

UC Riverside

2018 Publications

Title

Chemical speciation, including polycyclic aromatic hydrocarbons (PAHs), and toxicity of particles emitted from meat cooking operations

Permalink

<https://escholarship.org/uc/item/9s106353>

Journal

Science of The Total Environment, 633

ISSN

00489697

Authors

Gysel, Nicholas
Dixit, Poornima
Schmitz, Debra A
et al.

Publication Date

2018-08-01

DOI

10.1016/j.scitotenv.2018.03.318

Peer reviewed



Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Chemical speciation, including polycyclic aromatic hydrocarbons (PAHs), and toxicity of particles emitted from meat cooking operations

Nicholas Gysel^{a,b}, Poornima Dixit^{a,b}, Debra A. Schmitz^c, Guenter Engling^d, Arthur K. Cho^c, David R. Cocker^{a,b}, Georgios Karavalakis^{a,b,*}

^a University of California, Bourns College of Engineering, Center for Environmental Research and Technology (CE-CERT), 1084 Columbia Avenue, Riverside, CA 92507, USA

^b Department of Chemical and Environmental Engineering, Bourns College of Engineering, University of California, Riverside, CA 92521, USA

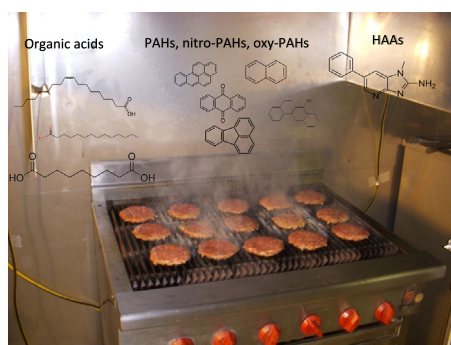
^c Departments of Molecular and Medical Pharmacology/Environmental Health Sciences, UCLA Center for Health Sciences, Los Angeles, CA 90095, USA

^d Desert Research Institute (DRI), 2215 Raggio Pkwy, Reno, NV 89512, USA

HIGHLIGHTS

- Uncontrolled meat cooking operations emit high concentrations of toxic and carcinogenic pollutants.
- The electrostatic precipitator was more efficient in reducing most harmful emissions.
- PAHs, nitro-PAHs, organic acids, and HAAs decreased with the control technologies.
- PM redox activity and electrophile content decreased with the control technologies.
- Particles contained higher levels of prooxidants and the vapors higher levels of electrophiles.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 5 December 2017

Received in revised form 10 March 2018

Accepted 25 March 2018

Available online 3 April 2018

Editor: P. Kassomenos

Keywords:

Meat cooking

PM emissions

Polycyclic aromatic hydrocarbons

Organic acids

Toxicity

ABSTRACT

We assessed the chemical properties and oxidative stress of particulate matter (PM) emissions from underfired charbroiled meat operations with and without the use of aftertreatment control technologies. Cooking emissions concentrations showed a strong dependence on the control technology utilized, with all emission rates showing decreases with the control technologies compared to the baseline testing. The organic acids profile was dominated by the saturated nonanoic, myristic, palmitic, and stearic acids, and the unsaturated oleic, elaidic, and palmitoleic acids. Cholesterol was also found in relatively high concentrations. Lower and medium-weight polycyclic aromatic hydrocarbons (PAHs) were the dominant species for all cooking experiments. Heavier PAHs were also detected in high concentrations, especially in the particle-phase. For the nitrated PAH emissions (nitro-PAHs), low molecular weight compounds dominated the cooking emissions. Under the present experimental conditions, the heterocyclic aromatic amines (HAAs) showed very low concentrations, which suggests these species are rarely formed in meat cooking PM. The most efficient control technology for reducing the majority of the toxic pollutants was the electrostatic precipitator, which resulted in total emissions reductions on the order of 95%, 79%, 90%, 96%, 90%, and 94%, respectively, for particle-phase PAHs, gas-phase PAHs, particle-phase nitro-PAHs, gas-phase nitro-PAHs, particle-phase HAAs, and gas-phase HAAs compared to the baseline testing. Our experiment showed that cooking aerosol contained higher levels of prooxidants in the particle-phase and the

* Corresponding author at: University of California, Bourns College of Engineering, Center for Environmental Research and Technology (CE-CERT), 1084 Columbia Avenue, Riverside, CA 92507, USA.

