C₆₀ fullerenes from combustion of common fuels

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Abstract

Releases of C₆₀ fullerenes to the environment will increase with the growth of nanotechnology. Assessing the potential risks of manufactured C₆₀ requires an understanding of how its prevalence in the environment compares to that of natural and incidental C₆₀. This work describes the characterization of incidental C₆₀ present in aerosols generated by combustion of five common fuels: coal, firewood, diesel, gasoline, and propane. C₆₀ was found in exhaust generated by all five fuels; the highest concentrations in terms of mass of C₆₀ per mass of particulate matter were associated with diesel and coal. Individual aerosols from these combustion processes were examined by transmission electron microscopy. No relationship was found between C₆₀ content and either the separation of graphitic layers (lamellae) within the particles, nor the curvature of those lamellae. Estimated global emissions of incidental C₆₀ to the atmosphere from coal and diesel combustion range from 1.6 to 6.3 tons yr⁻¹, depending upon combustion conditions. These emissions may be similar in magnitude to the total amount of manufactured C₆₀ produced on an annual basis. Consequent loading of incidental C₆₀ to the environment may be

several orders of magnitude higher than has previously been modeled for manufactured C₆₀.

Key words: nanomaterials, TEM, emissions

1. Introduction

Often regarded as the next industrial revolution, nanotechnology is projected to grow at an annual rate of 16.5% between 2014 and 2020.¹ As manufactured nanomaterials (MNM)s are produced in ever-greater quantities, releases of them to the environment through use, disposal, and accidents are inevitable.^{2, 3} While some manufactured nanoparticles may not have similar forms that already exist in nature, others such as several metal oxides⁴ may have analogues already present in the environment. These analogous particles may be formed naturally, or incidentally (unintentionally) through anthropogenic processes. Knowledge of the background concentrations of analogous particles will be important in order to understand the potential impacts of MNMs and formulate appropriate environmental policies for them.

Carbon-based nanomaterials (CNMs) are an important category of MNMs and encompass carbon nanotubes, fullerenes, and graphene. As with all MNMs, releases of manufactured CNMs to the environment may occur throughout their lifecycle. The resulting environmental concentrations of manufactured CNMs are projected to be low,⁵ but manufacturing volumes are highly uncertain.^{6, 7}

Some CNMs are formed by natural processes. C₆₀ has been identified in certain geological materials using mass spectrometry.^{8, 9} While successful extraction of C₆₀ from geological materials has historically been challenging,¹⁰ more effective extraction procedures have recently been developed.¹¹⁻¹⁴ These newer extraction procedures better enable the measurement of naturally occurring C₆₀, but the degree to which such C₆₀ molecules may be liberated from the material and become more mobile in the environment is uncertain.

In addition to having natural sources, C₆₀ may also be produced incidentally as a byproduct of anthropogenic activities. One potentially significant source of incidental CNMs is combustion. Forest fires have been cited as a source of fullerenes to the environment,^{15, 16} but results are not conclusive. Based on high-resolution transmission electron microscopy, Murr *et al.*¹⁷⁻¹⁹ asserted the presence of CNMs (both “fullerene” materials and carbon nanotubes) in exhaust from propane, natural gas, and other combustion processes. Utsunomiya *et al.*²⁰ identified “fulleroid” carbonaceous structures in ambient aerosols in Detroit, Michigan, and mass spectrometry suggested the presence of C₆₀ and C₇₀ (*m/z* 720 and 840, respectively) in the samples. The authors presumed coal combustion to be the source of these fullerenes.

Two publications to date have definitively identified C₆₀ and/or C₇₀ fullerenes in atmospheric aerosols via mass spectrometry. Sanchís *et al.*²¹ reported the presence of C₆₀ and C₇₀ in aerosol samples collected from ambient air over the Mediterranean Sea, and Benn *et al.*²² detailed the presence of C₆₀ in aerosol collected under a variety of ambient and source-specific conditions. While prior studies have identified fullerenes in combustion-generated and atmospheric aerosols, none of them utilized microscopy to examine particle morphology and structure in conjunction with quantification of C₆₀ content. The objective of this work is to provide a new combination of quantitative and qualitative characterization that provides insight into the contribution of specific sources to incidental C₆₀ in the atmosphere.

