



Review

Carbon black vs. black carbon and other airborne materials containing elemental carbon: Physical and chemical distinctions



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ARTICLE INFO

Article history:

Received 15 March 2013

Received in revised form

10 June 2013

Accepted 16 June 2013

Keywords:

Carbon black

Black carbon

Soot

Elemental carbon

Nanomaterial

ABSTRACT

Airborne particles containing elemental carbon (EC) are currently at the forefront of scientific and regulatory scrutiny, including black carbon, carbon black, and engineered carbon-based nanomaterials, e.g., carbon nanotubes, fullerenes, and graphene. Scientists and regulators sometimes group these EC-containing particles together, for example, interchangeably using the terms carbon black and black carbon despite one being a manufactured product with well-controlled properties and the other being an undesired, incomplete-combustion byproduct with diverse properties. In this critical review, we synthesize information on the contrasting properties of EC-containing particles in order to highlight significant differences that can affect hazard potential. We demonstrate why carbon black should not be considered a model particle representative of either combustion soots or engineered carbon-based nanomaterials. Overall, scientific studies need to distinguish these highly different EC-containing particles with care and precision so as to forestall unwarranted extrapolation of properties, hazard potential, and study conclusions from one material to another.

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1. Introduction

Carbon black (CB) is a manufactured product that has been in commerce for over a century. Consisting of a fine black powder of nearly pure elemental carbon (EC), it has numerous applications in a variety of commercial and consumer products. Its single largest use is as a reinforcing agent in vehicle tires and rubber automotive

Watson and Valberg (2001) demonstrated that CB and soot are physically and chemically distinct substances. CB is simply a quasi-graphitic form of nearly pure EC that is distinguished by its very low quantities of extractable organic compounds and total inorganics (generally <1% of each; IARC, 2010; McCunney et al., 2012; OECD, 2005; Wang et al., 2003; Watson and Valberg, 2001). In addition, CB has a characteristic particle morphology that consists of acini-

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factured by either partial combustion or thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions optimized to yield a variety of CB grades having specified ranges of properties (e.g., specific surface area, particle size and structure, conductivity, and color).

As discussed in a previous paper (Watson and Valberg, 2001), the terms carbon black and soot have often been used interchangeably despite the fact that soot by definition is an undesired byproduct of incomplete combustion of fossil fuels and biomass.

erates. In stark contrast, combustion soot is a highly heterogeneous substance that generally includes a major organic carbon fraction (oftentimes >50% of total mass) and significantly higher ash and extractable organic matter contents than carbon black. Its chemical and physical properties are highly variable depending on its source. As described previously by Watson and Valberg (2001), some soot forms such as diesel exhaust particulate (DEP) can have morphologies resembling the aciniform aggregates of carbon black, while other soots can exhibit significant variations in morphology.

Since the publication of the Watson and Valberg paper in 2001, there has been continued misuse of soot as a synonym for carbon black. In fact, the US National Library of Medicine's PubMed biomedical literature database uses soot as a MeSH (Medical Subject Headings) indexing term for carbon black. Adding to these errors in nomenclature, the term black carbon has gained widespread usage in recent years to describe light-absorbing carbonaceous aerosols that are now recognized as key climate-forcing agents (Andreae and

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Gelencsér, 2006). More specifically, black carbon has emerged as the leading term among climate modelers to describe the fraction of combustion-related carbonaceous aerosols that are strongly light-adsorbing (Bond and Bergstrom, 2005). Other terms like soot, elemental carbon, and graphitic carbon continue to be used synonymously with black carbon, although there are efforts to develop more precise nomenclature that distinguishes between these terms based on measurement techniques and light-absorbing properties (Andreae and Gelencsér, 2006; Bond and Bergstrom, 2005; Kupiainen and Klimont, 2004; US EPA, 2012). We will not enter this nomenclature debate, and for the purposes of this paper which is focused on differentiating CB from other airborne EC-containing materials, we will use the term black carbon (BC) particles as referring to EC-containing fine particles that are commonly found in ambient air due to emissions from incomplete combustion of fossil fuels and biomass. We will use the term black carbon rather than soot since there are other soot components that have little, if any, EC content; these include chars, coke-oven emissions, as well as a class of organic carbon-based particles, known as “Brown Carbon (BrC)”, that have received a great deal of recent research attention due to their light-absorbing properties (Andreae and Gelencsér, 2006; Kuhlbusch et al., 2009; US EPA, 2012). Termed brown carbon to reflect their characteristic brown appearance, BrC particles are found in the combustion soot of biomass and biofuels, and contain little, if any, elemental or black carbon (Andreae and Gelencsér, 2006; Chakrabarty et al., 2010).

Given the similarity in their names, it is not surprising that the terms carbon black and black carbon are often misused. Examples of the misuse of these terms are widespread in the scientific literature, including even in the March 2012 US Environmental Protection Agency (US EPA, 2012) Report to Congress on Black Carbon. Specifically, in Chapter 3 of this report that addresses black carbon effects on public health and the environment, US EPA referred to several studies (Tankersley et al., 2004, 2007, 2008) where laboratory animals were exposed to carbon black as providing evidence of the potential health effects of black carbon (BC). Confusing carbon black with black carbon, Büchner et al. (2013) repeatedly referred to ultrafine carbon black particles as being “one of the major constituents of air pollution”, stating that carbon black particles are “one of the major constituents of industrial and exhaust emissions” and that they are “produced not only by traffic and industry, but also in every household and office”. Similarly, Reisetter et al. (2011) referred to carbon black particles as being “found in many different environmental exposures” and as “a primary component in ambient pollution and diesel exhaust”. In a letter to the editor regarding the Reisetter et al. (2011) publication, Levy et al. (2011) clarified that these references would be more accurate for black carbon particles. As explained by Levy et al. (2011), unbound CB particles are not generally released into the environment from CB products like tires and other rubber products since they are tightly bound in product matrices. Other papers like Garza et al. (2008) and Murr (2008) have referred to “commercial black carbon”, which would appear to be a misnomer for “commercial carbon black” given that they refer to it as being a constituent of tires. To our knowledge, black carbon is not produced commercially.

Due to the continued misuse of soot and now black carbon as synonyms for carbon black (and vice versa), it is appropriate to update the Watson and Valberg (2001) analysis. Since the publication of this paper over ten years ago, there has emerged a greater understanding of the physical and chemical properties of the various forms of combustion-derived black carbon particles. This knowledge base has been improved as a result of the heightened efforts of researchers and regulators to better understand the climate-forcing properties and adverse health effects of black carbon (Janssen et al., 2011, 2012; UNEP, 2011; US EPA, 2012). In addition, with the

commercial development of several kinds of engineered carbon-based nanomaterials (e.g., fullerenes, single-walled and multi-walled carbon nanotubes, graphene) and the laboratory generation of ultrafine elemental carbon particles for toxicological study (e.g., spark-generated elemental carbon, SGEC; diffusion flame particles, DFP), the spectrum of carbonaceous particles is now broader than it was ten years ago. Since carbon black has gained usage as a test particle in numerous toxicology studies of various engineered nanomaterials including carbon nanotubes and fullerenes, there is a particular need to distinguish carbon black from engineered carbon-based nanomaterials. Focusing on physical and chemical characteristics, we thus examine how CB differs from black carbon and other EC-containing particles that might become airborne.

2. Overview of different airborne EC-containing materials

Table 1 summarizes some of the general differences between CB and other classes of airborne EC-containing materials. Below, we provide brief descriptions of each particle type, focusing in particular on their origins and sources and how we may come into contact with them. In subsequent sections, we focus on the physical and chemical properties of CB and contrast them to those of other airborne EC-containing materials.

2.1. Carbon black

CB is the name of a group of manufactured fine-particle products that have a variety of different trade names and physico-chemical properties, but share a chemical composition of nearly pure EC. CB has been commercially produced for over 100 years, and with 2008 worldwide production totaling approximately 9.8 million metric tonnes, it has been cited as one of the top 50 industrial chemicals manufactured worldwide (ICBA, 2004; McCunney et al., 2012). Rubber applications – tire-related automotive uses (tires, tubes, tread), rubber automotive products (e.g., belts, hoses, miscellaneous), and non-automotive industrial rubber products including industrial molded and extruded products – dominate worldwide CB use patterns, consuming approximately 90% of CB used in the US, Western Europe, and Japan (IARC, 2010; McCunney et al., 2012). The remaining 10% is divided among other special CB applications that include uses as a pigment, UV absorbing, and/or conducting agent in inks, coatings, and plastics (IARC, 2010; ICBA, 2004; McCunney et al., 2012; Wang et al., 2003).

The greatest potential for CB exposure is in CB manufacturing and its production, collection, and handling (IARC, 2010; McCunney et al., 2012). While CB continues to be manufactured via several well-established manufacturing processes (the oil furnace process, the thermal black process, the acetylene black process, the lamp black process, the channel black process, and the gas black process; for descriptions of each process, see McCunney et al., 2012; Wang et al., 2003), greater than 95% of both US and worldwide carbon black production is generated via the oil furnace process (IARC, 2010; McCunney et al., 2012; Wang et al., 2003). In the oil furnace process, heavy aromatic petroleum oils are pyrolyzed at extremely high temperatures (1400–1800 °C) to produce CB particles and tail gas (e.g., carbon monoxide, hydrogen, steam). As a continuous process that is conducted within a closed reactor, manufacturing conditions can be carefully controlled in the oil furnace process, such that a variety of carbon black grades with differing properties (e.g., surface area, aggregate size, structure, abrasion resistance, tint strength, etc.) can be produced. As discussed more later, furnace blacks and other carbon black products generally exist as complex particle aggregates and agglomerates in finished products rather than as free individual particles.

Table 1
General characteristics of the classes of elemental carbon-containing materials discussed in this article.