E-mail address: gkaraval@cert.ucr.edu (G. Karavalakis).

corresponding vapors contained higher levels of electrophiles. Overall, the use of control technologies reduced the redox and electrophilic activities of cooking PM.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Emissions from commercial cooking may contribute to exceedances of the Federal PM_{2.5} air quality standards in certain regions of the United States (US). In particular, in the South Coast Air Basin (CA), emissions from all restaurants produce approximately 10.4 tons/day of PM_{2.5}. Currently, commercial cooking operations, especially under-fired charbroilers, is the largest source of primary PM_{2.5} in the Basin, with primary PM_{2.5} emissions from residential fuel combustion and heavy-duty diesel trucks falling significantly behind (South Coast Air Quality Management District (SCAQMD), 2016). Previous studies have reported that emissions from meat cooking operations contribute significantly to ambient fine PM_{2.5} concentrations (Buonanno et al., 2009; Fine et al., 2004; Zhang et al., 2010). Hildemann et al. (1991) estimated that approximately 21% of all organic PM_{2.5} in Los Angeles was from meat cooking, while Schauer et al. (2002) estimated that 23% of the PM_{2.5} organic carbon mass emitted in Los Angeles was contributed from meat cooking activities. The magnitude of this problem has led to the inclusion of cooking aerosol as a component of PM in the US national emission inventory. Cooking operations are also major contributors of secondary organic aerosols (SOA), organic material, and volatile organic compounds (VOCs) in urban environments (Mohr et al., 2012; Sun et al., 2011). Mohr et al. (2009) showed that cooking organic aerosol contributes 17% to organic PM in Barcelona. Allan et al. (2010) estimated that the average contribution of cooking aerosol to organic aerosol was 22–30% in London. For southern California, in Riverside, it was estimated that food cooking operations contribute about 11% of fine organic aerosol mass (Williams et al., 2010).

The chemical nature of PM emissions from meat cooking activities is rich, with hundreds of organic compounds including saturated and unsaturated fatty acids (alkanoic and alkenoic acids), n-alkanes, dicarboxylic acids, furans, furanones, amides, steroids, polycyclic aromatic hydrocarbons (PAHs) and their nitrate derivatives (nitro-PAHs), and heterocyclic aromatic amines (HAAs) (Abdullahi et al., 2013; Elmore et al., 2004; Lewtas, 2007; Robinson et al., 2006; Rogge et al., 1991). Several studies have investigated PAH emissions from cooking activities, although the concentrations of these carcinogenic pollutants depend on parameters such as cooking style, ingredients, cooking procedures, and temperatures (Chen et al., 2007; He et al., 2004; Rogge et al., 1991). Rogge et al. (1991) showed that PAH emissions increased with increasing the fat content of meat. McDonald et al. (2003) reported that charbroiling emissions yielded an average of about 3–5 times more PAHs and about 20 times more cholesterol than grilling. Li et al. (2003a) compared the PAH emissions of different cooking styles and found that Chinese style cooking emitted the highest PAH concentrations, followed by Western style, fast food, and Japanese style. Rose et al. (2015) showed that there was little evidence of PAH formation during the grilling, frying, roasting, and toasting experiments, whereas barbecuing resulted in the formation of PAHs. They also showed that PAH levels increased when the food was barbecued closer to the heat source. In addition to PAHs, HAAs have also been classified as human carcinogens (Chiang et al., 1999). The amounts of HAAs can range from less than 1 ppb to greater than 500 ppb, and are dependent upon the type of meat, method of cooking, and the temperature and duration of cooking (Turesky, 2007). Ni et al. (2008) showed that barbecuing or pan frying produced larger amounts of HAAs than did oven broiling. Finally, Sinha et al. (1995) reported that the HAA content generally increases as a function of temperature and the duration of cooking.