2. Methods

2.1 Materials

C₆₀ (99.9%) and ¹³C₆₀ (99%) were purchased from MER Corporation (Tucson, AZ). ¹³C₆₀ was used as an extraction surrogate, as described below, and analytical standards were prepared using C₆₀ and ¹³C₆₀. Toluene (HPLC-grade, JTBaker) and methanol (acetone-free, Sigma-Aldrich) were used for preparation of standards and for sample extraction. Sample extractions were carried out in HPLC-

grade toluene. Absolute (acetone-free) methanol (Sigma-Aldrich, St. Louis, MO) was added to samples immediately prior to analysis.

2.2 Sources

Five combustion sources were selected on the basis of being suspected sources and widely used: coal-fired power plant, mixed hardwood fire, diesel-powered generator, gasoline-powered lawnmower, and propane grill. The power plant burned bituminous coal and was equipped with a baghouse filter. The mixed hardwood fire was lit in a backyard elevated fire pit under calm wind conditions using approximately 7 kg of wood; log size varied from 25 to 50 cm in length and from 10 to 20 cm in breadth. The diesel engine was a 32 kW generator (Kubota) operated at 0% load and 90% load.²³ A two-stroke lawnmower engine (6 HP, EPA Phase I compliant) was sampled during normal operation (i.e., while cutting grass), and a propane grill was operated at medium and low flame using a commercially available consumer propane tank.

2.3 Sample Collection

Particles in naturally diluted exhaust plumes (except where noted) were collected onto 47-mm Teflon membrane filters (1.0- μ m pore size, Millipore, Billerica, MA) using a stainless steel filter holder (Advantec, #02929-20, Cole Parmer, Vernon Hills, IL) and a battery-powered vacuum pump (Leland, #100-3002-S, SKC Inc., Eighty Four, PA). A size-selective inlet was not used, so the filter samples represented total suspended particulates (TSP). Prior to sampling, filters were stored in a desiccator for > 24 h at 21 °C and weighed (balance accuracy 100 μ g, detection limit 10 mg). Samples were collected using an initial flow rate of 9 L min⁻¹, which decreased as sampling progressed. During sampling, the flow rate decreased by 0 – 4 L min⁻¹ (resulting in final flow rates of 5 to 9 L min⁻¹), depending upon the sample type. Samples were collected for up to one hour or until the accumulated TSP on the filter posed too large a pressure drop for the pump to function, whichever was shorter. After sampling, filters were stored in individual plastic petri dishes at 4 °C until they were equilibrated in a desiccator for > 24 h at

21 °C and weighed immediately prior to extraction. Controls included seven field blanks that were loaded into the filter holder and removed without turning on the pump and five laboratory blanks.

Aerosol samples from the power plant were collected at several points throughout the plant: (1) after the boiler and economizer and before the cyclone, (2) before the baghouse damper and after the cyclone, and (3) at the baghouse outlet. For the mixed hardwood campfire, the sample inlet was located in the smoke plume, approximately 60 cm from the flame. Undiluted diesel engine exhaust was collected from a 0.8-cm diameter stainless steel tube attached (via a dilution manifold) to the 5 cm I.D. exhaust pipe. Samples from the lawnmower were collected via a tube fixed approximately 5 cm from the engine exhaust grate; the filter holder and pump were attached to the lawnmower. For the propane grill, the sample inlet was located approximately 30 cm above the burner unit.

Ash samples were collected in 50 mL polypropylene vials and stored at 21 °C. Fly ash, bottom ash, and pug mill ash (mixture of fly ash, boiler ash, and lime) were collected from the relevant capture devices within the power plant. Wood fire ash was sampled from the fire pit after the fire was extinguished. Immediately prior to extraction, ash samples from the power plant were pulverized in a ball mill to reduce particle size; ash from the wood fire did not require this pretreatment. Aliquots of the final ash materials were then extracted according to the procedure below.

