ISSN 1047-3289 *J. Air & Waste Manage. Assoc.* **50**:1619-1622

Combustion Aerosols: Factors Governing Their Size and Composition and Implications to Human Health

INVITED DISCUSSIONS

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Nearly a decade of epidemiologic research has indicated that exposure to elevated concentrations of ambient particulate matter less than 2.5 µm in size ($PM_{2.5}$) can adversely impact human health. Despite this, plausible mechanistic pathways remain poorly understood. This limited understanding stems in part from the complexity of the PM itself. Although epidemiologic studies often treat $PM_{2.5}$ as a single entity, in reality, it is broadly distributed in particle size, particle morphology, and particle composition. All of these factors may plausibly influence the interaction of the particles with the human airway.

In the Critical Review by Lighty, Veranth, and Sarofim, the authors provide a comprehensive review of these complexities associated with $PM_{2.5}$. In their paper, $PM_{2.5}$ formation in combustion systems, measurement methods for $PM_{2.5}$, and exposure studies associated with $PM_{2.5}$ are all discussed in an interrelated fashion. The synthesis of these three topics in one comprehensive review makes this paper a valuable resource for researchers in the field. The emphasis on following particles through their entire history, from formation to emissions and ultimately deposition and health effects, also makes this review particularly useful for researchers in one community seeking to understand the governing phenomena in another.

One particularly valuable aspect of the review is the discussion of particle formation in combustion systems from a fundamental perspective, followed by more detailed discussions addressing phenomena specific to individual fuels or combustion devices. This discussion is useful for its identification of the factors that remain poorly characterized and in need of additional study. For example, the authors present a stark contrast between the relatively well-characterized emissions of coal-fired utility plants and the poorly characterized emissions of domestic biomass combustion. Their comments suggest that coupling epidemiologic studies in regions burning diverse fuels with detailed particle size and composition distribution measurements would be quite useful in understanding the importance of particle size and composition on $PM_{2.5}$-induced health effects.

One aspect that is briefly addressed in their review is the overlooked importance of particle morphology. A particle of 1-µm aerodynamic diameter will have much lower surface area than will a fractal-like particle of equivalent size. Transition metals, which are often surface enriched in combustion-derived particles, have been suggested as one plausible damage-inducing species; if true, then the surface area and, hence, morphology of the PM is of considerable importance. Human airway deposition studies generally assume spherical particles, yet recent data from our laboratory indicate that 40–50% of the particles in a rural ambient air sample are nonspherical, ranging from elliptical and angular particles with an aspect ratio of 1.6 or greater to fractal-like soot and metal-derived aggregates consisting of much smaller 10–40 nm primary particles. As the authors suggest, this adds to the challenge of identifying the primary components of $PM_{2.5}$ responsible for the observed health effects.

The authors, in presenting a comprehensive summary of particle formation, particle emissions, and particle-associated health effects, have laid out the many remaining research challenges associated with this important problem. It is up to the research community to act upon these challenges and unravel the complex issues associated with this potential hazard to public health.

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The research team has written a comprehensive review of the existing data associated with combustion aerosols. With the recent revision of the National Ambient Air Quality Standards (NAAQS), this is both an important and timely subject. The authors covered a broad range of topics associated with combustion aerosols, and the resulting document is an excellent starting point for focused, future research.

Combustion aerosol formation and emissions involve a number of complex mechanisms. The review provides an in-depth study of particle formation and the factors that influence both particle size and composition. This is the one technical area where there have been considerable research and agreement. As in many cases, reviews of this nature often uncover additional questions. The authors correctly identify areas where more research is needed.

The major research areas include:

- improved understanding of combustion fundamentals,
- improved understanding of fine particulate and aerosols control,
- improved sampling and particle characterization methods, and
- improved understanding of the health effects.

The establishment of additional regulations and more stringent ambient particulate levels in the absence of solid health-effect data is distressing to the fossil-fuel industry and the energy consumer. The association between increased ambient particulate concentrations and adverse health effects without the identification of a toxicological mechanism clearly suggests that more research is needed prior to establishing $PM_{2.5}$ regulations. The authors correctly point out that the correlation of fine particulates with adverse health effects does not prove causality. Particle mass, or more specifically, particle concentration, is more likely a surrogate for harmful airborne species. What roles do natural source materials, uncontrolled by human activity, play? How do PM and weather conditions correlate and thus affect human health? Can correlated events be separated to determine causality? We must answer these questions to effectively address the health issues.