Class of Elemental Carbon-Containing Materials	Origin/Source	Starting Material	Approximate Elemental Carbon Content	Potentially Exposed Populations	References
Carbon Black (CB)	Large-scale commercially manufactured product via controlled combustion or thermal decomposition	Acetylene, natural gas, coal-tar residues, petroleum oils	>97% ^b	OCCUPATIONAL: Exposure is primarily to the aggregate and agglomerate forms at CB manufacturing plants and at user industries (e.g., tire manufacturers).	IARC, 2010; McCunney et al., 2012; Watson and Valberg, 2001
Ambient Air Black Carbon (BC) Particles	Unwanted byproduct from incomplete combustion or pyrolysis	Any carbon-containing material: waste oil, fuel oil, gasoline fuel, diesel fuel, coal, coal-tar pitch, oil shale, wood, paper, rubber, plastics and resins, or household refuse	Highly variable; oftentimes <50% ^b	ENVIRONMENTAL: Ubiquitous in the environment due to numerous anthropogenic and natural biomass burning sources.	US EPA, 2012; Watson and Valberg, 2001
Engineered Carbon-Based Nanomaterials (CNMs) (e.g., Fullerenes, Carbon Nanotubes Graphene-Family Nanomaterials ^a)	Smaller-scale commercially manufactured products and/or laboratory-scale materials; generated via a variety of methods, often involving metal catalysts	Hydrocarbon gases such as methane (e.g., for CNTs, fullerenes, graphene), graphite (for fullerenes, graphene)	Generally >90%, with the exception of unpurified CNTs and fullerenes ^b	OCCUPATIONAL: Highest exposures likely to occur during handling of dry powder, collection, weighing, blending, transferring to containers, bagging, and maintenance.	Aschberger et al., 2010; Bello et al., 2009; Donaldson et al., 2006; Sanchez et al., 2012
Laboratory-Generated Elemental Carbon Particles (e.g., Spark-Generated Elemental Carbon – SGEC; Diffusion Flame Particles – DFP)	Laboratory-scale particles generated either from graphite electrodes by spark discharge in anhydrous argon (SGEC), or from a diffusion flame (DFP)	Graphite electrodes or diffusion flame (fuels include ethylene gas, and a mixture of propane and air)	Variable depending on experimental conditions; generally >75% and potentially >90% ^b	HIGHLY LIMITED: Exposure is expected to be highly limited since particles are laboratory generated and not produced in significant commercial quantities.	Evans et al., 2003; Matuschek et al., 2007; Stoeger et al., 2006; Van Winkle et al., 2010

^a Adopting the nomenclature of Sanchez et al. (2012), Graphene-Family Nanomaterials (GFN) refers to a number of related, but physically and chemically different graphene materials, including few-layer graphene (FLG), ultrathin graphite, graphene oxide (GO), reduced graphene oxide (rGO), and graphene nanosheets (GNS).

^b See Table 2 for sources of this range.

Occupational CB exposures can also occur to workers in downstream user industries, such as in rubber manufacturing, ink manufacturing and printing, paint manufacturing, paper, plastics, ceramics, battery production, carbon electrode production, and in metallurgical processes like carburization (McCunney et al., 2012; OECD, 2005). Although CB is used in a number of common consumer products, IARC (2010) concluded that: “Exposure to [free, unbound] carbon black does not occur during the use of products in which carbon black is bound to other materials, such as rubber, printing ink or paint”. Consistent with this IARC conclusion, US EPA (2005) stated that: “There is a safe history of carbon black when used in tires, plastics, automotive components, inks, adhesives, paints, dyes and ceramics”. These conclusions regarding the low likelihood of significant CB exposure from consumer product usage are based on the fact that CB is generally bound within a product matrix – i.e., within the rubber of a tire. Even in toners used for photocopying machines or inks used in inkjet printers, CB is part of a matrix from which it is not liberated; moreover, such a matrix typically is contained within a sealed system of cartridges. As stated by OECD (2005), CB exposure associated with toner usage is expected to be insignificant under normal use conditions.

Finally, it is important to distinguish CB, which is produced from petrochemical feedstocks, from vegetable carbon products (also referred to as vegetable black) that are produced from materials of plant origin, including wood, cellulose residues, peat, and coconut and other shells. In addition to their different source materials, commercial vegetable carbon products have markedly larger characteristic particle size distributions than CB that are distinguished by the general absence of particles with diameters of less than 275 nm (EFSA, 2012).

2.2. Black carbon (BC)

Black carbon (BC) is a collective term that describes a range of carbonaceous substances from partly charred plant residues to highly graphitized (i.e., highly ordered molecular carbon structures as found in graphite) soot that are generated as products of incomplete combustion (Shrestha et al., 2010). In contrast to CB, there is no universally accepted chemical definition of the term “black carbon”, and it is oftentimes referred to as soot, graphitic carbon, and/or elemental carbon. Some definitions proposed for black carbon have focused on its chemical and/or physical properties (e.g., its light-absorbing properties), while others are operationally based and reflect the results of measurement and estimation approaches (Janssen et al., 2012; Kupiainen and Klimont, 2004; US EPA, 2012). For example, Andreae and Gelencsér (2006) define BC as “soot carbon” and “an impure form of near-elemental carbon with a graphite-like structure, which is formed in flaming combustion and in internal combustion engines”. Andreae and Gelencsér (2006) further define “Equivalent Black Carbon (BCE)” as “the amount of strongly light-absorbing carbon with the approximate optical properties of soot carbon that would give the same signal in an optical instrument (e.g., the aethalometer) as the sample”. In its recently finalized Report to Congress on Black Carbon, US EPA (2012) defines BC as the “carbonaceous component of PM that absorbs all wavelengths of solar radiation” (hence, the appropriateness of the term “black”). In its 2012 report, the Joint World Health Organization (WHO)/Convention Task Force on Health Aspects of Air Pollution similarly describes BC as “an operationally defined term which describes carbon as measured by light absorption” (Janssen et al., 2012).

BC particles are ubiquitous in urban and rural air, such that we are all routinely exposed to BC in ambient air from a variety of sources. As shown in Fig. 1, global BC emissions are estimated to be around 7600 Gigagrams (Gg; equivalent to 10^9 grams, or 1 kilotonne), with US emissions representing about 7.6% of this estimate, or approximately 580 Gg (US EPA, 2012). There is a diverse assortment of both anthropogenic and natural sources of ambient air BC particles, which thus typically include a complex mixture of materials. Anthropogenic sources include mobile and stationary diesel engines (particularly older engines), and to a lesser extent, spark-ignition (gasoline) engines; fossil fuel-based electric utility generating units (EGUs) and other power generation sources; industrial/commercial boilers; residential combustion sources, such as oil furnaces, fireplaces, and woodstoves in developed countries, and simple cookstoves and open fires in developing countries; and open biomass burning sources such as agricultural burning and prescribed forestry burning (Janssen et al., 2012; US EPA, 2012). In general, both mobile and stationary source emissions of black carbon are declining in many developed countries due to regulations relating to engine emission standards, cleaner fuels, and PM_{2.5} reduction technologies such as fabric filters (baghouses), electrostatic precipitators, and diesel particulate filters (US EPA, 2012). Wildfires are the dominant natural source of black carbon.

As discussed more later, BC particles have variable chemical compositions depending on their sources, sometimes being primarily EC, but often existing as complex mixtures of EC, organic carbon (OC), and other non-carbon species such as ionic species and trace metals.

2.3. Engineered carbon-based nanomaterials (CNMs)

Engineered carbon-based nanomaterials (CNMs) such as fullerenes (also commonly referred to as buckminsterfullerenes and buckyballs, with C₆₀ being a prototypical fullerene) and carbon nanotubes (CNTs) are among the more prominent engineered

carbon-based nanomaterials commercialized to date based on current applications and potential for widespread use (Hendren et al., 2011). Graphene has also garnered recent attention due to its unique electronic properties. As discussed below, each of these materials can be found in nanoparticle forms that have all three external dimensions at the nanoscale (i.e., between 1 and 100 nm). Note that other CNMs, such as carbon nanohorns, nanodiamonds, and nano-onions (i.e., multi-layer fullerenes), have also been discovered; however, they are not as far along in terms of their commercial development as fullerenes and CNTs, or projected to have the same revolutionary applications as graphene, and are thus not considered further.

Kroto and Smalley are credited with discovering the C₆₀ fullerene in 1985, and C₆₀ fullerenes are now recognized by chemists as one of the three forms of true EC (along with graphite and diamond) (Bond and Bergstrom, 2005). Combustion methods have been developed for mass-production of fullerenes, and they are projected to have far-reaching applications in such areas as photovoltaics, water treatment, materials science and optics, and biological applications such as imaging probes and drug carriers (Hendren et al., 2011). Based on production estimates from the recent Hendren et al. (2011) study, annual US production of fullerenes (lower and upper bounds of ~2–~70 metric tonnes per year, respectively) is a very small fraction of annual US commercial CB production (~10 million metric tonnes per year).

Carbon nanotubes (CNTs) are generally classified by the number of walls in the final structure, and include single-walled carbon nanotubes (SWCNT), double-walled carbon nanotubes (DWCNT), and multi-walled carbon nanotubes (MWCNT). CNTs can be open-ended, or closed with a hemispherical cap resembling half of a fullerene molecule. In addition to variations in their wall number, CNTs can be further classified by a variety of properties, including their length, shape, electric charge, surface modification, purity, and propensity to form agglomerates and aggregates (Aschberger et al., 2010). Several different methods have been developed for

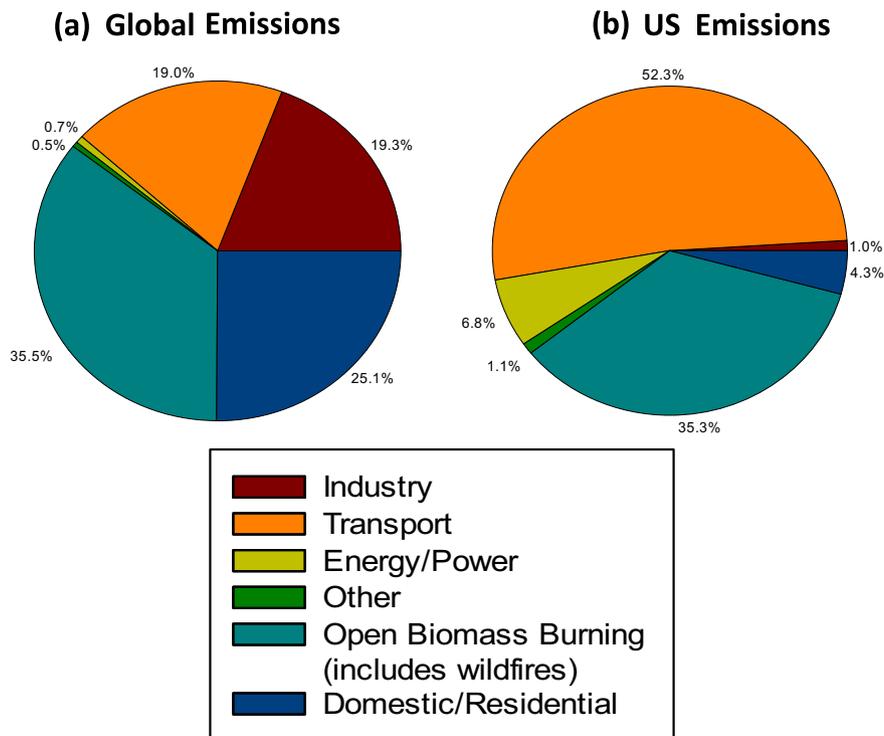


Fig. 1. Black carbon emissions estimates by major source category. Panel (a) shows global black carbon emissions (7600 Gg total; 2000 estimate), while Panel (b) shows US black carbon emissions (581 Gg total; 2005 estimate). All data from US EPA (2012).