Samples for transmission electron microscopy (TEM) were collected onto copper TEM grids with a lacey carbon coating (LC300-Cu, Electron Microscopy Sciences, Hatfield, PA). Aerosol particles were deposited onto the grids directly from the aerosol phase by affixing the grids to the second and third stages of an impactor with cutpoint diameters of 0.3 and 0.05 μm , respectively, (Microanalysis Particle Sampler, MPS-3, California Measurements, Inc., Sierra Madre, CA) using double-sided carbon tape. The impactor was operated at a flow rate of 2 L min⁻¹ for 30 – 120 s, depending upon the sample type. After collection, grids were stored in a desiccator until analysis. TEM samples for coal combustion were collected at the baghouse outlet, as other locations in the combustion train were not suitable for this

type of sampling due to elevated temperature and particle concentration. For the wood fire and propane grill, the impactor inlet tube was positioned approximately 60 cm and 30 cm from the flame, respectively. The same exhaust sampling apparatus was used for diesel TEM sampling as for filter sampling. TEM samples were not collected for the gasoline-powered lawnmower because the impactor was not easily portable.

2.4 Sample Preparation

All filter samples were extracted using ultrasonic-assisted extraction. The extraction protocol was developed by testing the influence of methanol, extraction time, and a silica gel cleanup step on the extraction efficiency of $^{13}\text{C}_{60}$ spiked onto filters. These three variables were also tested in the method development of Farré *et al.*²⁴ and Sanchís *et al.*²⁵ Both blank filters and filters bearing aerosol from a smoldering wood fire (intended as a proxy for all combustion aerosols) were used in the optimization.

Prior to sample extraction, 10 μL of a 10 ng μL^{-1} solution of $^{13}\text{C}_{60}$ was spiked onto filter samples as an extraction surrogate.²¹ After drying, filters were placed into 8-mL glass vials. Vials were filled with toluene and placed in an ultrasonic bath for 5 h.²⁵ Bath temperature was kept below $\sim 35^\circ\text{C}$ by periodic addition of crushed ice. Following sonication, filters were removed from the vials and centrifuged at 5000 rcf for 5 min if visible solids remained in the vial. This was true for one coal sample collected after the cyclone and before the baghouse (position #2 as described above) and one diesel sample collected at 90% load. Samples were concentrated by gentle blowing with nitrogen to evaporate the solvent, combined with heating to $< 40^\circ\text{C}$. Once sample volume fell below 0.5 mL, it was reconstituted using toluene to equal 0.5 mL. Finally, 0.5 mL of methanol was added to all samples, resulting in a 1:1 ratio of toluene to methanol, prior to analysis. Field blanks and extraction blanks were prepared in an identical manner.

2.5 Sample Analysis

Analytical standards containing C₆₀ and ¹³C₆₀ were prepared at concentrations ranging from 1 to 200 pg mL⁻¹ in toluene and methanol. Toluene and methanol used for liquid chromatography/mass spectrometry (LC/MS) analysis were HPLC grade (Fisher Scientific, Pittsburgh, PA). The analytical procedure was based on that previously published by Farre *et al*²⁴ and used by Sanchis *et al*,^{21, 25} with minor changes. Samples were analyzed by LC/MS using an Agilent HPLC 1100 (Wilmington, DE) and a Thermo TSQ triple quadrupole mass spectrometer (MS) (Thermo Finnigan, San Jose, CA) equipped with an electrospray ionization (ESI) source. The HPLC was equipped with an Agilent reversed-phase Eclipse XDB column (150 mm × 2.1 mm, particle size 5.0 μm), a column heater set at 40 °C, and a Thermo Survey (San Jose, CA) autosampler. The injection volume was 50 μL, and all separations were obtained isocratically using a 1:1 toluene:methanol mobile phase at flow rate of 0.3 mL min⁻¹.

