Physio-Chemical Analysis of Airborne Tire Wear Particles

Julie Panko[1], Britt L. McAtee[1], Marisa Kreider[1], Mats Gustafsson[2], Göran Blomqvist[2], Anders Gudmundsson[3], Len Sweet[1], Brent Finley[4]

1 ChemRisk, Pittsburgh, PA; 2 VTI, Linköping, Sweden; 3 Lund University, Lund,Sweden; 4 ChemRisk, San Francisco, CA

ABSTRACT

Respirable particulate matter (PM_{10}) has been associated with human morbidity/mortality. Tire wear particles (TWP), produced from the interaction of pavement and tire surface, are thought to contribute to PM_{10}; however, airborne TWP has not been well characterized. In order to characterize environmentally relevant TWP, PM_{10} samples were collected while running vehicle tires on a roadway simulator. The generation of PM_{10} was quantified with an Aerodynamic Particle Sizer (APS; 0.5 to 10 µm) and a Scanning Mobility Particle Sizer (SMPS; 8 to 311 nm). Elemental analysis (Particle Induced X-ray Emission: PIXE) and particle morphology (scanning electron microscopy) were also examined. APS and SMPS data show concentrations of particles generated was low, seldom greater than 10 to 20 µg/m³. APS data indicated a bimodal distribution of the mass of particles, with peaks around 1 µm and between 5-8 µm. The SMPS data identified a peak in the number of particles generated between 10-100 nm. PIXE analysis revealed that the coarse fraction of airborne particulate was dominated by pavement. Sulfur and zinc were both identified by PIXE. Sulfur is found in tires and bitumen, while zinc likely originates from the tires as zinc oxide is used as an activator for tire rubber vulcanization. While the ultrafine portion (<100 nm) of the PM_{10} generated from tires represents only a very small portion of the total mass of the PM_{10}, this size fraction does contain material originating from the tire. Overall, emission of PM_{10} from tires is low and predominantly originates from the road surface.

INTRODUCTION

- Tire wear particles (TWP) are generated from the friction produced at the pavement/tread surface interface during rolling of the tire.
- TWP consist of tread rubber and embedded minerals and other constituents of road dust and have an overall particle size distribution of ranging from <1 µm to ~200 µm (Panko et al. 2008).
- Ambient airborne particulate matter can include TWP, especially in urban environments and locations near roadways (Fauser, 1999; Schauer et al 2002; Kitamura et al., 2007).
- The purpose of this study was to characterize the size distribution and chemical composition of airborne TWP generated from three common types of passenger car tires.

METHODS

General

- Testing was conducted at the VTI (Swedish National Road and Transport Research Institute) road simulator laboratory in Linkoping, Sweden. (Figure 1)
- Test tires included
  - Silica-based summer tire (Michelin Pilot Primary)
  - Silica-based winter tire (Pirelli Sottozero)
  - Carbon-black based summer tire (Bridgestone Potenza)
- Pavement installed on the simulator was a dense asphalt pavement containing mostly diabase rock with a maximum stone size of 11 mm.
- Rolling conditions included constant speed of 70 km/h; air temperature of simulator room was 15°C for the summer tires and 5°C for the winter tire.

Sampling Methods

- PM_{10} and $PM_{2.5}$ samples were collected with IVL-type samplers using 11 electric vacuum pumps, which were situated outside of the simulator room. To supplement the $PM_{2.5}$ collection, an additional two PQ200 $PM_{2.5}$ air samplers were also used. Polycarbonate filters were used for samples undergoing microscopy and mixed cellulose ester filters were used for samples undergoing bioaccessibility analysis (See Eurotox 2009 Abstract #659)
- Particle size distribution was measured using
  - DustTrak for real-time monitoring of total PM_{10} and $PM_{2.5}$
  - Aerodynamic Particle Sizer (APS; model 3321, TSI, USA) measuring particles with an aerodynamic diameter from 0.5 to 10 µm.
  - Scanning Mobility Particle Sizer (SMPS; model 3934, TSI, USA which was calibrated to measure and count particles from 7.37 nm to 311 nm.
- 12-stage cascade impactor was coupled to the PM_{10}-inlet of the APS to sample particles from 0.04 to 10 µm.
- A supplemental 2-stage sampling device (PM_{10}-$_{2.5}$ and $PM_{2.5}$)–stacked filter unit (SFU) was also used
  - Samples were collected on NuclePore filter, which was coated with a thin layer of grease for subsequent elemental analysis.