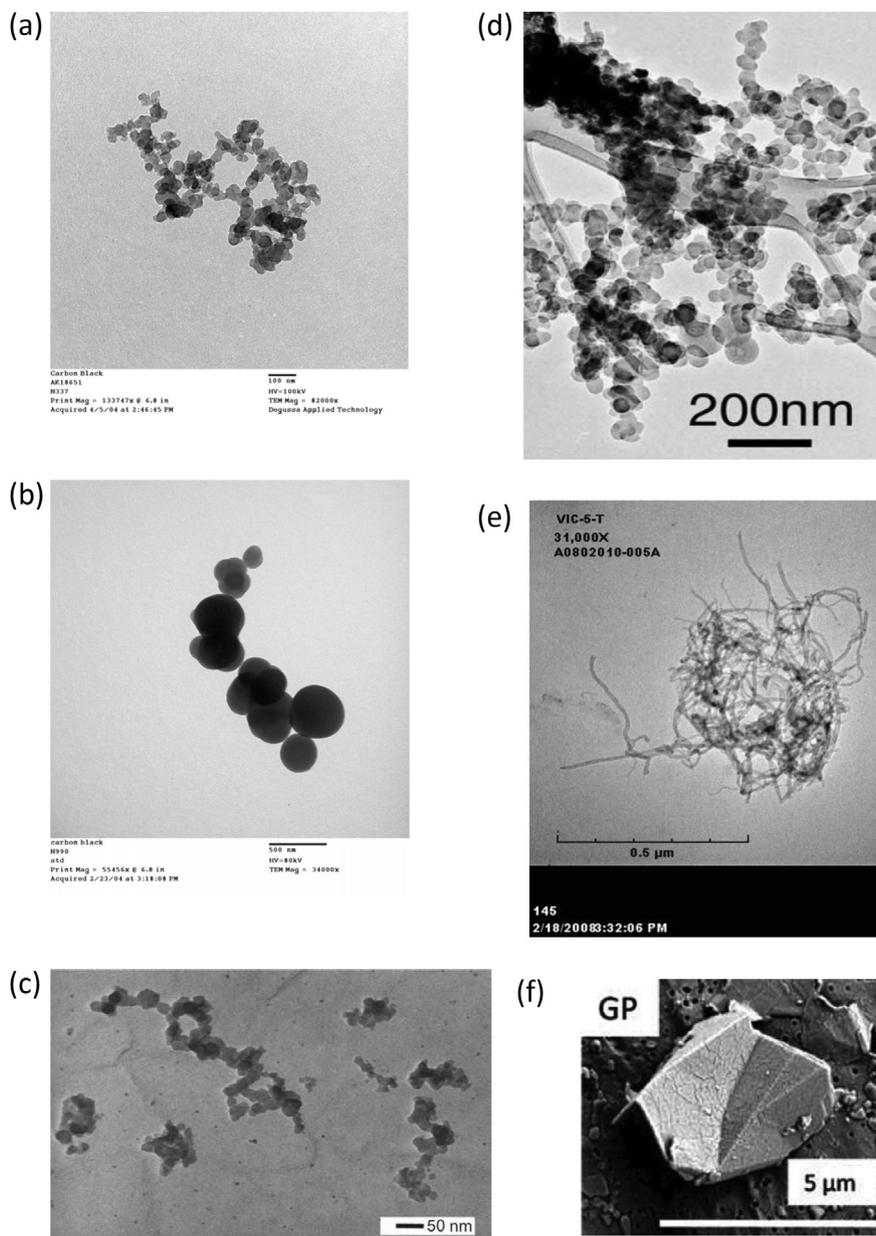


Fig. 2. TEM images of different types of elemental carbon-containing particles. Panel (a): N337 furnace black agglomerate (provided by Evonik Degussa GmbH); Panel (b): N990 thermal black (provided by Evonik Degussa GmbH); Panel (c): diesel exhaust particulate (Reprinted with permission from Shi et al. (2000). Copyright 2000 American Chemical Society); Panel (d): biomass smoke particles (Reprinted with permission from Pósfai et al. (2004). Copyright 2004 John Wiley and Sons); Panel (e): MWCNTs (from NIOSH, 2009); Panel (f): a graphene nanoplatelet (Reprinted with permission from Schinwald et al. (2012). Copyright 2012 American Chemical Society). Note that these images are not representative of the range of properties exhibited by these particle types (i.e., the size of the graphene nanoplatelet shown in (f) is not representative of the size of all graphene nanomaterials).

synthesis of CNTs, including arc discharge, chemical vapor deposition (CVD), and laser ablation (Donaldson et al., 2006). Their current commercial applications range from uses in a number of common consumer products (e.g., sporting goods, car parts, textiles) to applications in electronics, polymer composites, thermoplastics, coatings, and adhesives. Although US annual production of CNTs is estimated to be approximately 10–30 times that of fullerenes (Hendren et al., 2011), annual US production of CNTs (lower and upper bounds of ~50–~1000 metric tonnes per year, respectively) still remains a small fraction of annual US commercial CB production.

As with other engineered nanomaterials, there is the potential for unintended human exposures to fullerenes and CNTs from consumer products and environmental releases; however, the

greatest potential for human exposure is assumed to be for occupational workplaces like manufacturing facilities and research laboratories (NIOSH, 2009; Ramachandran et al., 2011). CNTs are currently used in a variety of everyday consumer goods such as sporting goods (e.g., tennis rackets, golf clubs, baseball bats) and car parts (e.g., bumpers and other plastic parts), but it is expected that any general population exposures to CNTs from use of these products are very low due to incorporation of the CNTs within solid product matrices (Aschberger et al., 2010). Interestingly, some researchers have reported the presence of fullerenes and CNTs in ambient air and indoor air samples, concluding that they are generated at low levels from common flame combustion sources such as natural gas kitchen burners and automobile exhaust (Lagally et al., 2012; Aschberger et al., 2010; Murr, 2008).

Table 2
Physical–chemical characteristics of various elemental carbon-containing materials.

Physical–Chemical Properties	Carbon Black (CB)	Ambient Air Black Carbon (BC) Particles				
		Diesel Exhaust Emissions (DEE) [Representative of 1990s-era Diesel Engine Technology]	Spark-Ignition (SI) Gasoline Engine Exhaust [Representative of Catalyst-Equipped 1990s-era Engines]	Open Biomass Burning Emissions	Biomass Fuel Combustion Emissions [Fuels representative of developing world regions – e.g., wood, crop waste, dried cattle dung]	Residential Wood-burning Emissions [Appliances representative of developed countries – e.g., domestic fireplaces, woodstoves]
<i>Morphology</i>						
General Morphology (shape, form)	Typically found in the form of aciniform aggregates and agglomerates, with aggregates being smallest indivisible entity ^{1,2,3,4}	Complex chains, aggregates, and agglomerated spherical particles ^{5,6}	Chain-like agglomerates, single particles with complex shapes ⁷	Chain aggregates, solid irregulars, liquid/spherical shapes ⁸	Dominant fraction of spherical organic carbon particles, lesser amounts of solid carbon aggregates (soot) and inorganic ash particles ⁹	Typically dominated by spherical organic carbon particles and solid carbon aggregates (soot), lesser fraction of sphere-like inorganic ash particles ⁹
Primary Particle Size (nm)	Typical diameters of ~15–300 nm ³	15–40 nm ^{5,6,14}	20–60 nm ⁷ ; <20 nm ¹⁵	Count median diameters in the range of 100–160 nm ⁸	Estimated count median diameter on the order of 150 nm ¹⁶	Solid carbon particles (soot): 20–50 nm; spherical organic carbon particles: 50–600 nm; inorganic ash particles: 50–125 nm ^{9,17}
Aggregate/Agglomeration State and Sizes	Aggregates with typical diameters between ~85 and 500 nm and agglomerates with typical diameters of ~1 µm up to 100+ µm ³	Agglomerate sizes ranging from several tens of nm to microns, with mean number diameters in the range of 60–100 nm ^{5,6}	100–300 nm ^{7,22}	Carbon and ash aggregates can form, with ash aggregates ranging in size up to a mm or more ⁸		Solid carbon aggregates that consist of tens to thousands of spherical primary particles: 50–300 nm ^{9,17}
<i>Chemical Composition</i>						
Total Carbon (TC) Content (%)	97–>99% ^{1,19}	~50–>90% ²⁵ ; 54–77% ⁵	63% ²⁶	~50–70% ^{8,27}	45–55% ¹⁶	28–62% ²⁸ ; median of 58% ²⁷ ; mean of ~83% ¹⁷
Elemental Carbon (EC) Content (% of Total Mass except where indicated to be % of Total Carbon (TC))	>97% ^{1,20}	Avg. 75%, range of 33–90% ²⁵ ; 25–52% ⁵	~25% for hot-stabilized engines, ~42% for cold-starts, and ~7% for smokers and high emitters ²⁵ ; ~10% ²⁶ ; ~20–50% ¹⁵	~8% ⁸ ; 2–10% ²⁷	2–35% ¹⁶	0.65–79%, but generally 5–20% ³¹ ; 3–38% ²⁸ ; median of 6% ²⁷ ; mean of ~47% ¹⁷
Organic Carbon (OC) Content (% of Total Mass except where indicated to be % of Total Carbon (TC))	<1% ²⁰ ; <2% ¹⁴	Avg. 19%, range of 7–49% ²⁵ ; 20–48% ⁵ ; 20% ¹⁴	~56% for hot-stabilized engines, ~46% for cold-starts, and ~76% for smokers and high emitters ²⁵ ; ~44% ²⁶	~55% ⁸ ; 40–71% ²⁷	21–50% ¹⁶	12–100% ³¹ ; 10–59% ²⁸ ; median of 53% ²⁷ ; mean of ~35% ¹⁷
Hydrogen to Carbon (H/C) Ratio	<0.008 ¹ ; 0.006 ³²	0.041 ³²				0.112 ³²
Trace Inorganic Species Content (%)	<1% ¹ ; below limit of detection ¹⁹	Avg. 2%, range of 1–5% ²⁵	~3% ²⁶ ; <5% ¹⁵	~<10% ⁸	2–12% ¹⁶	0.01–4% ³¹ ; <6% ⁹ ; 0.3–21% ²⁸
Solvent-Extractable Organic Matter (SEOM) (%)	0.02–0.14% ² ; <0.1% ³²	20% or less ²⁵ ; ~36% ³²				~35% ³²
Total PAH content (mg/kg)	~200–700 ² ; <0.01 ³⁴ ; 0.1–330 ³⁵ ; 0.075 ¹⁹	Up to about 10,000 ²⁵ ; 240–400 ⁵ ; ~85 ³⁴	226 ²⁶ ; <3–~3000 ³⁶	<10,000 ⁸		3200–4000 ⁹ ; 5.1–32,000 for particle-phase and 43.4–355 for vapor-phase ³¹ ; 9745 ¹⁷ ; ~8 ³⁴
<i>Additional Physicochemical Properties</i>						
Surface Area (m ² /g)	12–240 ^{1,2} ; 156.2 ³² ; 30–300 ¹⁴	30–90 ²⁵ ; 108 ^{14,32}				0.9 ³²
Density (g/cm ³)	1.76–1.90 ¹ ; 1.7–1.9 ³	1.5 ²⁵ ; <1–1.4 ⁵	1.42–1.82 ²²	1.20–1.4 ⁸		