The MS was operated in negative mode using single reaction monitoring (SRM). The MS ran at a spray voltage of 4000 V, sheath gas pressure of 49 psi, auxiliary gas pressure of 15 psi, and a capillary temperature of 300 °C. Monitored parent and product masses for C₆₀ and ¹³C₆₀ were 719.97-719.97 and 738.07-738.07 with CE values of 18 and 16, and tube lens values of 155, and 178, respectively. The instrument limit of detection (LOD) was determined daily by observing a signal-to-noise ratio greater than three, and ranged from 20 to 50 pg mL⁻¹. Detection limits thus ranged from 1 to 2.5 pg per injection.

The morphology and structure of aerosol particles were examined using a transmission electron microscope (JEOL 2100, Peabody, MA) with a Gatan CCD camera. Lamella separation was measured in DigitalMicrograph by selecting > 170 lamellae for each source. Tortuosity, an indicator of lamella curvature defined as the lamella length divided by the shortest straight-line distance between its two endpoints,²⁶ was measured in ImageJ by selecting 75 lamellae per source.

3 Results

3.1 C₆₀ content

Optimal extraction of C₆₀ from Teflon filters was obtained by using 100% toluene v. 1:1 methanol and toluene in the extraction vials, extracting via a bath sonicator for five hours v. a shorter period, and omitting a silica gel cleanup step. This method differs slightly from previously published procedures for extraction of fullerenes from wastewater effluent²⁴ and river sediment.²⁵ This extraction protocol resulted in $116 \pm 6\%$ extraction of ¹³C₆₀ from filters loaded with aerosol from a smoldering wood fire.

In total, 23 aerosol samples were collected. Specific details about them are shown in Table 1. Figure 1 shows the mass fraction of C₆₀ in TSP in each of 19 samples for which there was a measureable accumulation of TSP, enabling the calculation of a mass fraction. In eight of these, C₆₀ was below the limit of detection. These points have been coded with a mass fraction of zero in the figure and are depicted with open circles. The highest mass fraction was 41 µg g⁻¹ in exhaust from the diesel-powered generator at 90% load, although this point appears to be an outlier. Mass fractions above 1 µg g⁻¹ were also found in exhaust from the coal-fired power plant before the cyclone and after the baghouse and in exhaust from the propane grill at a low flame level. All samples from the propane grill and gasoline-powered lawnmower contained detectable, even if low, amounts of C₆₀, as did those from the diesel-powered generator at 90% load. However, samples from the diesel-powered generator operated at 0% load did not contain detectable amounts of C₆₀. While C₆₀ was found in combustion-generated particles from each of the source types, there was considerable variability in some cases. It is possible that transient variability in combustion conditions affected the amount of C₆₀ formed and/or its extractability from the particles. Extraction efficiency of the internal standard was low in certain cases, for example 10% for one of the samples from the coal-fired power plant and 11% for one of the samples from the diesel-powered generator, so these mass fractions and concentrations reported in Table 1 underestimate the actual values.

Figure 1: Mass fraction of C_{60} in TSP collected in the exhaust plumes of various combustion sources. Zero values are depicted with open circles, non-zero values with filled circles.

In samples containing measurable amounts of C_{60} , its mass concentration in the source plumes ranged over five orders of magnitude, from $4.1 \times 10^{-2} \text{ ng m}^{-3}$ in the plume of the propane grill running at a medium flame level to $2.3 \times 10^3 \text{ ng m}^{-3}$ in undiluted exhaust from the diesel-powered generator at 90% load. Table 1 shows C_{60} concentrations in the plume for each sample. C_{60} was not detected in any of the

four types of ash, nor was $^{13}\text{C}_{60}$ that was spiked into the samples recovered. Therefore, it is possible that the ash did contain C_{60} but that it was not extractable.

Table 1: C_{60} mass fraction in total suspended particles (TSP), airborne concentration, and extraction efficiency of $^{13}\text{C}_{60}$ extraction surrogate.