Numerous studies have reported that exposure to air pollution and, more specifically, PM is associated with adverse health effects (Sioutas et al., 2005). A recent study showed that more than three million people die prematurely each year from air pollution, more than malaria and HIV combined (Lelieveld et al., 2015). Airborne PM emissions may induce pulmonary inflammation at both epithelial and interstitial sites, as well as enter the circulation to reach other target sites, including the cardiovascular system (Kreyling et al., 2006). Organic species, such as PAHs, have been identified to induce a broad polyclonal expression of cytokines and chemokines in respiratory epithelium through the production of cytotoxic reactive oxygen species (ROS) (Li et al., 2003b). In respect to cooking activities, several epidemiological studies have reported that exposure to HAAs are linked to colorectal cancer, and less consistently, prostate and breast cancer (Cross and Sinha, 2004; Sinha, 2002). To the best of our knowledge, there is only one study that investigated the respiratory effects from PM emissions collected under controlled laboratory conditions of charbroiled meat cooking activities (Li et al., 2014). The authors showed that the organic material from meat cooking induced the expression of heme oxygenase-1 and cyclooxygenase-2 in BEAS-2B cells, as well as up-regulated the levels of IL-6, IL-8, and prostaglandin E2. The authors concluded that PM emissions from meat cooking could induce an inflammatory response in human bronchial epithelial cells.

Although previous studies have provided substantial data about indoor and outdoor cooking emissions, there is very limited data on the effects of aftertreatment control technologies on emissions from commercial cooking operations (Gysel et al., 2018). In California, and most of the United States, smaller restaurant chains operating with under-fired charbroilers are not required to control their PM emissions. Thus, it is necessary to study emissions from under-fired charbroiled meat cooking operations with and without aftertreatment control technologies. This work examines the chemical and toxicological characteristics of PM_{2.5} from meat cooking processes.

2. Experimental

2.1. Test facility, control technologies, and protocol

The meat cooking experiments were conducted at the University of California Riverside, Center for Environmental Research and Technology (CE-CERT) commercial cooking facility. The 1/3-pound meat patties used in this study were finished grind, pure beef hamburger, 21% fat by weight, 58–62% moisture, 3/8" thick, and 5" in diameter. Patties were cooked to an average internal temperature of 175 ± 5 °F, to attain a medium-well condition. Three control technologies were used in this study (hereinafter denoted as control technology 1 to control technology 3 (CT1, CT2, and CT3)). The first device was an in-hood dual stage filtration system located directly above the grill surface near the grease baffles. The second device was an aerosol grease removal based on a technology for particle (solid or liquid) separation from an incoming flow stream via boundary layer momentum transfer theory. The third device was an electrostatic precipitator (ESP). ESPs are proven technologies used to clean the effluents by using high voltage to ionize air molecules and having followed by both negative and positive charged collector plates to remove charged particles from the air. Subsequently, VOCs are removed by adsorption into an activated carbon bed. Detailed information about the test facility and protocol and description of the control technologies can be found elsewhere (Gysel et al., 2018).

