzel, T., Singer, B. C. and Slott, R. S., Some issues in the statistical analysis of vehicle emissions. *J. Transport. Stat.*, 2000, **3**, 31–14.
3. Virtanen, A. K. K., Ristimaki, J. M., Vaaraslahti, K. M. and Keskinen, J., Effect of engine load on diesel soot particles. *Environ. Sci. Technol.*, 2004, **38**, 2551–2556.
4. Frey, H. C., Rouphail, N. M., Zhai, H., Farias, T. L. and Gonçalves, G. A., Modeling and comparing real world fuel consumption for

diesel- and hydrogen-fueled transit buses and implication for emissions. *Transport. Res. D*, 2007, **12**, 281–291.
5. Lawson, D. R., Groblicki, P. J., Stedman, D. H., Bishop, G. A. and Guenther, P. L., Emissions from in-use motor vehicles in Los Angeles: a pilot study of remote sensing and the inspection and maintenance program. *J. Air Waste Manage. Assoc.*, 1990, **40**, 1096–1105.
6. Stedman, D. H., Bishop, G. A., Peterson, J. E., Guenther, P. L., McVey, I. F. and Beaton, S. P., On-road carbon monoxide and hydrocarbon remote sensing in the Chicago area. Final Report to Illinois Department of Energy and Natural Resources, Report ILENR/RE-AQ 91/14, ENR Clearing House, Springfield, IL, USA, 1991.
7. Stedman, D. H., Bishop, G. A., Beaton, S. P., Peterson, J. E., Guenther, P. L., McVey, I. F. and Zhang, Y., On-road remote sensing of CO and HC emissions in California, Final Report to California Air Resources Board, Contract No. A032-093, California Environmental Protection Agency, Air Resources Board, Research Division, Sacramento, CA, USA, 1994.
8. Bishop, G. A., Stedman, D. H., Peterson, J. E., Hosick, T. J. and Guenther, P. L., A cost-effectiveness study of carbon monoxide emissions reduction utilizing remote sensing. *J. Air Waste Manage. Assoc.*, 1993, **43**, 978–988.
9. Zhang, Y., Stedman, D. H., Bishop, G. A., Beaton, S. P. and Guenther, P. L., On-road evaluation of inspection/maintenance effectiveness. *Environ. Sci. Technol.*, 1996, **30**, 1445–1450.
10. Lawley, P. D., Mutagens as carcinogens: developments of current concepts. 1989, **213**, 3–25.
11. Boffetta, P., Dosemeci, M., Gridley, G., Bath, H., Moradi, T. and Silverman, D., Occupational exposure to diesel engine emissions and risk of cancer in Swedish men and women. *Cancer Causes & Control*, 2001, **12**, 365–374.
12. Lai, C. H. *et al.*, Exposure to traffic exhausts and oxidative DNA damage. *Occup. Environ. Med.*, 2005, **62**, 216–222.
13. Jung, K. H. *et al.*, Molecular signature for early detection and prediction of polycyclic aromatic hydrocarbons in peripheral blood. *Environ. Sci. Technol.*, 2011, **45**(1), 300–306; doi:10.1021/es101840s.
14. HEI. Diesel emissions and lung cancer: epidemiology and quantitative risk assessment. A special report of the Institute's Diesel Epidemiology Expert Panel, Health Effects Institute, Cambridge, MA, USA, 1999.
15. Zhang, K. M., Wexler, A. S., Zhu, Y. F., Hinds, W. C. and Sioutas, C., Evolution of particle number distribution near roadways. Part II. The 'road-to-ambient' process. *Atmos. Environ.*, 2004, **38**, 6655–6665.
16. Marshall, J. D. and Behrentz, E., Vehicle self-pollution intake fraction: Children's exposure to school bus emissions. *Environ. Sci. Technol.*, 2005, **39**, 2559–2563.
17. Maricq, M, M., Chemical characterization of particulate emissions from diesel engines: a review. *J. Aerosol Sci.*, 2007, **38**, 1079–1118.
18. Kittelson, D. B. *et al.*, On-road evaluation of two diesel exhaust after treatment devices. *J. Aerosol Sci.*, 2006, **37**, 1140–1151.
19. Matter, U., Siegmann, H. C., Kasper, M. and Burtscher, H., Distinction of volatile particles in exhaust of diesel engines with particulate traps. *J. Aerosol Sci.*, 1999, **30**, 471–472.
20. Liu, S., Xia, X., Zhai, Y., Wang, R., Liu, T. and Zhang, S., Black carbon (BC) in urban and surrounding rural soils of Beijing, China, spatial distribution and relationship with polycyclic aromatic hydrocarbons (PAHs). *Chemosphere*, 2011, **82**, 223–228.