Sample Name	Source	Conditions	C_{60} mass fraction, $\mu\text{g g}^{-1}$	C_{60} mass conc., ng m^{-3}	$^{13}\text{C}_{60}$ extraction efficiency (%)
C1	Coal-fired power plant	Before cyclone	N/A	0.0	58
C2			5.7	4.1×10^2	98
C3			BDL	0.0	10
C4			BDL	0.0	44
C5		After cyclone	5.0×10^{-1}	4.2×10^1	29
C6			BDL	0.0	33
C7		After baghouse	3.8×10^{-2}	1.9×10^{-1}	59
C8			1.9	1.3	93
W1	Wood fire	Stacked wood, open air	BDL	0.0	18
W2			BDL	0.0	34
W3			7.0×10^{-3}	3.4×10^{-1}	33
W4			BDL	0.0	26
D1	Diesel-powered generator	0% load	BDL	0.0	43
D2			BDL	0.0	36
D3		90% load	1.3×10^{-1}	5.0	11
D4			4.1×10^1	2.3×10^3	53
D5			N/A	1.7×10^2	55
G1	Gasoline-powered lawn	Mowing	1.2×10^{-1}	2.0	53
G2			4.4×10^{-2}	8.6×10^{-1}	46
P1	Propane grill	Low flame	1.6	1.2	59
P2			N/A	1.0×10^{-1}	54
P3		Medium flame	N/A	4.8×10^{-2}	47
P4			1.1×10^{-1}	4.1×10^{-2}	54
Bottom Ash	Coal-fired	From boiler	BDL	N/A	0.0

Fly Ash	power plant	Captured by	BDL		0.0
Boiler Ash		Bottom ash, fly	BDL		0.0
Wood Ash	Wood fire	Campfire residue	BDL		0.0

N/A: the mass fraction calculation yields zero due to a zero mass change, although the C_{60} content by mass spectrometry may be nonzero. BDL: C_{60} was below detection limit of mass spectrometer.

3.2 TEM results

Figure 2 shows representative TEM images of aerosols collected in exhaust plumes from the coal-fired power plant, wood fire, diesel-powered generator, and propane grill. Aerosols from all sources exhibited a structure consisting of short, irregularly shaped layers. The length and curvature of these layers (lamellae), as well as the spacing between them, varied across and within fuel types, as well as within individual particles. Average lamella spacing measurements, shown in Table 2, were not significantly different among any of the four sources. The distribution of lamella spacings within each source is shown in Figure S1. The distributions differed only slightly by source, indicating that aerosols generated by the diesel-powered generator may have had smaller spacings than did the other three sources. The average tortuosity (Table 2) did not vary by source, nor did the distribution of tortuosity, shown in Figure S2.

Figure 2: TEM images of combustion aerosols. Clockwise from top left: propane, diesel, wood, coal.

Table 2: Lamella separation and tortuosity (mean $\pm$ standard deviation) from TEM image analysis.

	Coal	Wood	Diesel	Propane
Lamella separation (nm)	0.38 ± 0.02	0.39 ± 0.03	0.37 ± 0.02	0.39 ± 0.01
Tortuosity	1.08 ± 0.09	1.05 ± 0.06	1.16 ± 0.35	1.12 ± 0.18

4 Discussion

4.1 Fullerene content

C_{60} concentrations in the exhaust plumes sampled in this work range over five orders of magnitude, $10^{-2} - 10^3$ ng m⁻³. These concentrations are at least one order of magnitude higher than those found by Benn *et al.*²² in ambient air in a parking garage (pg m⁻³) and are comparable to concentrations measured by Sanchís *et al.*²¹ over the Mediterranean Sea. There, the highest value reported is ~ 230 ng m⁻³, which is very similar to several values measured in coal and diesel exhaust in this work. The unexpected similarity between the ambient concentrations measured by Sanchís *et al.* and the exhaust concentrations measured in this work warrants further research, as sampling directly from a source should result in much higher concentrations than would one would expect to measure over the open sea. Low and variable extraction efficiencies of the internal standard $^{13}C_{60}$ from samples in this work may help to explain this discrepancy. One limitation of this study is that only one of each source type was investigated, and it is possible that there is a broad distribution in the amount of C_{60} emitted across different sources of the same type.