Compositional Analysis Methods

- Computer Controlled Scanning Electron Microscopy (CC-SEM) coupled with energy dispersive spectroscopy (EDS) was performed on six filters from PM_{10} samplers and six from $PM_{2.5}$ samplers. CC-SEM was used to characterize 900-1000 particles per filter. Field-emission SEM (FE-SEM) was also used to analyze particles less than one micron in diameter. FE-SEM was performed on filters from three $PM_{2.5}$ samples and 10 particles were characterized on each of these filters.
- Particle Induced X-ray Emission (PIXE) was used to conduct elemental analysis of the particles.
  - Analysis was conducted at Lund University in Sweden.
  - PIXE can only identify elements with an atomic number greater than that of aluminum (13), therefore elements with a lower atomic number, such as carbon, were not identified using this method.

Particles were categorized as either TWP or pavement based on the chemical composition. Based on our understanding of tire and asphalt composition, we identified the following categories as TWP: Zn-rich, C(S Zn), C(S) rich, C(Zn rich), and C-rich. Alternatively, Cu-rich, Fe/Zn, C(Cu) rich, Si/Al, Ca-Si rich, Si-rich, Ca-rich, and Fe-rich particles were not classified as TWP and were considered to be originating from the pavement.

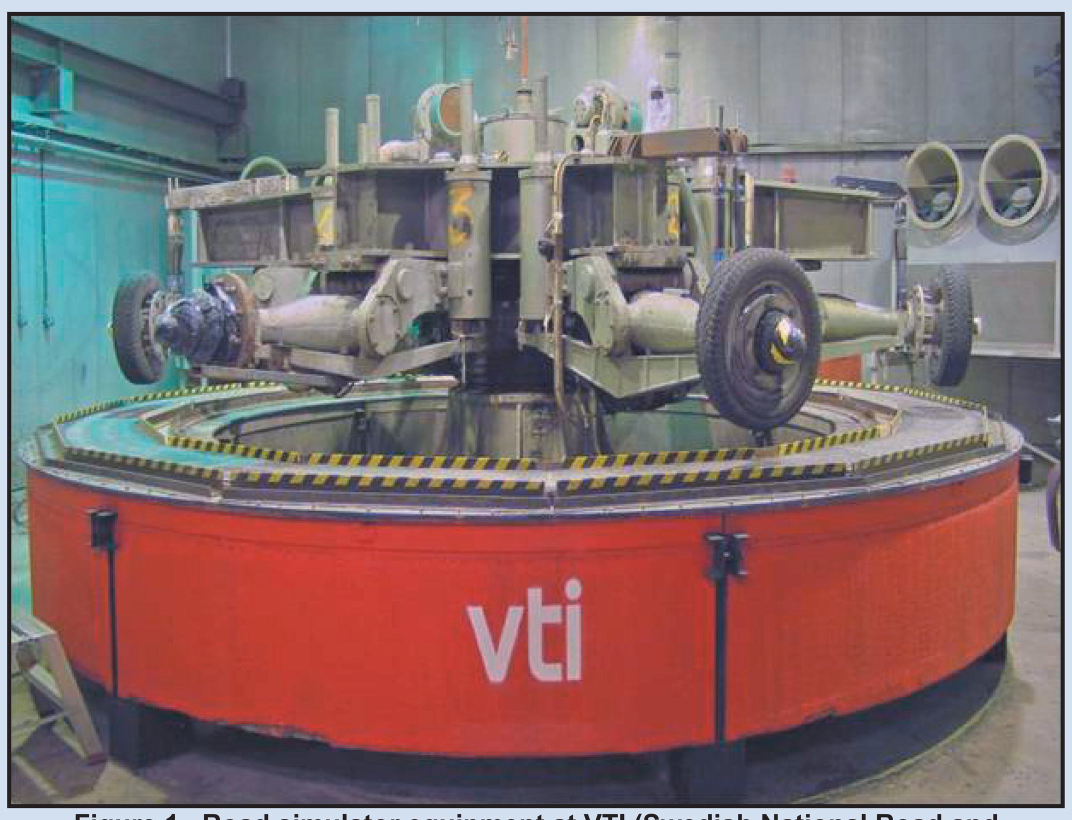


Figure 1. Road simulator equipment at VTI (Swedish National Road and Transport Research Institute) in Linkoping, Sweden.