21. Messerer, A., Niessner, R. and Pöschl, U., Comprehensive kinetic characterization of the oxidation and gasification of model and real diesel soot by nitrogen oxides and oxygen under engine exhaust conditions: measurement, Langmuir–Hinshelwood, and Arrhenius parameters. *Carbon*, 2006, **44**, 307–324.
22. Shah, S. D., Cocker, D. R., Miller, J. W. and Norbeck, J. M., Emission rates of particulate matter and elemental and organic carbon from in-use diesel engines. *Environ. Sci. Technol.*, 2004, **38**, 2544–2550.
23. Kumar, M., Kichambare, P. D., Sharon, M., Ando, Y. and Zhao, X., Synthesis of conducting fibres nanotubes and thin films of carbon from commercial kerosene. *Mater. Res. Bull.*, 1999, **34**(5), 791–801.
24. Lyonsm, J. and Johnston, H., Aromatic hydrocarbons from vehicular exhausts. *Br. J. Cancer*, 1956, **11**, 60–66.
25. Ludema, K. C., *Friction, Wear, Lubrication, A Textbook in Tribology*, CRC Press, Boca Raton, Florida, USA, 1996, pp. 124–134.
26. Morawska, L., Ristovski, Z., Jayaratne, E. R., Keogh, D. U. and Ling, X., Ambient nano and ultrafine particles from motor vehicle emissions: characteristics, ambient processing and implications on human exposure. *Atmos. Environ.*, 2008, **42**, 8113–8138.
27. Cao, W., Dong, G., Chen, W., Wu, J. and Xie, Y. B., Multisensor information integration for online wear condition monitoring of diesel engines. *Tribol. Int.*, 2015, **82**, 68–77.
28. Liati, A., Eggenschwiler, P. D., Schreiber, D., Zelenay, V. and Ammann, M., Variations in diesel soot reactivity along the exhaust after-treatment system, based on the morphology and nanostructure of primary soot particles. *Combust. Flame*, 2013, **160**, 671–681.
29. Kleeman, M. J., Schauer, J. J. and Cass, G. R., Size and composition distribution of fine particulate matter emitted from motor vehicles. *Environ. Sci. Technol.*, 2000, **34**, 1132–1142.
30. Burtscher, H., Physical characterization of particulate emissions from diesel engines: a review. *J. Aerosol Sci.*, 2005, **36**, 896–932.
31. Morawska, L., Bofinger, N. D., Kocis, L. and Nwankwoala, A., Submicrometer and supermicrometer particles from diesel vehicle emissions. *Environ. Sci. Technol.*, 1998, **32**, 2033–2042.
32. Ristovski, Z. D., Morawska, L., Bofinger, N. D. and Hitchins, J., Submicrometer and supermicrometer particulate emission from spark ignition vehicles. *Environ. Sci. Technol.*, 1998, **32**, 3845–3852.
33. Chakrabarty, R. K. *et al.*, Emissions from the laboratory combustion of wildland fuels: particle morphology and size. *J. Geophys. Res.*, 2006, **111**, D07204.
34. Huang, X. F., Yu, J. Z., He, L. Y. and Hu, M., Size distribution characteristics of elemental carbon emitted from Chinese vehicles: Results of a tunnel study and atmospheric implications. *Environ. Sci. Technol.*, 2006, **40**, 5355–5360.
35. Harris, S. J. and Maricq, M. M., Signature size distributions for diesel and gasoline engine exhaust particulate matter. *J. Aerosol Sci.*, 2001, **32**, 749–764.
36. Mathis, U., Mohr, M., Kaegi, R., Bertola, A. and Boulouchos, K., Influence of diesel engine combustion parameters on primary soot particle diameter. *Environ. Sci. Technol.*, 2005, **39**, 1887–1892.
37. Santamaria, A., Mondragon, F., Molina, A., Marsh, N. D., Eddings, E. G. and Sarofim, A. F., Characterization of the products of an ethylene inverse diffusion flame. *Combust. Flame*, 2006, **146**, 52–62.
38. Santamaria, A., Yang, N., Mondragon, F. and Eddings, E. G., Chemical and morphological characterization of the soot produced in an inverse diffusion flame with aromatic and aliphatic fuels. *Combust. Flame*, 2010, **157**, 33–42.
39. Manoj, B., Sreelakshmi, S., Mohan, A. N. and Kunjomana, A. G., Characterization of diesel soot from the combustion in engine by X-ray and spectroscopic techniques. *Int. J. Electrochem. Sci.*, 2012, **7**, 3215–3221.

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