Concentrations measured by Benn *et al.*²² are several orders of magnitude lower than were measured in this work. Given the potential presence of diesel-powered vehicles within or near the parking garage described in Benn *et al.*²² and the naturally occurring dilution with ambient air within a garage, this relationship

may be reasonable. Comparison of airborne C₆₀ concentrations between this study and the work of Utsunomiya *et al.*,²⁰ Murr *et al.*,^{18, 19} or Laitinen *et al.*²⁷ (which documents the observation of C₆₀ and higher fullerenes in ambient urban air) is not possible, as those works do not report C₆₀ quantitatively.

Soil samples collected near Latin America's largest coal-fired thermoelectric plant have been shown to contain C₆₀.²⁸ The finding of C₆₀ in exhaust from a coal-fired power plant in this study supports the suggestion by Sanchís *et al* (2015)²⁹ that coal was the source of C₆₀ found in those samples. Global incidental production of C₆₀ from coal combustion may be estimated by using C₆₀ mass fractions measured after the baghouse (0.97 µg g⁻¹). The PM emission factor for a power plant equipped with particulate control technology may range from 0.22 to 0.88 g kg⁻¹, assuming the US average ash value of 9.36%.^{30, 31} Using these emission factors and a global coal consumption estimate of 7.4×10^{12} kg yr⁻¹,³² global incidental C₆₀ production from coal combustion is estimated to range from approximately 1.6 to 6.3 tons yr⁻¹. Actual values may be somewhat higher, as some coal is burned in uncontrolled circumstances (uncontrolled power plants, residential use, etc.), and coal outside the US may differ in ash content. Coal type may significantly affect the coal PM emission factor in uncontrolled circumstances; for example, anthracite and bituminous coal PM emission factors for residential burning in China are 0.78 and 16.77 g kg⁻¹, respectively.³³

Global diesel emissions may also be an important source of incidental C₆₀ to the environment, as diesel is widely used and global consumption averages approximately 2.5×10^7 gallons d⁻¹.³⁴ Estimation of this loading based on data in this work is precluded by the limited sample size and wide variability in results.

Considering only coal, then, total loading of incidental C₆₀ to the global environment may range from 1.6 to 6.3 tons yr⁻¹. This estimate does not include the burning of other fossil fuels (propane, gasoline, fuel oil, etc.) for power generation or other applications, nor any biomass burning. Global production rates of manufactured C₆₀ are highly uncertain, but have been estimated to be between 1 and 40 tons yr⁻¹.⁶ Incidental production, then, may be approximately equal to total manufactured production.

While the C_{60} concentrations measured in partially diluted exhaust do not translate directly to concentrations in ambient air, they may be used to estimate the quantity of incidental C_{60} that is released to the atmosphere, which would then be deposited to Earth's surface via normal atmospheric processes. Upon deposition, as with any previously airborne pollutant, the incidental C_{60} would accumulate in soil or sediments, and contaminate surface water, where it may be indistinguishable from manufactured C_{60} . If incidental C_{60} production is significant, as these results suggest, modeling studies predicting environmental C_{60} concentrations that consider only manufactured sources may need to place their results in the context of "background" or "incidental" C_{60} concentrations. The same may not be true for certain functionalized fullerenes that have manufactured sources only.

The emphasis of this work was characterizing C_{60} emissions from specific sources under realistic conditions. A primary limitation of this work is the small number of samples. While this sample set does not constitute a robust accounting of all common combustion processes, we can conclude that C_{60} is released to the environment from incidental sources. Future studies should incorporate a larger number of samples from a larger number of sources of the same type (e.g., several different diesel engines) and employ a longer sampling time and/or higher flow rate to collect more mass. The relatively short sampling times in this study of exhaust plumes were selected on the basis of reported concentrations of C_{60} found in ambient air.²¹

Future research concerning incidental C_{60} should more thoroughly investigate diesel as a source, as engine loads of only 0% and 90% were studied here. While not common in the United States, wood (or wood pellet) combustion is a common method of heating residential homes in Europe;³⁵ investigation of this potential source may be valuable. Lastly, as C_{60} is prone to oxidation at atmospherically relevant levels of ozone,³⁶ it remains uncertain how oxidation of C_{60} , when in a complex carbonaceous matrix to which the molecule could become oligomerized, may affect the extraction of C_{60} from that matrix. Differences in extraction efficiency caused by atmospheric oxidation could have significant implications for the environmental concentrations of incidentally produced C_{60} .