2.2. Sampling and emissions analysis

A sampling system was devised to simultaneously collect multiple filter and gas samples, as shown in Figure SM1, Supplementary Material (SM), and described in detail elsewhere (Gysel et al., 2018). The samples were isokinetically withdrawn from the stack at a fixed flow rate and diluted with VOC and particle-free air using a partial flow venturi dilution system. Particulate PAH and nitro-PAH samples were collected on 47 mm Teflon® filters. Amberlite XAD-4 polyaromatic absorbent resin (Aldrich Chemical Company, Inc.) was used to collect the semi-VOCs. PAH and nitro-PAH species for the cooking aerosol were collected in duplicate samples for the baseline and each control technology. More details on the PAH and nitro-PAH collection, handling, and analyses are given in the SM. Polar organic compounds, including organic acids, and HAAs were collected on pre-cleaned quartz-fiber filters (QAT Tissuquartz Pall-Gelman, Ann Arbor, MI, USA) in duplicate for the baseline and each control technology. HAAs were also quantified in the semi-volatile fractions, utilizing the XAD-4 resin bed extract used for the PAH and nitro-PAH collection. Additional information on the analysis methods for polar organic compounds and the HAAs is provided in the SM. Trace elements and metals were collected onto 47 mm Teflon® filters and subsequently analyzed using the X-Ray fluorescence (XRF) method as per EPA IO-3.3.

2.3. DTT and GAPDH assays

The oxidative potential of cooking emissions (gas- and particle-phase) was measured through the dithiothreitol (DTT) assay. Particle and semi-volatile fractions were collected using a filter based collection system containing a XAD-4 resin bed below the 47 mm Teflon® filters. This assay measures the prooxidant content of the sample based on its ability to transfer electrons from dithiothreitol (DTT) to oxygen (Cho et al., 2005; Kumagai et al., 2002). In the procedure, the sample to be analyzed is incubated with DTT for varying times, the reaction quenched by addition of 5,5'-dithiobis(2-nitro)benzoic acid (DTNB) and the remaining DTT measured by its absorption at 412 nm. Rates are calculated averaging duplicate runs, and are blank corrected. The units used are the nanomoles of DTT consumed per minute per m³ of air sample. Since DTT can be oxidized by high concentrations of metal ions (Netto and Stadtman, 1996), the contribution of metals to the DTT-based redox activity was also determined by adding the metal chelator, diethylenetriaminepentaacetic acid (DTPA) (20 μM), to one set of the samples.

The GAPDH assay measures the content of electrophiles in the sample, based on their ability to inhibit or inactivate the thiolate enzyme glyceraldehyde-3-phosphate dehydrogenase (GAPDH), through covalent bonding. Inhibition of GAPDH by vapor and PM2.5 samples was determined under anaerobic conditions according to the method described previously (Shinyashiki et al., 2008). In brief, a mixture of 1 unit of rabbit GAPDH was incubated with aliquots of the organic extracts of vapors and particles or water suspension under argon gas at 25 °C for 120 min. The reaction was quenched by adding an equal volume of cold DTT solution, and GAPDH activity, measured as the rate of nicotinamide adenine dinucleotide (NADH) formation, was monitored by its absorption at 340 nm. The ability to inactivate the enzyme is expressed as the equivalents of *N*-ethylmaleimide (NEM), the standard electrophile. Samples were run in triplicate and values reported as averages. The units used are the equivalents of *N*-ethylmaleimide per sample.

3. Results and discussion

3.1. Organic acids and other polar compounds

Organic acids dominate emissions from meat cooking operations. Meat used in cooking contains fats made up of saturated and

unsaturated fatty acid esters of glycerol in the form of triglycerides and phospholipids. The chemical processes that typically occur during high temperature treatment of meat are the degradation of sugars, pyrolysis of proteins and amino acids, and the degradation of fats, which result to the production of free fatty acids, free glycerol and mono- and diglycerides (Abdullahi et al., 2013; Nolte et al., 1999). Our results show that the *n*-alkanoic acids were generally the most abundant class, followed by *n*-alkenoic acids, *n*-alkanedioic acids, aromatic monocarboxylic acids, and sterols. Normal alkanolic and *n*-alkenoic acids were by far the most abundant individual species in any of the polar compounds classes shown in Fig. 1 and Table SM1. In particular, the highest emission rates were observed for the saturated nonanoic, myristic, palmitic, and stearic acids, whereas for the *n*-alkenoic acids the highest emission rates were identified for oleic, elaidic, myristoleic, and palmitoleic acids. Nonanoic acid emission rates were found at the highest levels for all the C₆ and up to C₁₃ *n*-alkanoic acids (60,916 μg/kg of meat cooked for the baseline experiment). The high emission rate of nonanoic acid could be due to the breakdown of the monounsaturated oleic acid (one double bond in the C₉ position) (Schauer et al., 2002). Similar distributions of fatty acids have been observed in previous studies when investigating the emissions from Chinese cooking, meat cooking, and seed oil cooking (He et al., 2004; Schauer et al., 2002; Rogge et al., 1991; Zhao et al., 2007a). Other studies have reported that oleic and palmitoleic acids were emitted by far the largest rates from meat cooking operations, and they serve as key tracers for aerosols from food cooking in urban areas (Robinson et al., 2006; Schauer et al., 1996).