Future research in these areas is being driven by the proposed revision to the ambient air quality standard. A number of organizations, including the U.S. Environmental Protection Agency, U.S. Department of Energy, EPRI, and industry, are conducting ambient particulate ($PM_{2.5}$) measurement and characterization programs. The objective of these programs is to develop a database of fine particulate ambient concentrations and speciation. Another objective of these studies is to identify the impact of outdoor air quality on indoor air quality and the influence of indoor air quality and personal exposure on human health. CONSOL is participating in a study that specifically addresses this issue. In response to the need for improved mass concentration and speciation data, a new generation of ambient samplers has been developed and improved chemical speciation techniques are being utilized. We may soon have an improved understanding of "how much" and "what types" of particles are in the air. However, this information can only be applied into effective regulations when coupled with accurate health information.

In summary, all environmental regulations carry some economic costs. This fact is recognized in this review. The authors of this review are applauded for the completeness and accuracy of this summary of the body of knowledge associated with combustion aerosols. The information provided in this review should serve to focus future research that will bridge the data gaps to assure that future regulations are based on sound science.

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The authors have done an excellent job on this review. Various aspects of combustion aerosols, from the sources and control to the health impact, are covered to provide a clear and integrated picture of this subject. Of special importance is the manifestation of the direction for future research. Cross-disciplinary research that involves both engineers and health professionals is certainly a must.

There are several supplemental issues that I would like to address here. First, as shown in the review, combustion aerosols are generally in the submicrometer size range, with their primary particles in the size range of nanometers. With the enthusiastic pursuit of the nanotechnology today, numerous types of nanoparticles of large quantities are being manufactured and applied. For example, nanosized titania has been commonly applied to windows, cosmetics, and air purification. The introduction of these nanosized particles into our daily life, which results from attrition and subsequent suspension, may pose significant impact on the environment (e.g., enhancing photocatalysis in the ambient air) and human health. Their effects are expected to be much more acute than those of the submicron particles due to their size effect. In addition, certain materials that are nontoxic in the larger size range have been shown to cause adverse effects when they are in the nanosized range. However, the impact of these manufactured products has not been quantified yet. This is certainly an area that needs to be extensively and urgently researched.

The second issue is related to the control of heavy metals from combustion sources. While many of the metals are toxic to the environment and human beings, they are also valuable resources with high market values. For example, the price of ferrovanadium is $12.75 per kg, much higher than the $0.10 per metric ton for Fe. Recycling these materials is certainly meritorious, both economically and environmentally. Currently, ~2000 metric tons of vanadium is recovered from petroleum residues annually, which accounts for 45% of U.S. consumption. The development of new techniques that can effectively retrieve various precious metals from combustion systems will provide attractive incentives for industry and should be encouraged.

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The material presented has convinced me that a substantive body of scientific knowledge exists concerning both the character of combustion aerosols and their implications to human health. So, after having established what these aerosols are, and what hazards they present to the population, I think that the next logical question is: Shouldn't we now also investigate in parallel the *technical* solutions for the control of this problem, rather than just studying, in relative isolation, the *science* of the sources, nature, and consequences of the problem? I propose that the former path is by far the wiser, and that it makes excellent sense to begin searching now for effective technical means for air pollution control (APC) of these submicron combustion aerosols.

The history of similar problems (low-level radiation, water pollution, air pollution, hazardous waste disposal, etc.) shows that the lapse of a significant period of time (measured in decades) is to be expected between the identification of such problems and the effective implementation of remediation, nationwide. This produces the curious result that the scientists who initially identify and quantify the problem might anticipate that their grandchildren may well enter adulthood, without effective protection from the consequences of the problem, before it has been fixed.

An extensive delay between discovery and cure is not particularly desirable, appropriate, or even necessary. Rather, the search for effective APC solutions for these combustion aerosols should be pursued, as a companion and parallel research endeavor, for the specific objective of reducing this delay.

Natural processes continuously introduce submicron particulates into the atmosphere, and consequently, other natural processes that remove them must exist in balance. Therefore, it seems rational that effective APC technologies might well utilize some of the same phenomena involved in these latter, particulate "removal" processes. Some of these processes occur within clouds, where nucleation, condensation, and electrostatic forces are particularly active. In fact, at least two such commercial technologies already exist, utilizing such phenomena, and each has been investigated to some extent for use in the APC of similar submicron particulates. Better yet, pilot scale equipment for each technology exist that would permit the evaluation of the effectiveness of these technologies for the APC of these aerosols.

The first technology is the so-called condensing heat exchanger (CHE). In the form described here, the CHE was developed to recover waste heat from boilers. Fuel combustion typically produces acidic flue gas. Boilers are designed to avoid corrosion from acidic flue gas by being operated above that temperature at which any condensate can form, the so-called dew point. This standard operating practice results in boiler flue gases being released to the atmosphere at temperatures typically between 300 and 400 °F. The consequent lost energy can be partially recovered in a CHE by using the otherwise wasted energy to heat a cold fluid, typically cold water.