¹Wang et al. (2003), ²IARC (2010), ³ICBA (2004), ⁴Gray and Muranko (2006), ⁵Shi et al. (2000), ⁶Burtscher (2005), ⁷Chakrabarty et al. (2006), ⁸Reid et al. (2004), ⁹Kocbach Bølling et al. (2009), ¹⁰Bond et al. (2006), ¹¹Sanchez et al. (2012), ¹²Evans et al. (2003), ¹³Van Winkle et al. (2010), ¹⁴Stoeger et al. (2006), ¹⁵McDonald et al. (2008), ¹⁶Habib et al. (2008), ¹⁷Kocbach et al. (2006), ¹⁸Aschberger et al. (2010), ¹⁹Jacobsen et al. (2009), ²⁰Bello et al. (2009), ²¹Matuschek et al. (2007), ²²Robert et al. (2007), ²³Donaldson et al. (2006), ²⁴Roth et al. (2004), ²⁵US EPA (2002), ²⁶Schauer et al. (2002), ²⁷US EPA (2012), ²⁸Rau (1989), ²⁹Plata et al. (2008), ³⁰Ferge et al. (2006), ³¹Naehner et al. (2007); ³²Fernandes et al. (2003), ³³Schinwald et al. (2012), ³⁴Fernandes and Brooks (2003), ³⁵Borm et al. (2005), ³⁶Schauer et al. (2008), ³⁷Lu et al. (2006).

Graphene is constructed from single-atom, two-dimensional sheets of hexagonally arranged carbon atoms, which were first isolated from three-dimensional graphite in 2004 (Sanchez et al., 2012). It can be found in a variety of forms, including as mono-

layer graphene (often simply referred to as graphene), platelets consisting of stacks of 2–10 graphene layers (known as few-layer graphene), ultrathin graphite, graphene oxide, reduced graphene oxide, and graphene nanosheets. Sanchez et al. (2012) have termed

Engineered Carbon-Based Nanomaterials (CNM)					Laboratory-generated ultrafine elemental carbon particles	
Industrial Boiler Emissions [Modern boiler burning natural gas and/or fuel oil]	Single-Walled Carbon Nanotubes (SWCNT)	Multi-Walled Carbon Nanotubes (MWCNT)	Fullerenes	Graphene-Family Nanomaterials (GFN)	Spark-Generated Elemental Carbon (SGEC)	Diffusion Flame Particles (DFP)
Fractal-aggregate particles ¹⁰	Fiber-shaped, consisting of single tube of graphene rolled into a seamless cylinder	Fiber-shaped, consisting of many single-walled tubes stacked within each other	Closed-cage structures of 20 or more carbons, with C60 being a typical fullerene	Produced in several different forms, including a single one-atom-thick, two-dimensional sheet of hexagonally arranged carbon atoms (mono-layer graphene, or graphene), and 2–10 graphene sheets with a platelet-like shape (few-layer graphene, or FLG) ¹¹	Consists primarily of ultrafine aggregates and agglomerates, but includes some more complex chain-like structures ¹²	Consists of round primary particles formed into larger fractal aggregates ¹³
5–200 nm ¹⁰	Diameter: ~1–5 nm; length: ~1 nm – ~1 mm ¹⁸	Diameter: ~5–50 nm; length: up to >1 μm ¹⁸	For C60: 0.7 nm ¹⁹ ; >20 nm ²⁰	Graphene: 0.34 nm thickness; FLG: average diameter of 5000 nm and average thickness of 10 nm ¹¹	5–50 nm ¹² ; 7–12 nm ^{14,21}	8–16 nm ^{14,21} ; 20–40 nm ¹³
	Known to form complex bundles and ropes consisting of tens of tubes and greatly increasing both length and width ^{18,23}	Known to form complex bundles and ropes consisting of tens of tubes and greatly increasing both length and width ^{18,23}	C60 reported to form aggregates and agglomerates larger than 1 μm in suspensions ¹⁹		Aggregate-agglomerate size reflected in reported mean diameters in the range of 50–80 nm, some as large as 4 μm ¹² ; count median (mobility) diameter of ~90 nm ²¹ ; modal diameters of 25–150 nm ²⁴	Aggregate-agglomerate size reflected in reported count median (mobility) diameter of ~90 nm ²¹ and geometric mean (mobility) particle size of 192 nm ¹³
Residual oil: ~50% ¹⁰ ; distillate oil: 35% ²⁷ ; natural gas: 63% ²⁷ Residual oil: 38% ¹⁰ ; distillate oil: 38% ²⁷ ; natural gas: 10% ²⁷	>85% ²³ ; 60–97% ²⁹ ; ~95% ¹⁹	>85% ²³	For C60: 99.9% ¹⁹	Assumed to be high (e.g., >95%) due to use of graphite parent material	>~95% ²⁴ ; ~80% ³⁰	73–87% ³⁰
	87–98.9% of TC ²⁰	91.3–97.9% of TC ²⁰	49–65% of TC ²⁰	Assumed to be high (e.g., >95%) due to use of graphite parent material	~75–94% ²⁴ ; ~70% ³⁰	~90% of TC ¹³ ; 54–83% ³⁰
Residual oil: 15% ¹⁰ ; distillate oil: 25% ²⁷ ; natural gas: 25% ²⁷	1.1–13% of TC ²⁰	2.1–8.7% of TC ²⁰	35–51% of TC ²⁰	Assumed to be low (e.g., <1%) due to use of graphite parent material	<5% ²¹ ; 17% ¹⁴ ; ~10% ³⁰	7–19% ¹⁴ ; ~10% of TC ¹³ ; <1–18% ³⁰
Residual oil: <50% ¹⁰	Up to 15% residual metal ²³ ; ~2% ¹⁹ ; 1.3–4.1% in purified SWCNTs and 14–29% in unpurified SWCNTs ²⁹ ; ~0.5–0.6% ²⁰ For purified SWCNTs, <1% in dichloromethane, <5% in toluene ²⁹	Up to 15% residual metal ²³ ; 0.5–5.3% ²⁰	Negligible ²⁰	Negligible ³³	<0.002% (based on ash content of graphite parent material) ¹²	
Residual oil: ~30% ¹⁰	0.4 ¹⁹ ; up to ~155 based on data for 8 PAH species ²⁹		0 (i.e., below the level of detection) ¹⁹			110 ¹³
	~1300 theoretical value for discrete tubes, but ~300 or less in practice due to bundling ²³ ; 342.9–510.5 ²⁰ 1.7–2.1 ³⁷	Few hundred ²³ ; 99.7–229.1 ²⁰	For C60: <20 ¹⁹ ; 0.2–1.3 ²⁰	Mono-layer graphene: theoretical maximum of 2600 ¹¹ ; FLG: in practice ~100 ³³	300–900 ¹² ; 807 ¹⁴ ; 750 ²⁴	268–441 ¹⁴
		2.1 ³⁷		FLG: ~2 ³³	1.78 ¹²	

this collection of graphene-related materials as Graphene-Family Nanomaterials (GFNs).

Although GFNs are projected to have a diverse set of potential engineering applications (e.g., microchip components, structural composites, conducting polymers, battery electrodes,

supercapacitors, transport barriers, printable inks, antibacterial papers, biomedical technologies), they remain highly expensive to produce and largely a subject of research and development (R&D) rather than commercial development at the current time (Sanchez et al., 2012). Potential human exposures to GFNs are thus assumed

to be primarily limited to academic laboratories and commercial R&D facilities.

2.4. Laboratory-generated ultrafine elemental carbon particles

Laboratory-generated ultrafine elemental carbon particles are yet another distinct form of airborne EC-containing materials. They include DFP generated from burning a mixture of air and a hydrocarbon fuel source (e.g., propane, natural gas, etc.), and SGEC particles produced from spark generators operated using graphite electrodes and argon gas. Both DFP and SGEC particles are commonly referred to as ultrafine carbon particles since their particle size distributions are dominated by particles with diameters of less than 100 nm (Brown et al., 2000; Evans et al., 2003; Roth et al., 2004; Van Winkle et al., 2010). Typically, these particles are used in controlled laboratory studies (e.g., fine-particle physics or toxicology studies) when a uniform diameter and specific surface area are required (see Evans et al., 2003; Roth et al., 2004; Stoeger et al., 2006). Thus, the overall scale of production of DFP and SGEC and the potential for human exposure are highly limited, as these particle types are not produced in any significant quantity for commercial applications.

3. CB physical properties vs. other EC-containing materials

Fig. 2 shows transmission electron microscope (TEM) images of several of the different kinds of EC-containing particles discussed above. Recognizing that these images are not representative of the wide range of properties exhibited by these particle types (i.e., the size of the graphene nanoplatelet shown in Fig. 2(f) is not representative of the size of all graphene nanomaterials), they nonetheless illustrate some similarities in structure (e.g., carbon black and diesel exhaust particulate), as well as large differences (e.g., carbon black vs. MWCNTs and graphene). Below, we explain in detail the intricacies of CB morphology as it exists in CB products (i.e., outside the production reactor), focusing primarily on furnace black but also noting some differences in morphology for other CB types (e.g., thermal black). We next contrast CB physical properties with those of other EC-containing particles. In support of this analysis, we prepared a compilation (Table 2) of published data on the physicochemical properties of CB, ambient air BC particles, CNMs, and other EC-containing particles. Although we have attempted to include data from multiple literature sources to reflect some of the variability in the physicochemical properties reported for these classes of particles, it is also important to note that differences in sample collection and measurement techniques between studies also contribute to some of the variability indicated in the table. In addition, there are differing amounts of properties data available for the different particle types; in particular, CB and DEP are examples of highly-studied EC-containing particles with an abundance of properties data in the scientific literature, while far fewer data are available for CNMs and even for BC particles from gasoline engines. As noted by McDonald et al. (2008), gasoline engine emissions have received relatively limited study, especially compared to diesel engine emissions, despite the fact that they can be dominant sources of ambient carbonaceous particulate matter in urban areas.