Dicarboxylic acids were measured in the range of C₄ to C₁₂ and were generally found in lower concentrations than *n*-alkanoic and *n*-alkenoic acids. The predominant compounds were the traumatic (trans-2-dodecenedioic acid) acid, hexanedioic (adipic) acid, succinic acid, glutaric acid, and azelaic acid. The results reported here differ from other studies reporting that azelaic (nonanedioic) acid was the predominant dicarboxylic acid emitted from Chinese cooking (He et al., 2004; Zhao et al., 2007b), but agree with Rogge et al. (1991) showing that the saturated hexanedioic (adipic) acid had the highest concentration from meat charbroiling operations. This study is the first to report that charbroiled meat cooking may produce significant concentrations of the monounsaturated traumatic acid relative to the saturated dicarboxylic acids. Dicarboxylic acids are released from the oxidation of

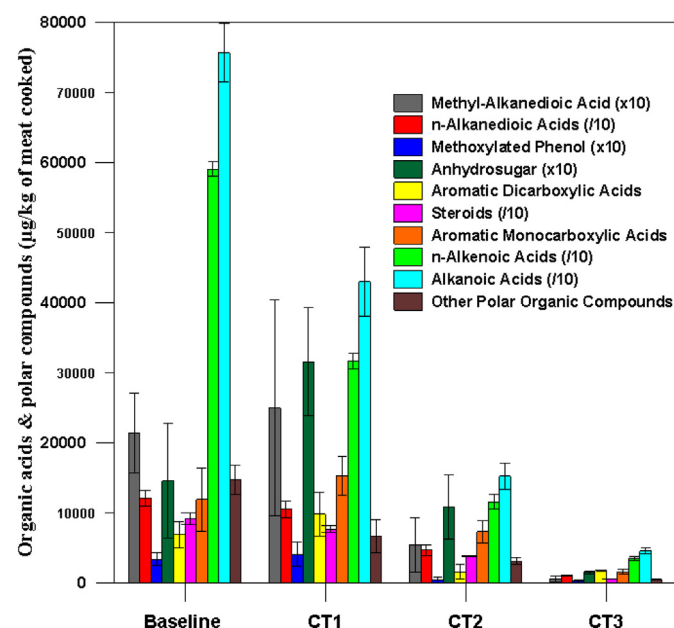


Fig. 1. Organic acids and other polar compounds for the baseline testing and the three control technologies.

dialdehydes during autoxidation of unsaturated lipids (Rogge et al., 1991). It is worth mentioning that *cis*-pinonic acid, which is not usually found in meat and serves as a marker for biogenic SOA, was measured in relatively high concentrations (13,596 $\mu\text{g}/\text{kg}$ of meat cooked for the baseline experiment). *cis*-Pinonic acid is related to the photochemical oxidation of biogenic volatile α -pinene (Cheng et al., 2004). It is theorized that α -pinene, which can be found in several muscles, was oxidized during thermal stressing forming *cis*-pinonic acid.