The most commonly used CHE commercially available uses low alloy construction, with the surfaces exposed to condensing flue gas being Teflon-coated.[1,2] The company manufacturing this technology, CHX,[2] markets it for heat-economizing, but it is obvious from their marketing video that particulates can also be captured and removed with the condensate. The video shows a sample of the low-pH condensate, which is black like India ink. This observation led Consolidated Edison Co. of New York to investigate the use of the CHE in an integrated design, for the purpose of combined heat recovery and pollution control, including particulate pollution control.[1] Although the results were measured as total particulate loading in LB/million BTU, it was reported that "1/4 condensation also occurs on submicron-size particulate, enhancing their removal" by "causing particle growth through agglomeration, and ultimately removing the fine particulates." Also reported were significant Hg removal efficiencies, ~50%.

The second technology is the so-called Cloud Chamber Scrubber (CCS).[3] This technology was developed to simulate conditions within clouds for the purpose of cleaning gases while using very modest amounts of both water and electricity. It is specifically marketed as an APC technology for "all generators of particulate under 1 micron."[4] Very fine droplets of water are generated and electrically charged. It was reported that "as they (droplets and particulates) approach 10 microns of separation, electrical attraction causes the particulate to enter the droplet" and "the CCS has been shown to be 99%+ efficient for the collection of all particulate from 0.1 to 3.0 microns."

These two technologies are not presented here because they are the solutions to the APC of the submicron combustion aerosols. Rather, they are presented as existing, commercially available, working technologies that *might* be adapted for this use. The advantage is that they are available today, as working systems. They can be quickly pilot-tested on actual source streams to determine their effectiveness. If these results are promising, the technologies can then be further investigated, scientifically, for the purpose of determining the practicality of adapting them for the effective APC of these submicron combustion aerosols.

What has been presented here is not a technical means for the APC of combustion aerosols. Rather, a recommendation has been made for the search for such a means, employing technological "gatekeeping," to identify and then attempt to adapt existing technology for this role. Two examples were briefly described. By investigating in parallel both the scientific fundamentals of the nature of the problem of these aerosols and the technical means for their control, the lapse of time between the discovery and the effective cure for this problem could be significantly reduced.

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$PM_{2.5}$ and smaller PM biology is different from that of other larger PM and gas-phase molecules that follow the partition coefficient between the gas and lung cell surface aqueous secretion—a reversible process. The chair of the Critical Review committee pointed out that drugs can be given by aerosol inhalation in sizes ~0.1 μm (e.g., insulin) with nearly 90% uptake. Consider only the consequences of inhalation of ambient PM of less than 2-μm diameter, the "garbage bags of pollution" and the villains of air pollution, which are very effectively taken up by the alveolar cells, and often engulfed by macrophages in the presence of surfactants, with some possibly going directly into circulation and arriving in the heart. There is no return channel for these particles and their absorbed baggage of chemicals; they are delivered into the inner workings of the cells with the potential to release all the chemicals they carry. "Aged PM" may carry chemicals that are significantly different from those originally absorbed due to chemical reactions on their surfaces, which are probably also accelerated due to catalytic effects.

At least six groups of health effects associated with air pollution can be clinically recognized, and in some, the pollutants that seem most closely associated with the clinical condition identified may overlap:

(1) watery/itching eyes—association unidentified;

(2) reduced lung diffusion capacity—associated with exposure to carbonaceous $PM_{2.5}$ and acid aerosols (sulfuric, sulfurous, nitric, or others);

(3) cancers, possibly birth defects—specific pollutant association in doubt, but probably nitro-PAHs;

(4) child lung-growth impairment—associated air pollutant is undetermined; and

(5) heart failure—shown in a multitude of epidemiologic studies. Associated with $PM_{2.5}$-bearing transition metals, extractable by dilute acids.

In rats with mild lung inflammation, heavy oil-derived $PM_{2.5}$ inhalation can cause cardiac dysrythmia and death.[1] As Lighty pointed out, these carry more V and Fe than PM from other sources do. Smog-related dysrythmia has been recorded in humans.

Molecular sequences phagocytose metal-bearing PM. The heart is mediated by cytokines, including tumor necrosis factor and others that may be involved in the biological chain reactions connecting the organs. TMF is a cardiac muscle depressant decoupling energy generation and contraction. This is not a clearly defined molecular sequence, and there may be more than one connecting mechanism, but it provides a basis for elucidation of the mechanisms. Defining the triggers for these health effects is important in order that selective control mechanisms can be developed and implemented in place of across-the-board reductive control of $PM_{2.5}$.

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