RESULTS

- Particle concentration was low in general; rising initially and then decreasing to a constant level of 6-10 µg/m³, indicating an overall low particle emission. (See Figure 2)
- Particle size distribution
  - APS data indicated a bimodal distribution of the particles, with a peak around 1 µm and a second peak between 5 and 8 µm. (See Figure 3)
  - SMPS data generally indicated a peak in the number of particles generated between 10 and 100 nm. (See Figure 4)

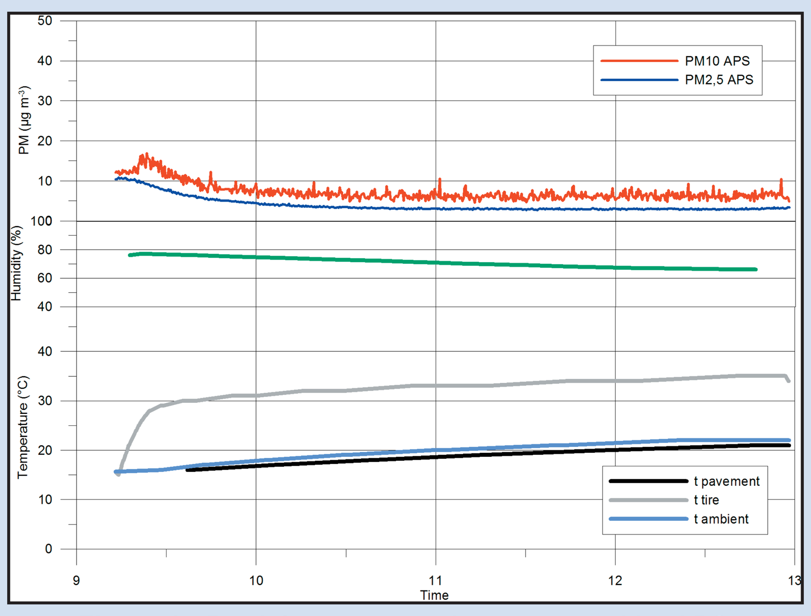


Figure 2. Particle concentration measured by APS, temperatures and relative humidity during the test of the silica-based summer tire.

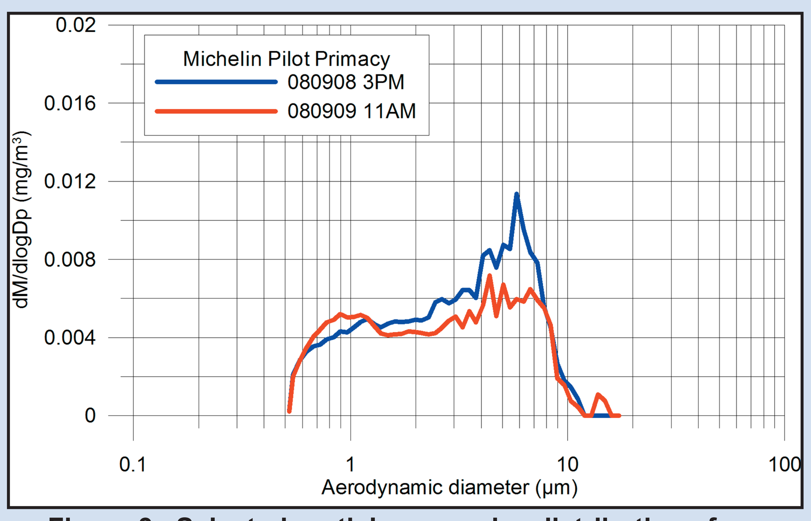


Figure 3. Selected particle mass size distributions from stable periods (APS)

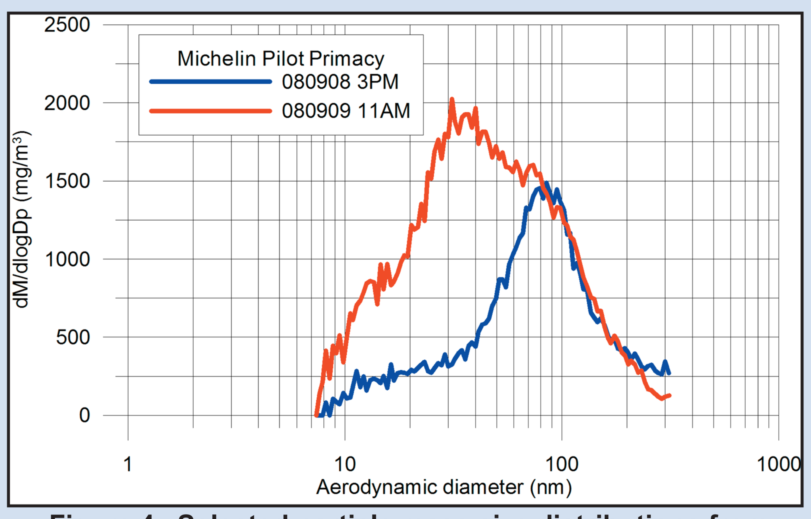


Figure 4. Selected particle mass size distributions from stable periods (SMPS)