A number of molecular biomarkers, which are organic compounds of biological origin, were also identified and quantified in cooking PM. The two major biomarker classes were monosaccharide anhydrides (mannosan and levoglucosan) and sterols (cholesterol and β -sitosterol), as shown in Table SM1. Sterols were found in higher emission rates than those of monosaccharide anhydrides, with cholesterol being the dominant biomarker in meat cooking PM, followed by levoglucosan, the pyrolysis product of cellulose in biomass burning, as the monosaccharide anhydride with the highest mass fraction. Although levoglucosan is usually recognized as a tracer for biomass burning, other studies have shown relatively high levels of levoglucosan in the PM emissions from different cooking styles (He et al., 2004; Pei et al., 2016; Zhao et al., 2007a; Zhao et al., 2007b). Studies have also shown that cholesterol was the dominant organic compound from meat cooking operations and suggested cholesterol as the main biomarker for the aerosol released from meat cooking (McDonald et al., 2003; Robinson et al., 2006; Rogge et al., 1991; Schauer et al., 1999). Cholesterol is biosynthesized by higher animals and found in body tissues such as animal fats and oils (Nolte et al., 1999; Rogge et al., 1991).

The use of control technologies showed reductions in most organic compounds, with CT3 having the larger reductions in PM-bound organic compounds compared to the baseline testing. The reductions in total organic compounds emissions were on the order of 40%, 77%, and 94%, respectively, for CT1, CT2, and CT3 relative to the baseline testing. The majority of the reductions in organic compounds compared to the baseline testing were statistically significant and ranged from 31%–74% for nonanoic acid, 46%–94% for myristic acid, 41%–95% for palmitic acid, and 71%–96% for stearic acid. Similar reductions were also seen for oleic acid and palmitoleic acid relative to the baseline testing, ranging from 32%–92% and 56%–95%, respectively. Large emissions reductions were also observed for the dicarboxylic acids compared to the baseline testing, with traumatic acid and azelaic acid showing emissions reductions ranged from 45%–94% and 55%–92%, respectively. Cholesterol and levoglucosan emission rates were also statistically significantly lower for CT2 and CT3 compared to the baseline testing, but not for CT1.

3.2. PAH and nitro-PAH emissions

More than 100 gaseous and particle-phase PAH compounds were identified and quantified for the baseline cooking experiment and the three control technologies, including non-substituted PAHs, methyl- and ethyl-substituted PAHs, biphenyls, and oxygenated PAHs, as shown in Fig. 2 (a–b) and Table SM2 and Table SM3. The PAH emission rates were dominated by lower and medium molecular weight PAH compounds. In contrast to previous studies (Chen et al., 2007; McDonald et al., 2003; Schauer et al., 1999), under the present test conditions, particle-phase PAHs were found in higher concentrations than gas-phase PAHs. The distribution in the particle phase emissions showed that phenanthrene, anthracene, fluoranthene, pyrene, fluorene, and methyl- and dimethyl-phenanthrenes were the most abundant PAHs. Heavier PAH compounds were also detected in the particle-phase, with benzo(*ghi*)fluoranthene, cyclopenta(*c,d*)pyrene, benzo(*a*)pyrene, indeno[123-*cd*]pyrene, coronene, and benzo(*ghi*)perylene showing relatively high concentrations for all cooking experiments. McDonald et al. (2003) reported similar PAH distributions and emission rates from charbroiled meat cooking. Our results also agree with other studies showing higher pyrene emission rates compared to different

