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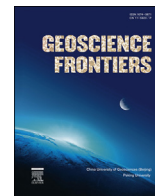


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Focus Paper

# Ambient nanoparticles/nanominerals and hazardous elements from coal combustion activity: Implications on energy challenges and health hazards

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## ABSTRACT

Coal is the most abundant fossil fuel in the world. Because of the growth of coal mining, coal-fired power plants and coal-burning industries, the increase of the emission of particulates (coarse, fine or ultrafine) is of great concern. There is a relationship between increasing human morbidity and mortality and progressive environmental air pollution caused by these types of particles. Thus, the knowledge of the physico-chemical composition and ambient concentrations of coal-derived nanoparticles will improve pollution control strategy. Given the current importance of this area of research, the advanced characterization of this coal combustion-derived nanoparticles/nanominerals as well as hazardous elements is likely to be one of the hottest research fields in coming days. In this review, we try to compile the existing knowledge on coal-derived nanoparticles/nanominerals and discuss the advanced level of characterization techniques for future research. This review also provides some of aspects of health risks associated with exposure to ambient nanoparticles. In addition, the presence of some of the hazardous elements in coal and coal combustion activities is also reviewed.

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## 1. Introduction

Despite concerns about the environmental impacts of coal use, in particular the contribution of CO<sub>2</sub> to climate change, enormous amounts of coal are still being burned annually to produce electricity, heat for industry and homes, coke for steel manufacturing, and feed stock for synthetic gas and numerous chemicals. Projections indicate that coal use will continue to rise by 0.6% annually through 2040 ([www.iea.org](http://www.iea.org)).

Coal is a complex organic-rich sedimentary rock that is typically enriched in S, As, Hg, Pb, Se, etc., elements that are potentially harmful to the environment and human health. Coal combustion

generates substantial amounts of ultrafine/nanoparticles formed primarily by mineral transformation during the high temperature combustion process. Most modern coal-fired power plants have sophisticated pollution control systems (electrostatic precipitators, bag houses, flue gas desulfurization units, etc.) that capture much of the particulates, sulfur dioxide, and trace elements liberated by coal combustion. However, these pollution control systems are inefficient in capturing the finest particles like ultrafine particles (Sambandam et al., 2014).

Generation of anthropogenic carbonaceous matter and mixed crystalline/amorphous mineral ultrafine/nanoparticle by worldwide coal-fired power plant represents serious environmental problems due to their potential hazards (Ribeiro et al., 2013). Ultrafine particles and nanoparticles are similar term with 1 to 100 nm in size. Thus, the use of coal to produce energy increases illness and death in the general population mainly because of air pollution (Garcia et al., 2014; Agudelo-Castaneda et al., 2016; Schneider et al., 2016). Moreover, coal burning in power plants also

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produces other airborne pollutants such as coarse particulate matter (2500 and 10,000 nm in size), sulfur dioxide, oxides of nitrogen, carbon dioxide, acid gases (HCl, HF), and hydrocarbons (PAHs) in addition to the emission of nanoparticles. Thus, each of the steps in the coal life cycle, starting from mining to transportation in addition to coal combustion, generates nanoparticle contamination (Oliveira et al., 2012a, b, 2014; Ribeiro et al., 2013). Exposure to emissions from coal-fired plants depends on factors such as temperature, precipitation, wind direction and speed, and topographical features of the local area (Hower et al., 2013; Wilcox et al., 2015). Emissions may be local or regional, causing health effects to those living near or far from power plants. Several researchers had clearly indicated the relationship between increasing human morbidity and mortality due to increasing air pollution caused by ultrafine/nanoparticles (Suzuki et al., 2002; Chen et al., 2004; Tatar et al., 2005; An et al., 2007; Effros, 2009; Rastogi et al., 2009). Due to the greater surface area of a nano-material/nano-mineral (any material/mineral with single unit size is <100 nm), they are more environmentally active with respect to bio-uptake and associated health risks as compared to larger particles with the same chemical compositions (Gilmour et al., 2004; Oberdorster et al., 2005; Xia et al., 2006a, b).

Nanoparticles carry considerable amounts of air toxics, including the largest fraction of polycyclic aromatic hydrocarbons (PAHs) by mass (Eiguren-Fernandez et al., 2003; Li et al., 2003). PAHs are found in gas-phase and as sorbet to aerosols in the ambient air. PAHs are known as mutagenic and carcinogenic in the animal system (Abdel-Shafy and Mansour, 2015). PAHs are generally emitted from residential heating, coal gasification and liquefying plants, carbon black, coal-tar pitch and asphalt production, coke production, catalytic cracking towers and related activities in petroleum refineries as well as motor vehicle exhaust. Estimated PAHs emission rate from coal is 0.95 mg/kg (Oros and Simoneit, 2000). Some PAHs such as anthracene (Ant), phenanthrene (Phe), benzo(a)anthracene (BaA), and chrysene (Chry) were found to be emitted from coal combustion (Harrison et al., 1996; Saikia et al., 2016a, b). Coal tar pitch, a known Group-1 carcinogen contains about 200 PAH compounds, which are transported by wind and rainwater to nearby soil sediments, water and air, leading to increased cancer risk for human beings (Mahler et al., 2012). Many developed countries such as USA, Canada, etc. use coal-tar-based sealcoat pavements which contains high PAHs. Volatile PAHs in coal-tar-based sealcoat are released into the air and other non-volatile PAHs get transported into the soil sediments and water bodies due to abrasion and storm runoff.