3.1. CB morphology and particle size dimensions

By way of the well-studied carbon black manufacturing process and extensive materials characterization data, CB is known to consist predominantly of particle aggregates and agglomerates having sizes exceeding 100 nm and ranging up to hundreds of microns (Figs. 2(a) and 3) (McCunney et al., 2012; Wang et al., 2003). In fact, due to its structure of aciniform (grape-like)

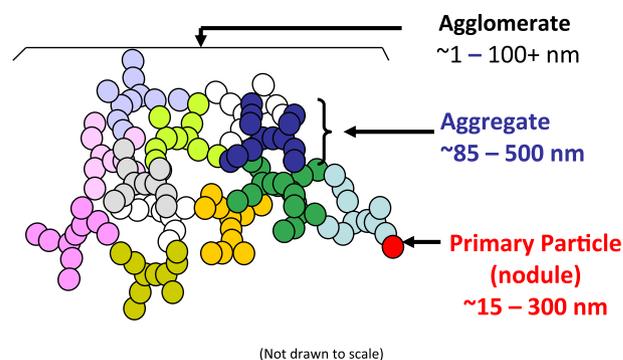


Fig. 3. Structure of carbon black. (Adapted with permission from Gray and Muranko (2006). Copyright 2006 Lippincott Williams & Wilkins, Inc.) Size ranges represent approximate diameters of typical CB structural entities, as reported in ICBA (2004).

aggregates, CB is a member of the class of substances known as Industrial Aciniform Aggregates (IAA), which also include precipitated amorphous silica, pyrogenic silica, titania, and pyrogenic alumina. For these substances, the aggregate is widely regarded as the smallest indivisible entity; this is supported by the ASTM International (2005) definition for a carbon black aggregate: “a discrete, rigid, colloidal mass of extensively coalesced particles; it is the smallest dispersible unit”. Based on a review of the physical characteristics of commercial CB and findings from experimental studies of the robustness of CB aggregates and similarly structured materials such as titanium dioxide in both high-energy artificial systems and biologic systems (e.g., Creutzenberg et al., 2012; Gray and Muranko, 2006; Maier et al., 2006; Porter et al., 2008; NanoCare, 2009), Levy et al. (2012) recently concluded that the available evidence indicates that CB aggregates do not break down into smaller aggregates or primary particles in lung fluid.

Primary carbon black particles (also known as nodules) with typical diameters in the range of 15–300 nm are the basic building blocks of commercial CB products (ICBA, 2004; Levy et al., 2012). Composed of randomly stacked, concentric sheets of condensed aromatic ring systems (i.e., graphite platelets), CB primary particles are distinguished by their so-called turbostratic arrangement (Wang et al., 2003). Importantly, CB primary particles generally exist only within the production reactor vessel due to the rapid and irreversible formation of fused aggregates within which the fused primary particles no longer have discrete physical boundaries (Gray and Muranko, 2006; ICBA, 2004; McCunney et al., 2012). As reflected in Fig. 3, typical CB aggregates are reported to have approximate diameters in the range of ~85–500 nm (ICBA, 2004; Levy et al., 2012). In contrast to other CB products, thermal blacks (N990 Series) can contain some discrete primary particles interspersed among aggregates (see Fig. 2(b)); however, as reflected in Table 3, primary particles produced via the thermal black process have characteristic diameters of greater than 100 nm that thus fall outside the nano-size region. Table 3 shows how different CB grades have characteristic primary particle and aggregate sizes, as well as surface areas that span more than an order of magnitude.

As reflected in Fig. 3, once both nodule formation and aggregation have ceased, larger clusters known as agglomerates are typically formed, ranging in diameter from approximately 1–100+ μm (ICBA, 2004; Levy et al., 2012; McCunney et al., 2012). CB agglomerates generally consist of tens to thousands of strongly adhering aggregates held together by van der Waals forces rather than chemical bonds (ICBA, 2004; Kuhlbusch and Fissan, 2006; McCunney et al., 2012). Although agglomerates can be viewed as temporary structures due to the absence of chemical bonds or welding that hold aggregates together, Gray and Muranko (2006) concluded that both experimental evidence and particle size

Table 3
Summary of carbon black morphology for different CB grades (data from Wang et al., 2003).

ASTM designation	Primary Particle Size, $D_{wm}^{a,b}$ (nm)	Aggregate Size $D_{wm}^{a,b}$ (nm)	D_{st}^c (nm)	Surface area ^a (m^2/g)
N110	27	93	76–111	143
N220	32	103	95–117	117
N234	31	109	74–97	120
N326	41	108	98	94
N330	46	146	116–145	80
N339	39	122	96–125	96
N351	50	159	127	75
N375	36	106	91	105
N550	93	240	220–242	41
N660	109	252	227–283	34
N774	124	265	261	30
N990	403	593	436	9

^a Measured by TEM.

^b D_{wm} = weight mean diameter = $\frac{\sum nd^4}{\sum nd^3}$.

^c D_{st} = Stokes diameter by centrifugal sedimentation from various sources.

measurements at CB manufacturing plants support the persistence of large CB agglomerates under typical manufacturing and use conditions. In particular, Kuhlbusch et al. (2004) measured particle size distributions at several carbon black manufacturing plants, demonstrating that airborne carbon black in bagging areas has a minimum size distribution larger than $\sim 0.4 \mu m$ and is dominated by micron-sized particles. As a result, CB agglomerates are considered to represent the predominant carbon black entity at CB manufacturing plants (Gray and Muranko, 2006; ICBA, 2004; McCunney et al., 2012). As a final processing step to reduce dust generation and facilitate shipping and handling, CB agglomerates are often pelletized into large grains, with diameters falling between 100 and 1000 μm (ICBA, 2004; Kuhlbusch and Fissan, 2006).

3.2. CB vs. ambient air BC particles

As indicated by the TEM images in Fig. 2(a), (c), and (d), there can be similarities between the morphology of CB and ambient air BC particles. In particular, diesel exhaust particulate (DEP) emitted by traditional diesel engines (i.e., pre-2007 diesel engine technologies; see Hesterberg et al. (2011) for discussion of the physical and chemical changes to DEP from post-2006 on-road diesel engine technologies equipped with diesel oxidation catalysts and diesel particulate filters and operated using ultra-low sulfur diesel fuel) is well-known to form complex chains and agglomerates of spherical primary particles. Diesel exhaust primary particles, which have solid EC cores, tend to have smaller diameters than many primary CB particles (15–40 nm for DEP vs. typical CB primary particle diameters of 15–300 nm; see Table 2). Given their similar morphological structures composed of aggregated nano-sized primary particles, DEP and CB can both have high surface area per mass values (Table 2). However, a notable difference between CB morphology and that of DEP involves the layer of volatile and semi-volatile hydrocarbons and sulfates that typically lies atop of the solid EC cores of DEP (Kittelton, 1998; Shi et al., 2000; US EPA, 2002); this surface layer contributes to the significant differences in chemical composition between CB vs. DEP that are discussed in the next section.

In addition to DEP, BC particles from biomass combustion are another example of BC particles that can be commonly found in the form of chain-like aggregates of spherical primary particles (Chakrabarty et al., 2010; Kocbach et al., 2006; Kocbach Bølling et al., 2009). Kocbach Bølling et al. (2009) described one form of residential woodsmoke particles as consisting of complex aggregates of tens to thousands of spherical 20–50 nm diameter primary carbon particles; as shown in Table 2, these aggregates are reported to have diameters in the range of 50–300 nm. Based on TEM

micrographs, Kocbach et al. (2006) concluded that primary particles in residential woodsmoke had turbostratic microstructures (i.e., concentric carbon layers) similar to those reported for CB.

Due to large variability in fuel properties and combustion conditions (e.g., temperature, residence time), BC particles from biomass burning can also be found in a variety of other forms that are strikingly different from CB morphology. In particular, Kocbach Bølling et al. (2009) reported that woodsmoke particles can also contain spherical particles with high organic carbon (OC) contents, as well as sphere-like particles with high ash contents. Reid et al. (2004) reported that particle emissions from open biomass burning sources include a mixture of chain aggregates, solid irregulars, and liquid/spherical shapes. Similar to what has been reported for DEP, Reid et al. (2004) also cited evidence showing biomass smoke particles to consist of “semi-spherical/semi-liquid droplets with solid complex cores”. Fernandes et al. (2003) reported only a minor fraction of aciniform carbon-containing aggregates for chimney soot from residential wood-burning. Instead, they observed a significant fraction of large (>1 micron) liquid-like agglutinated structures that lacked well-defined boundaries, as well as hard-edge planar structures. Although few surface area data were identified for woodsmoke particles, Fernandes et al. (2003) reported a very low surface area (0.9 m^2/g) for their wood-burning chimney soot sample; as shown in Table 2, this is below even the low-end of reported surface areas for CB.

Recent studies have probed the atomic structure of environmental BC particles, allowing comparisons to the turbostratic arrangement of CB primary particles (Hays and Vander Wal, 2007; Müller et al., 2007). For example, Müller et al. (2006) reported evidence of substantially higher graphitization of a commercial CB sample vs. a DEP sample, with the latter containing a greater fraction of carbon of an aromatic nature. Following up on this study, Müller et al. (2007) used high-resolution transmission electron microscopy (HRTEM) to identify graphene-like layers as the basic structural units of both CB samples and a DEP sample; however, they observed evidence of a higher degree of defects in the graphene-like structures of the DEP sample, as reflected in smaller and more strongly bent graphenes. Interestingly, they correlated the number of defects in the graphene-like structures with the extent of surface functionalization, finding substantially higher incorporation of surface oxygen and hydrogen for the DEP sample than for CB samples. Finally, Hays and Vander Wal (2007) reported evidence of the heterogeneity of soot structures at the nanoscale among several types of BC particles generated for different fuels and combustion conditions, including emissions from an electric utility boiler burning No. 6 residual fuel oil, an industrial boiler burning No. 2 distillate oil, a heavy-duty diesel truck, and a forest wildfire.

3.3. CB vs. engineered carbon-based nanomaterials (CNMs)

Based on the TEM images in Fig. 2(a), (e), and (f), it is clear that there are dramatic morphological differences between CB and CNMs. In particular, each of these prominent CNMs is distinguished by their unique shapes that differ from those of the aciniform aggregates of CB (Table 2). For example, SWCNTs and MWCNTs are both fibrous materials with high aspect ratios, and their needle-like fiber shapes have drawn comparisons with asbestos (Aschberger et al., 2010; Poland et al., 2008). Fullerenes such as C60 are characterized by their symmetrical closed-cage structures that consist of hexagonal and pentagonal rings. Graphene-family nanomaterials (GFNs) can have a number of several different forms, including as a single one-atom-thick, two-dimensional sheet of hexagonally arranged carbon atoms (e.g., mono-layer graphene), and as platelet-like structures made up of stacks of 2–10 graphene sheets (e.g., few-layer graphene).