One important factor affecting the quantitative determination of C_{60} content of combustion materials is extraction efficiency. The C_{60} content of all ash samples was below the detection limit. Similarly, Benn *et al.*²² did not detect C_{60} in most of the tested solid (non-aerosol) phase soot samples, which were scraped from the relevant surface or otherwise collected in solid form: soot from a candle, shotgun, fireplace, fire pit, biomass burning chamber, and prescribed pine burn. They all had undetectably low C_{60} concentrations.²² While C_{60} was not detected in our ash samples, the $^{13}C_{60}$ extraction surrogate was also not detected. This substrate may be acting as a sink under the conditions encountered here. Strong sorption relationships exist among carbonaceous materials: polycyclic aromatic hydrocarbons (PAH) adsorb to carbon nanomaterials³⁷ and to black carbon.³⁸ Since urban soils may contain varying amounts of black carbon,³⁹ the extraction of C_{60} from either its carbonaceous aerosol matrix, or from soil to which the aerosol is deposited, may vary widely. Given the wide variety of matrices and particle sizes in which C_{60} (regardless of source) may enter a natural environment, assessing the potential ecological impact of engineered C_{60} is highly challenging.

4.2 Particle Structure

Lamella separation, visible in Fig. 2, may hold potential to serve as a fuel-specific fingerprint of soot particles.²⁶ The average lamella spacings measured in this work (0.38 – 0.41 nm, see Table 2) are comparable to those measured by van der Wal *et al.*²⁶ in soot from a variety of engines and oil boilers. In contrast, the spacings measured here are larger than those measured by Toth *et al.*⁴⁰ in soot from burning 3-6-ring feedstocks, and slightly smaller than those measured in diesel soot in the presence of an oxidation catalyst, as oxidation state can widen lamella separation.⁴¹ While C_{60} content in this work varied by over five orders of magnitude, lamella separation showed no distinguishable differences between aerosols derived from fuels that produce high C_{60} concentrations (diesel, coal) compared to those

that produce lower concentrations (wood, propane). Lamella spacing may serve as a source (fuel) marker for soot, but it does not appear to be suggestive of C₆₀ content.

Curvature of graphitic layers within soot may be quantified in several ways.⁴²⁻⁴⁴ Tortuosity is defined as the curved path length of a graphitic layer divided by the straight-line distance between the layer's endpoints,⁴⁵ and is the metric used here. This calculation results in tortuosity values ranging from 1 for a perfectly straight layer, or fringe, to infinity for a closed shape such as a circle. Lamella curvature (however termed) has been shown previously to correlate positively with fullerene content in soot generated during a fullerene synthesis process.⁴² This is because fullerenes are formed from graphene sheets that curve upon incorporation of five-membered rings. Aerosol samples from each of the fuels sampled here show no significant difference in tortuosity, as shown in Table 2.

Tortuosity distributions (Figure S2) show no notable differences among the four fuel types, except perhaps that propane combustion particles may exhibit a small number of higher-tortuosity graphitic layers. It is possible that this result depends on which microscopy images were selected for tortuosity measurement. While the correlation between tortuosity and fullerene content revealed by Goel *et al.*⁴² may in theory apply to soot containing incidentally produced fullerenes, the dramatic differences in concentration between a fullerene synthesizing flame⁴⁶ and these incidental sources (at least three orders of magnitude) likely means that an exhaustive TEM survey and image analysis effort would be required to observe the relationship, should it exist. As such, lamella tortuosity is likely not usable as a proxy for C₆₀ content in atmospheric aerosols from a practical perspective. Mass spectrometry, especially with recent methodological advances,^{11-14, 25, 28} still appears to be the most appropriate way to determine concentrations of C₆₀ in various environmental media.

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