Nanoparticles that are emitted from coal combustion as well as coal-handling activities are unintentional by-products, and in most cases, encapsulate several hazardous elements (Chen et al., 2005; Giere et al., 2006; Hower et al., 2008). It is reported that coal combustion activities also release aggregates of Fullerene (C<sub>60</sub>) in terms of mass of C<sub>60</sub> per mass of particulate matter (Tiwari et al., 2016; Saikia et al., 2016b). The gases generated from coal burning are also enriched volatile organic compounds, toxic and greenhouse gases, organometallic compounds, and other gas components (Hower et al., 2013; Ribeiro et al., 2013). Some researchers reported that the fly ash were generated from coal combustion activity consists of finer-sized particles, ranging from 0.01 to 200 μm (Baba, 2002; Ribeiro et al., 2013). Due to their small size and larger surface area, these ash particles have a greater tendency to absorb hazardous elements that are transferred from coal to waste products during combustion (Gulec, 2001). So far, very few studies have been conducted on the emission of nanoparticles from coal combustion activities. Apart from use in electricity generation, coal is also used in other industries like cement, steel, tea processing, brick kilns, coke ovens as well as in household activities for

**Table 1**

The elements concentration determined in the four Assam coals (ppm: mg/kg ash basis) (after Saikia et al., 2009).

Metal	Ledo	Bragolai	Tikak	Tipong	World coal	Indian average	US average
Fe	6240	4582	3990	3576	—	—	—
Mg	424.35	603	752	928			
Bi	7	4.50	5.2	2.69	2–20		
Al	1315	632	1003.2	1825.4			
V	64	58.72	76.2	58	2–100		
Mn	14	13.40	35.2	65.50	5–300	100	100
Pb	10	5	8.6	9.60	2–80	15	15
Cd	5	5	n. d.	4.04	0.1–65	1.3	1.3
Cr	n. d.	n. d.	0.3	n. d.	0.1–60	70	15
Ni	5	1.50	1.6	9.60	0.5–50	45	15
Co	3	5	8.50	9.20	0.5–30	11	7
Cu	45	23	55	69.60	0.5–50	20	19
Zn	35	10	10	14	5–300	40	39

Note: n. d. – not detected.

combustion purposes. Thus, there is an urgent need of reviewing the current status of research on coal combustion-derived nanoparticles and/or nanominerals, and their characterization techniques for the benefit of future researchers. The aim of this paper is to critically review the existing knowledge on the properties of coal-derived nanoparticles/nanominerals and their available advanced characterization techniques. The human health effects of ambient nanoparticles and hazardous elements emitted from coal combustion activities are also given special emphasis in this paper.

## 2. Characteristics of coal-derived ultrafine/nanoparticles

Airborne nanoparticles consist of over 95% of particulate matter when the number of particles is considered (Whitby, 1978; Kittelson, 1998; Oberdorster et al., 2005). It was found that the particles below 100 nm and below 300 nm contribute more than 80% and 99% of the total number of particles irrespective of the measurement locations and meteorological conditions (Heal et al., 2012). Nanoparticles emitted from coal combustion contain major elements such as Al, C, Ca, Fe, Mg, Na, S, Si, and trace elements such as As, Ba, Cd, Cr, K, Mo, Mn, Nd, Pb, Rh, Se, Ti, V, and Zn (Sambandam et al., 2014). Swaine and Goodarzi (1995) reported that, based on environmental relevance, the trace elements present in coal are in four groups: Group I elements (As, Cd, Cr, Hg, Se), which are known to be hazardous in some circumstances; Group IIA elements (B, Cl, F, Mn, Mo, Ni, Pb); and Group IIB elements (Be, Cu, P, Th, U, V, Zn); and Group III elements (Ba, Co, Sb, Sn, Tl). The concentration of the elements present in the coal varies with ash yield, source areas and geologic history (Gluskoter, 1975; Swaine, 1990). Saikia et al. (2009) also reported the presence of hazardous elements in few high sulfur coals (see Table 1), which are regarded as Hazardous Air Pollutants (HAPs) in the 1990 Clean Air Act Amendments (CAA) USA. Another study carried out by Baruah and Khare (2010) on trace element concentration of high sulfur coals and their associated coal mine rejects showed that most of the hazardous elements are enriched in the coal mine rejects (see Table 2).

Particulates emitted from coal combustion process whether they may be coarse, fine or ultrafine mainly originates from the heterogeneous nature of the mineral matter present in coal. During the coal combustion process, the highly volatile trace elements such as As, Cd, Pb, Hg, Sn, Zn, Sb, etc., are likely to go into the air by emission whereas, other elements like Cr, V, Zr, Mn, Co, Cu, etc., are retained in the ash and may also be responsible for soil and ground water contamination (Saikia et al., 2009). A number of studies show that submicron (partial size <1 μm) and ultrafine coal fly ash particles typically contain a large number of alkali and alkaline earth

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