As shown in Table 2, CNMs are also characterized by their unique nanoscale dimensions – i.e., they can have multiple dimensions on the order of 100 nm or less and thus meet definitions of nanoparticles (all three external dimensions at the nanoscale) or nano-objects (one, two, or three external dimensions at the nanoscale) adopted by such groups as the International Organization for Standardization (ISO) Technical Committee (TC) 229 and the Organisation for Economic Co-operation and Development Working Party on Manufactured Nanomaterials (OECD WPMN) (EC JRC, 2010). As described in the recent Aschberger et al. (2010) review, SWCNTs have typical diameters in the range of about 1 (ca. 10 atoms around the cylinder)–5 nm, with tube lengths that are variable over 6 orders of magnitude (e.g., from 1 to 1 mm). The diameters of MWCNTs are typically in the range of 5–50 nm, depending on the number of walls, with maximum lengths of several micrometers (Aschberger et al., 2010). C60 fullerenes are reported to have diameters as small as 0.7 nm (Jacobsen et al., 2009), and both mono-layer graphene and few-layer graphenes generally have thicknesses of 10 nm and smaller (Sanchez et al., 2012).

In contrast to CNMs that can have significant fractions of individual nano-sized particles, CB can be more aptly described as a nano-structured material – i.e., having an internal or surface structure at the nanoscale (as defined by the OECD WPMN) (EC JRC, 2010) – than a nanoparticle or nano-object. As discussed earlier, this is because CB aggregates and agglomerates are formed from nano-sized primary particles, but the strongly fused CB aggregates, rather than the primary particles, constitute the smallest indivisible entities in commercial CB products. While there is also extensive evidence demonstrating the strong tendency of CNMs such as CNTs and fullerenes to agglomerate in both gaseous and liquid phases, these agglomerates (e.g., CNT ropes) are held together by van der Waals forces and represent more temporary structures compared to fused CB aggregates (ASTM International, 2005; Donaldson et al., 2006; Wang et al., 2003).

In practice, due to their strong tendency to agglomerate, CNMs such as CNTs and GFNs are reported to have surface areas similar to those of CB (Table 2). However, as shown on Table 2, discrete CNTs and mono-layer graphene can theoretically have surface areas far in excess of CB (Sanchez et al., 2012). Few data were found to characterize the surface areas of fullerenes, although available data for C60 fullerenes indicate smaller surface areas than those of the other CNMs and CB (see Table 2).

Lastly, again delving down to the atomic structure, CB's turbostratic arrangement, which has been characterized as quasi-graphitic (Wang et al., 2003), distinguishes it from highly graphitic GFNs.

3.4. CB vs. laboratory-generated ultrafine elemental carbon particles

As shown in Table 2, both SGEC and DFP have morphologies that bear similarities to those of CB, as well as DEP and woodsmoke aggregates. In particular, they both are reported to consist primarily

of complex aggregates and agglomerates formed from spherical primary particles (Evans et al., 2003; Van Winkle et al., 2010). Based on published studies, primary particle diameters are in the range of <10–50 nm (Brown et al., 2000; Evans et al., 2003; Matuschek et al., 2007; Stoeger et al., 2006; Van Winkle et al., 2010), and thus are smaller than those of many CB products. Reported surface areas (in the range of ~300–900 m²/g; see Table 2) appear to be slightly higher than those of CB commercial products, reflecting the smaller primary particle sizes. As shown in Table 2, size distribution data show a sizable fraction of aggregates and agglomerates with diameters of less than 100 nm (Evans et al., 2003; Matuschek et al., 2007; Roth et al., 2004; Van Winkle et al., 2010).

4. CB chemical composition vs. other EC-containing materials

As discussed below, CB is a high-purity substance, consisting of greater than 97% EC. CB thus stands in stark contrast to most ambient air BC particles that are highly heterogeneous in chemical composition and frequently contain a significant organic carbon (OC) fraction. In addition, available data indicate that OC and metals contents of many of the CNMs can well exceed those of CB. Table 2 provides a compilation of chemical composition data for each of the EC-containing materials.

4.1. CB chemical composition

Given its high EC content (>97%), other CB chemical components, such as oxygen, hydrogen, sulfur, OC and extractable organic materials, and ash, are generally present at only very low levels of <1% (McCunney et al., 2001, 2012). The high purity of CB is reflected in the very low ratios of hydrogen–carbon (H/C) that have been reported in the literature – i.e., 0.008 in Wang et al. (2003) and 0.006 in Fernandes et al. (2003). Solvent-extractable organic materials (typically obtained via rigorous laboratory analytical procedures that include prolonged Soxhlet extraction using organic solvents and high temperatures) generally are in the range of tenths of 1% by weight of carbon black; they include a mixture of polycyclic aromatic hydrocarbons (PAHs), lesser amounts of other polynuclear aromatic hydrocarbons (PNAs), and sulfur and sulfur compounds (IARC, 2010; McCunney et al., 2001, 2012). Although a few inorganic elements have been identified in CB (e.g., calcium, copper, iron, manganese, potassium, lead, arsenic, chromium, selenium, and zinc; as reported in IARC, 2010), the trace inorganic metal content of CB is typically below 1% (Wang et al., 2003).

The PAH content of CB has been extensively studied, with OECD (2005) reporting that the concentrations of individual PAHs vary from less than 0.01 to 800 mg/kg and seldom are in excess of 200 mg/kg. As shown in Table 4, PAH concentrations provided in Borm et al. (2005) for particle extracts prepared by 8-h Soxhlet extraction with toluene support the OECD (2005) observations. The

Table 4
Individual PAH concentrations determined using organic-solvent extracts of carbon black (data from Borm et al., 2005).

PAH Species	PAH Concentrations for Different CB Commercial Products (mean mg PAH/kg CB)			
	Printex 90 (Degussa) 300 m ² /g SA	Sterling V (Cabot) 30–40 m ² /g SA	N330 (Columbian) 70–90 m ² /g SA	Lampblack 101 (Degussa) 20 m ² /g SA
Phenanthrene	0.039	8.8	2.4	0.057
Anthracene	0.001	0.4	0.2	0.002
Fluoranthene	0.01	21.5	7.2	0.05
Pyrene	0.065	202.5	191	0.813
Benzo(a)pyrene	ND	6.8	1.4	0.011
Benzo(ghi)perylene	0.008	89.7	44.8	0.172
TOTAL	0.123	329.7	247.0	1.105

ND = not determined; SA = surface area.

Borm et al. (2005) data also suggest that the PAH content of CB materials can be variable.

Importantly, a number of studies have investigated the bioavailability of PAHs found on CB surfaces, and reported findings indicating that PAHs and other organics are tightly adhered to CB particles (Bevan and Yonda, 1985; Borm et al., 2005; Buddingh et al., 1981; Hamm et al., 2009; Locati et al., 1979). Overall, these studies demonstrate that rigorous laboratory extraction with organic solvents (e.g., benzene, toluene) are needed to effectively desorb PAHs from CB surfaces, and that the PAHs are tightly bound and resist being mobilized in the face of extraction using physiologically relevant media. For example, despite testing CB products with benzo(a)pyrene levels (determined by organic extraction) ranging up to 6.8 mg/kg (Table 4), Borm et al. (2005) observed no detectable leaching of PAHs from CB samples exposed to a saline or surfactant-containing extraction procedure. Most recently, Hamm et al. (2009) quantified PAH migration into aqueous media (drinking water, artificial sweat, saliva, and rainwater) following 7-day immersion tests of cured rubber materials containing CB and CB-associated PAHs. They observed only negligible amounts of PAHs (i.e., concentrations 100,000–1,000,000-fold lower than PAH concentrations in the cured rubber materials themselves) in the aqueous extracts.

4.2. CB vs. ambient air BC particles

As shown in Table 2, the chemical composition of ambient air BC particles exhibits large variability not only for different BC source types, but also within the same source type. Similar to the variation in physical properties, it is well-established that the chemical composition of BC particles is highly dependent on fuel properties (e.g., carbon content, ash content, moisture content, density, texture) and combustion conditions (e.g., temperature, residence time). Notwithstanding the significant variation in the chemical composition of different kinds of BC particles, there are some distinguishing features that differentiate the composition of BC particles from that of CB. Focusing on DEP and open biomass burning particles, Fig. 4 illustrates some of the major differences in chemical composition between different kinds of EC-containing materials.

As shown in Table 2, the EC content of most ambient air BC particle types is generally less than 50%. For example, Reid et al. (2004) reviewed composition data for a variety of open biomass burning sources and concluded that black carbon (i.e., EC) contributes approximately 8% of the fresh fine-particle mass emissions. Habib et al. (2008) reported a range of EC contents of 2–35% for combustion of biomass fuels commonly used in developing world regions (e.g., wood species, crop waste, cattle dung), while various sources (Kocbach et al., 2006; Naeher et al., 2007; Rau, 1989; US EPA, 2012) indicate that the EC content of woodsmoke from fireplaces and wood-burning appliances is generally less than 50%, and frequently in the range of 5–20% (Table 2).

We identified only DEP from 1990s-era diesel engine technologies as major BC particle types having EC contents that are on average greater than 50%. As shown in Fig. 4, US EPA (2002) reported an average EC content of approximately 75% for DEP; however, they also reported a range of 33–90% given that DEP composition is well-known to be influenced by a variety of factors, including engine design, load, operating speed, fuel composition, and the presence of engine emission controls. As reviewed in Hesterberg et al. (2011), aftertreatment technologies such as diesel oxidation catalysts and diesel particulate filters have contributed to significantly lower EC emissions for post-2006 on-road diesel engine technologies. Although variable, the available data for particulate emissions from gasoline engines indicate lower EC fractions

(e.g., ~10% up to 50%) than those for DEP from traditional diesel engines (Table 2).

As shown in Table 2, the OC fraction commonly exceeds the EC fraction for ambient air BC particles. This is particularly true for biomass burning emissions, with Reid et al. (2004) reporting an average OC content of approximately 55% for fresh fine-particle emissions from a variety of open biomass burning sources (Fig. 4). In addition, Naeher et al. (2007) compiled fine-particle composition data from several studies where OC contents of 12–~100% were observed for residential wood combustion in fireplaces. Table 2 shows that DEP generally has an OC content of 20% or higher, while the available data indicate that the OC content of particulate emissions from gasoline engines is generally greater than 40%. Consistent with the higher OC contents of BC particles compared to CB, Table 2 shows that higher percentages of solvent-extractable organic matter (SEOM) have also been reported for BC particles, including 20% or less for DEP (US EPA, 2002) and 35% for wood-burning chimney soot (Fernandes et al., 2003).