- Elemental composition by PIXE:
  - The course fraction of airborne particulate was dominated by silica, calcium, iron, and potassium and these particles likely result from the pavement (Figure 5a). When silica is removed from the tire profile, it is possible to see the contribution of the lesser elements (Figure 5b).
  - The fine fraction (<1 µm) contained a significant amount of sulfur, which while present in tread rubber (~1%), is also present at higher concentrations in the asphalt pavement (3.2%) used at the simulator laboratory.
  - Zinc and copper were also found in several size bins and appeared to be related in that they peaked in nearly the same bins for each tire analyzed. Zinc has been used as a tracer for TWP in the literature and likely originates from the tires as it was not detected in the pavement from the road simulator. The source of copper is unknown as it was not detected in the pavement and is not used in rubber compounding because of its oxidizing properties.

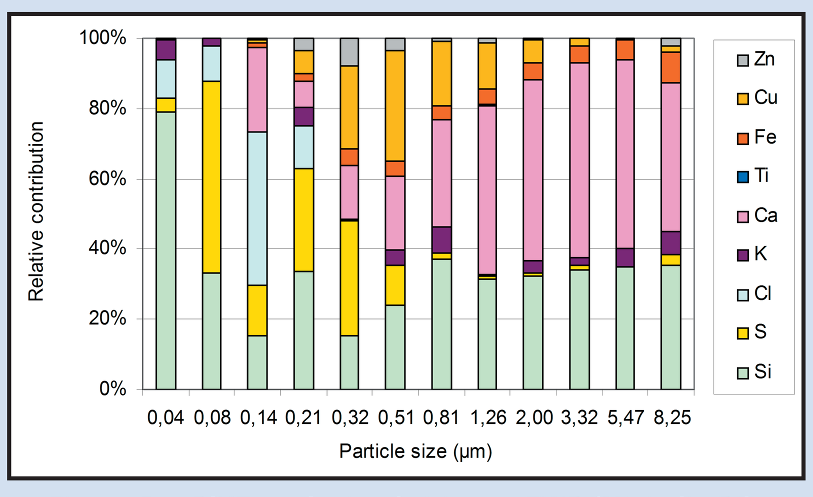


Figure 5a. PIXE analysis of airborne TWP (Michelin Pilot Primacy shown)

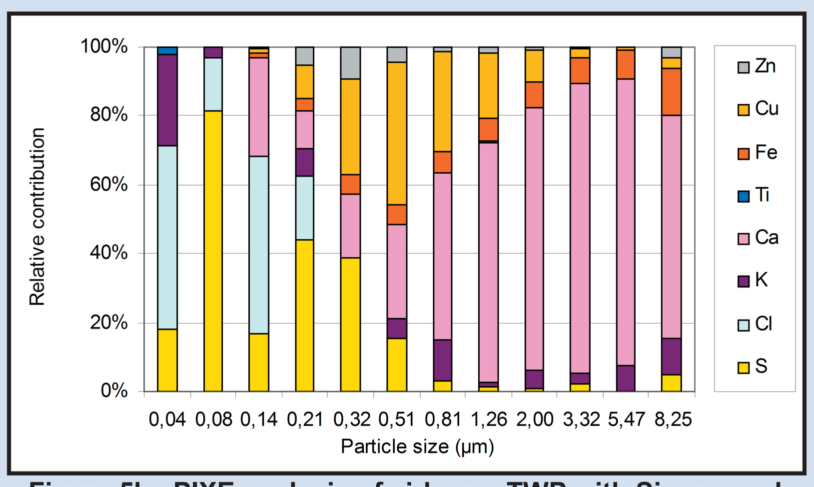


Figure 5b. PIXE analysis of airborne TWP with Si removed (Michelin Pilot Primacy shown)