Precise chemical characterization of the numerous organic species in BC particles is very challenging, with Reid et al. (2004) observing that there is an absence in the scientific literature of any full quantification of the organic compounds species making up the carbon-based components of biomass smoke particles. PAHs are among the organic species that have been quantified in a range of BC particle source types (see Table 2). As previously discussed by Watson and Valberg (2001), the comparison of PAH data across studies and particle types is fraught with uncertainty; uncertainties can arise from differences in collection or extraction methods, lack of uniform analyte specification (i.e., only some analytes are measured or reported), reporting of particulate vs. vapor phase organics, and differences in data presentation. Recognizing these uncertainties, Table 2 shows that BC particles have been reported to have total PAH concentrations as high as 10,000 mg/kg (1%), and thus substantially above even the higher PAH levels reported for some CB products. In support of this idea, Fernandes and Brooks (2003) reported 100-fold and larger differences in the PAH contents of a commercial rubber-grade CB sample vs. several varieties of BC-containing particles (e.g., DEP, wood-burning chimney smoke).

The contributions of heteroatoms, such as hydrogen and oxygen, are also significantly different between CB and BC particle types. As discussed previously, Müller et al. (2007) demonstrated a correlation between the degree of structural imperfections (i.e., bent graphene structures) in a variety of EC-containing particles (e.g., lamp black, furnace soot, various DEP samples, and spark-discharge model soot) and the degree of surface functionalization with hydrogen and oxygen atoms. For example, they reported a surface oxygen content of 0.5% for the lamp black (CB) sample, but levels ranging from 3 to approximately 17% for the various BC samples. The Müller et al. (2007) data suggest that CB and BC are fundamentally different with respect to the reactivity and oxidation behavior of the inherent microstructure. Supporting the Müller et al. (2007) findings, Reid et al. (2004) reported that approximately 20–30% of the fine-mode mass of fresh open biomass burning particle emissions is contributed by elements such as hydrogen, oxygen, and nitrogen.

Finally, Table 2 shows that BC particles also typically contain greater amounts of trace inorganic species than CB. In particular, Reid et al. (2004) reported a value of ~10% as representative of the trace inorganic species content of fresh open biomass burning fine-particle emissions. They highlighted potassium, chlorine, and calcium as major trace inorganic species. Notably, Bond et al. (2006) showed that approximately 54% of the fine-mode mass in particle emissions from an industrial boiler burning residual oil consists of water, mineral ash, ionic compounds, and hydrogen and oxygen associated with organic carbon compounds.

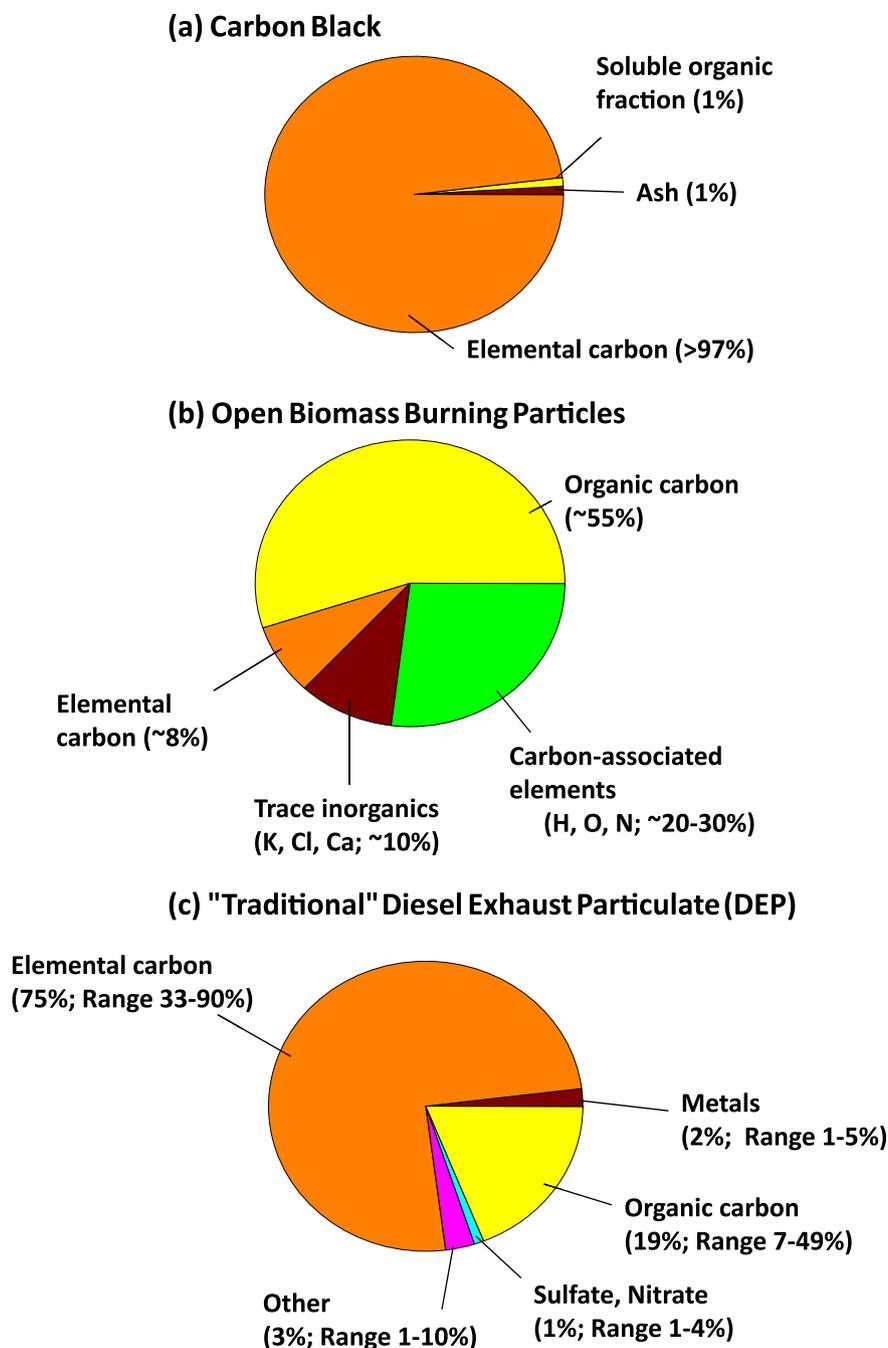


Fig. 4. Comparison of chemical composition among different elemental carbon-containing particles. Elemental carbon-containing particles include (a) carbon black (data from Watson and Valberg, 2001) and two dominant forms of black carbon or "soot", namely (b) particulate emissions from open biomass burning (data from Reid et al., 2004) and (c) "traditional" diesel exhaust particulate representative of 1990s-era diesel engine technologies (data from US EPA, 2002).

4.3. CB vs. engineered carbon-based nanomaterials (CNMs)

Few data were identified for the speciation of carbon in CNMs, but the available data indicate that the carbon content of high-purity CNTs is dominated by EC (Table 2). Specifically, Bello et al. (2009) reported approximately 87–99% of the total carbon in several SWCNT and MWCNT products to be EC based on a modified NIOSH 5040 thermal-optical analysis. Only a refined fullerene product and a purified fullerene product were found to have major OC fractions, with OC comprising 35 and 51% of the total carbon content, respectively. Bello et al. (2009) also quantified EC and OC in

several CB products, observing greater than 99% of the total carbon in each product to be EC. No literature data were identified for the EC and OC contents of GFNs, although it is expected that GFNs produced from a high-purity graphite parent material would have a high (>95%) EC content. Although more data are clearly needed, it thus appears that some CNMs likely have high EC:OC ratios approaching those of CB. The Plata et al. (2008) findings of low quantities of solvent-extractable organic matter (<1% in dichloromethane and <5% in toluene) for purified SWCNT products provide additional confirmatory evidence for the low OC content of high-purity CNT products. The Bello et al. (2009) data suggest a high

OC fraction in some fullerene products, although [Jacobsen et al. \(2009\)](#) reported an absence of detectable levels of the 16 US EPA priority PAHs in a C60 fullerene product.

Despite hypotheses that PAHs can be co-formed with CNTs at the elevated temperatures achieved during CNT synthesis ([Plata et al., 2008](#)), we identified just two studies that have investigated the PAH content of CNTs. For analyses of the 16 US EPA priority PAHs, [Jacobsen et al. \(2009\)](#) reported a concentration of 0.417 mg/kg for a high-purity SWCNT product, whereas they reported a lower concentration (0.075 mg/kg) for a CB sample. Following a toluene extraction procedure, [Plata et al. \(2008\)](#) identified low molecular weight PAHs (<200 amu) in various SWCNT samples. With summed PAH concentrations ranging up to approximately 155 mg/kg, all samples were found to contain naphthalene and several contained a full suite of PAHs, including acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, as well as benzo[b]fluoranthene. According to [Plata et al. \(2008\)](#), however, isotopic analyses indicated that the PAHs may have been derived from the environment – i.e., were the result of post-production contamination rather than from co-formation during synthesis. Thus, [Plata et al. \(2008\)](#) speculated that common air contaminants may be adsorbed on SWCNTs during manufacture, transport, storage, and use. Although limited, available data thus suggest that CNMs have PAH contents in the range of those reported for CB products.

In contrast to CB, however, industrially synthesized CNTs may contain elevated levels of a number of metals that are used as catalysts during their synthesis ([Donaldson et al., 2006](#); [Plata et al., 2008](#)). These common metal catalyst contaminants include cobalt (Co), iron (Fe), nickel (Ni), and molybdenum (Mo). While post-production refinement can remove the majority of the residual metal species, [Donaldson et al. \(2006\)](#) reported that purified CNTs from at least one manufacturer can contain up to 15% residual metal by mass. [Plata et al. \(2008\)](#) reported lower levels of residual metals in purified SWCNT products (1.3–4.1% total metals content), but residual metals contents as high as 29% in unpurified CNTs ([Table 2](#)). While these contributions of catalyst metals are not unexpected, [Plata et al. \(2008\)](#) also reported the presence of other metals (Cr, Cu, Pb) in purified SWCNT products at concentrations ranging from 20 to 300 mg/kg. The investigators hypothesized that residual acid from the acid treatments commonly used in the SWCNT purification process may promote the transfer of trace metals from metallic manufacturing equipment to SWCNTs.