RESULTS CONTINUED

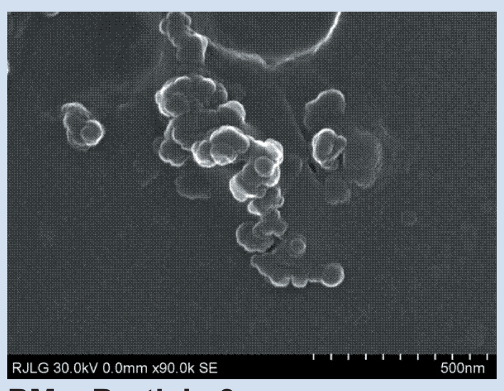
- Microscopy using CC-SEM/EDX of PM_{10} and $PM_{2.5}$ filters
  - TWP represented approximately 38% by particle number count and 8.5% by mass of the total sample (Table 1 and 2). Of the 38% identified as TWP by number, the vast majority were found in the 0.2 to 1.0 µm size range (31.8% out of 38.2%; Table 1). When binned according to mass, the TWP was found mostly in the 1.0 to 2.5 and 2.5 to 5 µm range (Table 2).
- Microscopy using FE-SEM
  - Particles <200 nm were observed on the $PM_{2.5}$ samples.
  - Most of the particles have a composition which includes strong carbon peak.
  - Variety of particle shapes, some agglomerated particles (Figure 6).

Table 1. Average PM_{10} size distribution by number of particles

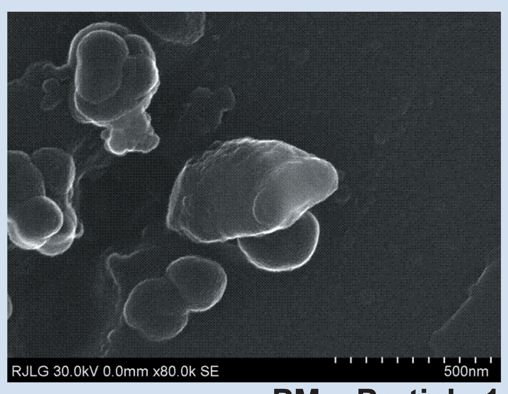
Classes	Number %	0.2 - 1.0 µm	1.0 - 2.5 µm	2.5 - 5.0 µm	5.0 - 7.5 µm	7.5 - 10.0 µm	>10µm
Total	**100**	**66.65**	**28.95**	**3.9**	**0.4**	**0.05**	**0.00**
Percent totals by number count of TWP							
Zn-rich	0.733	0.184	0.152	0.268	0.002	0.005	0.122
C (S ZN)	0.367	0.367	0.000	0.000	0.000	0.000	0.000
C(S) rich	6.183	5.201	0.941	0.040	0.001	0.001	0.000
C(Zn) rich	2.400	2.164	0.235	0.002	0.000	0.000	0.000
C-rich	28.517	23.907	4.344	0.247	0.005	0.000	0.000
TWP total	**38.2**	**31.8**	**5.7**	**0.56**	**0.007**	**0.006**	**0.12**

Table 2. Average of mass by size distribution for total PM_{10} samples

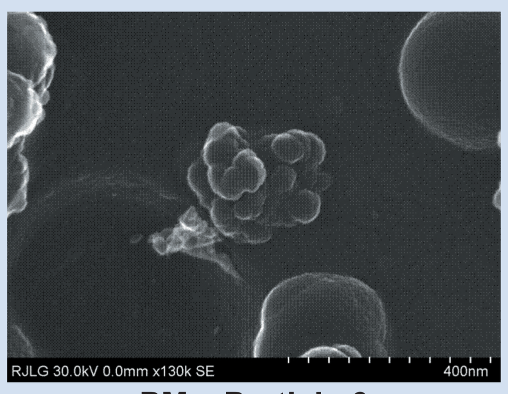
	Mass %	0.2 - 1.0 µm	1.0 - 2.5 µm	2.5 - 5.0 µm	5.0 - 7.5 µm	7.5 - 10.0 µm	>10µm
Total	**100**	**3.8**	**27**	**35.3**	**19.3**	**7.4**	**7.2**
Percent totals of mass of TWP							
Zn-rich	2.900	0.080	0.550	1.634	0.101	0.038	0.497
C (S ZN)	0.033	0.033	0.000	0.000	0.000	0.000	0.000
C(S) rich	1.133	0.204	0.574	0.220	0.015	0.094	0.025
C(Zn) rich	0.217	0.132	0.068	0.011	0.000	0.006	0.000
C-rich	4.217	0.741	2.042	1.098	0.235	0.071	0.029
TWP total	**8.5**	**1.2**	**3.2**	**2.9**	**0.4**	**0.2**	**0.6**



$PM_{2.5}$ Particle 9



$PM_{2.5}$ Particle 1



$PM_{2.5}$ Particle 6

Figure 6. FE-SEM photographs of ultrafine airborne particles collected at VTI

DISCUSSION

- The airborne particle concentration measured during the tests indicated low amounts (6-10 µg/m³) of PM_{10} and $PM_{2.5}$ are generated from the tire/pavement interface. This is consistent with the particle size distributions measured on bulk TWP collected as the tire rolls against the pavement, where less than 1% by volume were smaller than 10 µm (Kreider et al. 2009).

- The results of the compositional analysis performed using PIXE and CC-SEM/EDX are consistent; both indicating that TWP are mostly found in the size range greater than 0.2 µm. Sulfur, which is present in both tread rubber and the pavement was detected primarily in size fractions <0.5 µm. The source of the sulfur in the ultrafine fraction is unknown; although it has been hypothesized that the ultrafine particles are from condensation of oils volatilized from tire tread (Dahl, et al. 2008), or other tread compounds (Cadle and Williams, 1978). Tire temperatures >200°C (temperature required for decomposition of tread rubber) are rarely measured during driving; and the maximum tire temperature measured during the tests was <40°C. However, Cadle and Williams (1978) hypothesized that the gaseous emissions from tires that they measured including sulfur compounds (followed by subsequent condensation on chamber walls) may occur if local temperatures in small areas of the contact patch greatly exceeded the temperature of the bulk tread. Therefore, further work is required to understand the source and mechanism of generation of the ultrafine particles.

- Analytical results produced by the FE-SEM/EDX technique provides an opportunity to visualize the particles formed in this size range, but the data are limited to the particles actually analyzed and cannot be extrapolated to understand the composition of the whole fine particle fraction. Further the use of EDX on particles less than 100 nm has limited accuracy in terms of composition analysis because the electron beam is larger than many of the particles.

- Although this study indicated that the emission of PM_{10} from tire wear is low, additional research is necessary to understand the overall contribution of TWP to airborne particulate matter in the ambient environment.

ACKNOWLEDGEMENT

The work presented here was funded by the Tire Industry Project, an international consortium of 11 tire manufacturers, collaborating to understand the human health and environmental impact of tires, under the oversight of the World Business Council for Sustainable Development. We would also like to acknowledge RJ Lee Group, Pittsburgh, PA for the CC-SEM and FE-SEM analysis and Lund University, Lund Sweden for the PIXE analysis.

REFERENCES

Cadle, S.H.; Williams, R.L. (1979). Gas and particle emissions from automobile tires in laboratory and field studies. Rubber Chem Technol , 52, (1), 146-158.

Dahl, A.; Gharibi, A.; Swietlicki, E.; Gudmundsson, A.; Bohgard, M.; Ljungman, A.; Blomqvist, G.; Gustafsson, M. (2006). Traffic-generated emissions of ultrafine particles from pavement–tire interface. Atmospheric Environment, 40, 1314-1323.

Fauser, P.; Tjell, J.C.; Mosbaek, H.; Pilegaard, K., Quantification of tire-tread particles using extractable organic zinc as tracer. Rubber Chem Technol 1999, 72, (5), 969-977.

Kitamura, Y.; Kuroiwa, C.; Harada, M.; Kato, N. (2007). Analysis of Rubber Fraction in Suspended Particulate Matter (SPM) on Road. 172th Technical Meeting of the American Chemical Society, Inc. Cleveland, OH.

Kreider M., McAtee, B., Sweet, L., Panko, J., Finley, B. (2008). Physical and Chemical Characterization of Tire Related Particles: Comparison of Particles Generated Using Different Methodologies. 174th Technical Meeting of the Rubber Division of the American Chemical Society, Inc. Louisville, KY

Panko, J., Kreider, M., McAtee, B, Sweet, L., Finley, B (2008). Methods for Collecting Tire Wear Particles. 174th Technical Meeting of the Rubber Division of the American Chemical Society, Inc. Louisville, KY

Schauer, J. J.; Fraser, M. P.; Cass, G. R.; Simoneit, B. R., Source reconciliation of atmospheric gas-phase and particle-phase pollutants during a severe photochemical smog episode. Environ Sci Technol 2002, 36, (17), 3806-14.