4.4. CB vs. laboratory-generated ultrafine elemental carbon particles

As shown in [Table 2](#), studies have shown that both SGENC and DFP can have chemical compositions dominated by high EC fractions – e.g., [Roth et al. \(2004\)](#) reported the generation of SGENC particles containing less than 6% organic volatile material by weight after replacement of the organic compound components in their generating system with pure inorganic components. However, [Roth et al. \(2004\)](#) reported a significant organic volatiles content (~25%) when their generating system contained organic compound components, and other studies ([Ferge et al., 2006](#); [Matuschek et al., 2007](#); [Stoeger et al., 2006](#); [Van Winkle et al., 2010](#)) have reported data indicating that both particle types can have significant organic carbon contents (as high as nearly 20%; [Table 2](#)). Besides EC and OC, few other chemical composition data were identified for either type of laboratory-generated ultrafine elemental carbon particles. [Van Winkle et al. \(2010\)](#) reported data indicating a low PAH content of approximately 110 mg/kg for DFP. It is assumed that levels of trace inorganic species are similarly low for SGENC particles as CB based on testing data from [Evans et al. \(2003\)](#) indicating the low

ash content (<0.002%) of the graphite electrodes that are the parent material for the SGENC particles.

5. Discussion and conclusions

5.1. Discussion

With the exception of the laboratory-generated EC particles that are highly limited both in terms of their production and exposure potential, each of the EC-containing particle classes considered in this paper is currently at the forefront of regulatory attention. CB was among 12 substances nominated by the US National Toxicology Program (NTP, 2012) in 2012 for possible review in a future edition of the Report on Carcinogens. The climate effects and public health impacts of atmospheric black carbon have been the subject of a number of major reports, including a US EPA (2012) Report to Congress, a United Nations Environment Programme (UNEP)/World Meteorological Organization (WMO) assessment ([Shindell et al., 2012](#); [UNEP, 2011](#)), and a Joint World Health Organization (WHO)/Convention Task Force on Health Aspects of Air Pollution report ([Janssen et al., 2012](#)). In addition, the International Agency for Research on Cancer (IARC) re-evaluated the carcinogenicity of diesel exhaust and gasoline engine exhaust in June 2012, upgrading diesel exhaust from a Group 2A probable human carcinogen to a Group 1 known human carcinogen, but retaining gasoline engine exhaust as a Group 2B possible human carcinogen ([Benbrahim-Tallaa et al., 2012](#)). As noted above for CB, DEP was also nominated for possible NTP (2012) review. Engineered nanomaterials, and particularly CNTs and fullerenes, have been the subject of regulatory scrutiny for over a decade now, as regulatory agencies attempt to assess whether potential exposures and health risks posed by engineered nanomaterials can be addressed under existing regulatory frameworks or whether new regulatory paradigms are needed.

Given the more extensive health effects database that is available for CB vs. other carbon-based materials (aside from DEP), there are prominent examples where scientists and regulatory agencies have turned to the CB health effects literature for insights on the potential health hazards of lesser-studied EC-containing particles, such as CNMs and lesser-studied BC particles. As discussed earlier, in its March 2012 Report to Congress on Black Carbon, US EPA (2012) referred to several studies ([Tankersley et al., 2004, 2007, 2008](#)) where laboratory animals were exposed to carbon black as providing evidence of the biological plausibility for a long-term effect of BC particles on cardiovascular health. In addition, [Jackson et al. \(2012\)](#) referred to Printex 90 CB particles as being “representative of a [sic] engineered carbonaceous nanoparticles”, while [Bourdon et al. \(2012\)](#) characterized Printex 90 CB particles as “an ideal model for exploring systemic effects of NP exposure”.

However, due to the significant physical and chemical differences between CB and other carbon-based materials discussed in this paper, we caution that any extrapolation of the potential health effects across these different carbon-containing particle types is fraught with uncertainty. Based on both toxicological and epidemiologic evidence, it is now well-accepted that an array of physical and chemical properties can play a role in mediating the health hazards posed by fine and ultrafine particles such as the EC-containing particles considered in this paper ([Castranova, 2011](#); [EC SCENIHR, 2006](#); [US EPA, 2007](#)). Among the particle properties that have been proposed to be of toxicological relevance are particle size, surface area, shape, crystal structure, chemical composition, surface chemistry, and solubility ([Hansen et al., 2007](#); [Kobach Bølling et al., 2009](#)). Although much work remains to be done to characterize the relationships between specific physicochemical properties and hazard potential, it should be assumed that

differences in physicochemical properties translate into differences in hazard potential unless otherwise demonstrated.

There are now numerous study findings indicating that differences in physical–chemical properties contribute to differences in the health hazards posed by CB vs. other EC-containing particles. As one example from this large body of literature, [Stoeger et al. \(2006\)](#) observed significant differences in acute lung inflammatory responses of mice exposed to different EC-containing particles (CB, DEP, SGEC, and DFP) via intratracheal instillation. In addition, using the acellular Ferric-reducing ability of serum (FRAS) assay, [Bello et al. \(2009\)](#) reported marked differences in biological oxidative demand (BOD) between three CB commercial products differing in their primary particle sizes and surface areas, multiple fullerenes differing in their purity, and a series of MWCNTs and SWCNTs varying in length and purity. Finally, the [Poland et al. \(2008\)](#) study provided qualitative evidence that particle shape, and in particular fibrosity, plays a greater role than “simple graphene chemistry” in determining asbestos-like, length-dependent pathogenic behavior. In this pilot study where mice were given intraperitoneal injections containing different types of MWCNTs or CB, long-fiber MWCNTs were shown to induce inflammation, foreign body giant cell formation, and granulomas either 24-h or 7-days post-instillation that were “qualitatively and quantitatively similar to the foreign body inflammatory response caused by long asbestos”; however, no such responses were observed for either the curled/tangled MWCNT samples or the non-fibrous CB sample.

Epidemiological studies have also yielded disparate conclusions regarding the health hazards posed by CB vs. ambient air BC particles (note that we are not aware of any epidemiological studies that have been conducted for engineered carbon-based nanomaterials; this is assumed to be due to the small sizes of potentially exposed populations and the limited durations of possible exposures). For example, occupational epidemiology studies of CB manufacturing workers and CB user populations do not show consistent evidence of excess mortality for CB-exposed workers, and in fact provide some evidence of mortality reductions compared to general population referent populations ([Abraham et al., 2011](#); [Dell et al., 2006](#)). In contrast to these results for CB, numerous environmental epidemiologic studies report statistical associations between surrogate measures of ambient air BC particles (e.g., optical measures of black smoke, black carbon, and absorption coefficient; thermal-optical measures of elemental carbon) and excess mortality and morbidity health risks (e.g., [Janssen et al., 2011, 2012](#)); however, it is important to mention that the observational epidemiology studies reporting these statistical associations are subject to numerous confounders and uncertainties in interpretation. As discussed previously, there are particularly large differences in chemical composition between CB and the various BC particles, such that it is not recommended that epidemiologic study findings be extrapolated among the different particle types.

Some similarities in biological responses have also been observed between CB and other EC-containing particles. [Donaldson et al. \(2005\)](#) discuss how EC-containing particles may share mechanisms of harm, namely an oxidative stress pathway. However, they acknowledge that oxidative stress elicited by these materials may arise from different chemical components. Perhaps the most notable similarity involves the rat-lung response to overload exposure conditions for both CB and DEP. As discussed in greater detail in the [Valberg et al. \(2006\)](#) review of the carcinogenic risk of CB, chronic inhalation bioassays conducted in the mid-1990s reported that laboratory rats inhaling high levels ($>1000 \mu\text{g}/\text{m}^3$) of either CB or DEP developed lung tumors near the end of lifetime exposure. The lung tumor rate in rats increased with increasing particle exposure concentration, but was independent of the type of particulate used. As discussed in [Valberg et al. \(2006\)](#), there is

now a sizable body of laboratory studies that support the conclusion that the mechanism of tumorigenicity of CB and DEP in rats arises from the rat-lung reaction to particle overload per se, and not from the particles' nature – i.e., is the same (in this specific animal model) for any poorly soluble particle. Both CB and DEP are poorly soluble particles that are not readily cleared by the rat; the same is true for other poorly soluble particles such as titanium dioxide, talc, coal dust, and volcanic ash. Importantly, it is now well-recognized that rats exhibit a unique severe lung inflammation response to all inert inhaled particles; and available evidence, including inconsistent findings of lung cancer risk in epidemiologic studies of CB worker populations, suggests this response is not relevant to humans ([Elder et al., 2005](#); [McCunney et al., 2001](#); [Valberg et al., 2006, 2009](#)).

5.2. Conclusions

Significant physical and chemical differences exist between CB and other airborne EC-containing materials. Compared to the nearly pure EC content and highly controlled properties of CB, BC particles typically exhibit substantial heterogeneity in chemical and physical properties, including higher OC content and levels of PAHs. CB should not be considered a model particle representative of various engineered carbon-based nanomaterials, in particular those that have a significant fraction of individual particles with diameters of less than 100 nm, because (1) CB is not found in the form of unbound, nano-sized particles in commercial products, and (2) there are significant differences in other properties, including size distributions, agglomeration state, shape, structure, and impurities content. Based on these significant physicochemical differences, and the growing evidence linking physicochemical properties with biological responses, we recommend that CB be viewed as being toxicologically distinct from other airborne carbon-based materials.

Greater care is thus needed in referring to these very different carbon-based materials in the scientific literature so as to forestall unwarranted extrapolation of properties, hazard potential, and study conclusions from one material to another. Any projection of health risks potentially associated with CB should be based on characteristics of CB per se. There is a lack of scientific support for the extrapolation of epidemiological and toxicological findings for various types of BC particles to risks associated with CB exposure.

Conflict of Interest

This paper was prepared with financial support provided by the International Carbon Black Association (ICBA) to Gradient. ICBA, which includes as member companies CB manufacturers headquartered in the United States, Europe, and Canada, is a scientific, non-profit organization that sponsors, conducts, and participates in investigations, research, and analyses relating to the health, safety, and environmental aspects of the production and use of carbon black. Drs. Christopher M. Long, Marc A. Nascarella, and Peter A. Valberg are scientists in the Cambridge, MA office of Gradient, an environmental consulting company that provides toxicology and risk assessment services to a variety of parties, including industry (e.g., utilities, engine manufacturers), governmental agencies, regulators, and law firms. Both Drs. Valberg and Long have offered testimony and served as expert witnesses in litigation concerning airborne particle issues. The final work product reflects the professional opinions of the authors and the writing is solely that of the authors. The analysis and conclusions drawn are those of the authors and do not necessarily reflect the views of their employer or ICBA.

Acknowledgments

The authors thank the members of ICBA's Scientific Advisory Group (SAG) for insightful comments on a draft of the manuscript. We also thank Jasmine Lai of Gradient for text processing assistance.

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