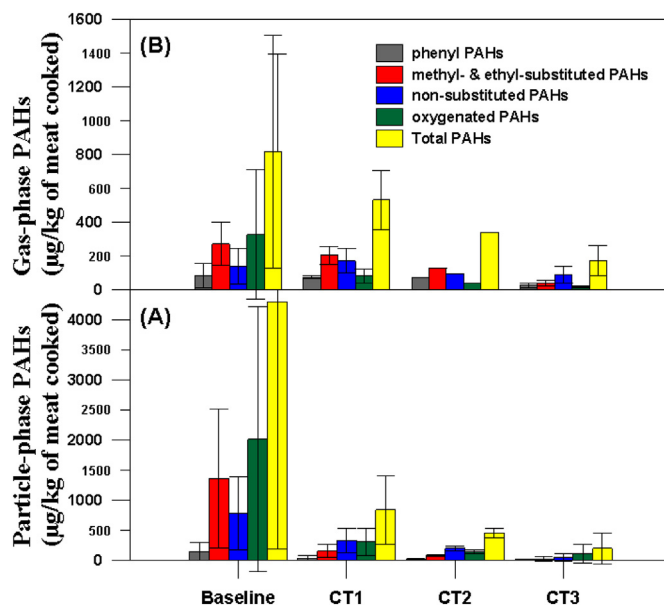


Fig. 2. (a–b): Particle-phase PAH emissions (A) and gas-phase PAH emissions (B), expressed in $\mu\text{g}/\text{kg}$ of meat cooked, for the baseline testing and the three control technologies.

cooking styles, including meat charbroiling and Chinese cooking (Chen et al., 2007; He et al., 2004; Zhao et al., 2007b).

It is worth to be mentioned that the majority of the published literature do not report oxygenated PAH (oxy-PAH) emissions from cooking operations. Oxy-PAHs, such as quinones, have been found to generate ROS resulting in oxidative stress that can lead to allergic diseases, and polycyclic aromatic ketones, quinones and anhydrides are well known mutagenic compounds (Knecht et al., 2013). Oxy-PAH compounds are emitted mainly from combustion processes, and they can also originate from heterogeneous reactions between PAHs and ozone. In contrast to their parent PAHs, most of the oxy-PAHs found in PM are directly toxic and mutagenic (Durant et al., 1996). This is the first study to report that oxy-PAHs dominated the particle-phase meat cooking PAH emissions profile. The most abundant oxy-PAH compounds were fluorenone, benzanthrone, perinaphthenone, 1,4-naphthoquinone, 9-anthraaldehyde, xanthone, and anthraquinone. Similar to their parent PAHs, oxy-PAHs were seen in substantially higher concentrations in the particle-phase than the gas-phase, revealing that most of these compounds, which were light molecular-weight, three-membered ring PAHs, existed in the particle-phase.

The highest contributors to the gas-phase PAHs were mainly the two-membered ring compounds and their ethyl- and methyl-substitutes. These were naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, 2,6 + 2,7-dimethylnaphthalene, 1,3 + 1,6 + 1,7-dimethylnaphthalene, acenaphthylene, 1 + 2 ethylnaphthalene, and some trimethylnaphthalenes. The next major contributors to the gas-phase PAHs were three-membered ring PAH compounds, including fluorene and phenanthrene. Our results are consistent with the study by Chen et al. (2007), in which naphthalene was the dominant gas-phase (unsubstituted) PAH compound from samples collected from Chinese restaurants, Western restaurants, and Western fast-food restaurants. However, the oxygenated 1,4-naphthoquinone and perinaphthenone compounds made up the majority of the gas-phase mass emissions in this study.

PAHs are formed between 550 °C and 950 °C, and maximum PAH production occurs at approximately 780 °C (Commins, 1969). Under the present experimental conditions, the surface of the charbroiled meat did not reach such high temperatures, while the meat itself did not contain any PAH compounds. Therefore, the relatively high PAH concentrations were likely not emitted directly from the meat itself, but from the direct access of lipids and fats onto the natural gas open

hot flame that favored the formation of PAHs via pyrolysis and subsequent volatilization and partly re-deposition on the meat surface (McDonald et al., 2003; Lijinsky, 1991; Rogge et al., 1991). PAH production from charbroiling cooking is a function both of the fat content of the meat and the proximity of the food to the heat source, and can be reduced by cooking for longer periods at lower temperatures (Phillips, 1999). Previous studies have shown that meat charbroiling processes exhibit higher PAH emissions than other cooking styles (McDonald et al., 2003; Wang et al., 2015).

Nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) can be either directly produced from combustion sources by electrophilic aromatic substitution reactions between nitrating agents, such as nitrogen dioxide (NO_2), and the parent PAHs, or formed from their parent PAHs by atmospheric OH or NO_3 radical initiated reactions (Miet et al., 2009). To date, there is little information available on nitro-PAH emissions from meat cooking processes. Fig. 3 shows the total gas- and particle-phase nitro-PAH emissions, whereas Table SM4 and Table SM5 list the individual nitro-PAH compounds for each phase. Analogous to their parent PAHs, particle-phase nitro-PAH were found in higher concentrations than the gas-phase compounds, with both light molecular weight compounds, such as 1-methyl-5-nitronaphthalene, 2-methyl-4-nitronaphthalene, 1-methyl-6-nitronaphthalene, 9-nitroanthracene, 2-nitroanthracene, and 1,8-dinitronaphthalene, and higher nitro-PAHs, such as 3-nitrophenanthrene, 2-nitrofluoranthene, 4-nitropyrene, 1-nitropyrene, and 7-nitrobenz(a)anthracene being dominant for all cooking experiments. Note that 1-nitropyrene, a compound that usually partitions exclusively in the particle-phase and a possible human carcinogen, was found in relatively high concentrations in the gas-phase.

Generally, PAH emissions decreased with the use of control technologies. The reductions in total particle-phase PAH and gas-phase PAH emissions ranged from 80% to 95% and from 35% to 79%, respectively. CT1 appeared to be the least effective technology in oxidizing light and heavier PAH compounds from meat cooking processes, with CT3 being the most effective technology in reducing these pollutants. It should be noted that heavier PAH compounds, such as benzo(a)pyrene, benz(a)anthracene, chrysene, indeno[123-cd]pyrene, dibenzo(ah)anthracene, benzo(ghi)perylene, and benzo(k)fluoranthene all decreased with the aftertreatment control technologies compared to the baseline testing. The use of control technologies also reduced nitro-PAH

emissions, including 1-nitropyrene and other nitrated species that have been identified as possible human carcinogens (i.e., 4-nitropyrene). It is hypothesized that the relatively high levels of 1-nitropyrene and 4-nitropyrene emissions in the particle-phase were likely due to electrophilic aromatic substitution reactions between parent pyrene and nitrogen containing cations such as NO_2^+ , as well as other nitrogen containing species in meat cooking (e.g., amides, etc.). The reductions in total nitro-PAH emissions ranged from 55% to 90% and from 26% to 96% for the particle-phase and gas-phase, respectively. It has to be noted that both total particle-phase PAH and particle-phase nitro-PAH emissions exhibited reasonable good correlations with PM mass, as previously reported by Gysel et al. (2018), with measured R^2 values of 0.62 and 0.82, respectively.

3.3. Trace elements and metals

Table SM6 lists the metal emissions, expressed in $\mu\text{g}/\text{kg}$ of meat cooked, for all cooking experiments. The elemental matrix showed that sulfur (S), potassium (K), chloride (Cl), and phosphorus (P) were the dominant elements, with our findings being consistent with previous studies (38–39, 45). The use of control technologies resulted in reductions for S, K, Cl, and P emissions compared to the baseline testing, with CT3 being the most efficient technology in reducing these species, as shown in Fig. 4. The reductions for the sum of metal species were on the order of 19%, 14%, and 89%, respectively, for CT1, CT2, and CT3. These reductions are in line with those found for the PM mass (Gysel et al., 2018), with the exception of CT2 suggesting this technology was not so efficient in reducing metals associated in the PM phase. For the redox active transition metals, iron (Fe), copper (Cu), and chromium (Cr) were the most prominent metals for all cooking processes, with their concentration showing both increases and decreases with the control technologies. Trace elements and metals emissions may be attributed to their presence in the meat or contamination during its processing. For example, K can be used as a marker of cooking PM emissions. Other metals such as Fe, Cu, and nickel (Ni) can be leached from the stainless steel surfaces under high cooking temperatures (Wang et al., 2015) or even the control technologies themselves (e.g., the stainless steel in-hood cartridges utilized in CT1).

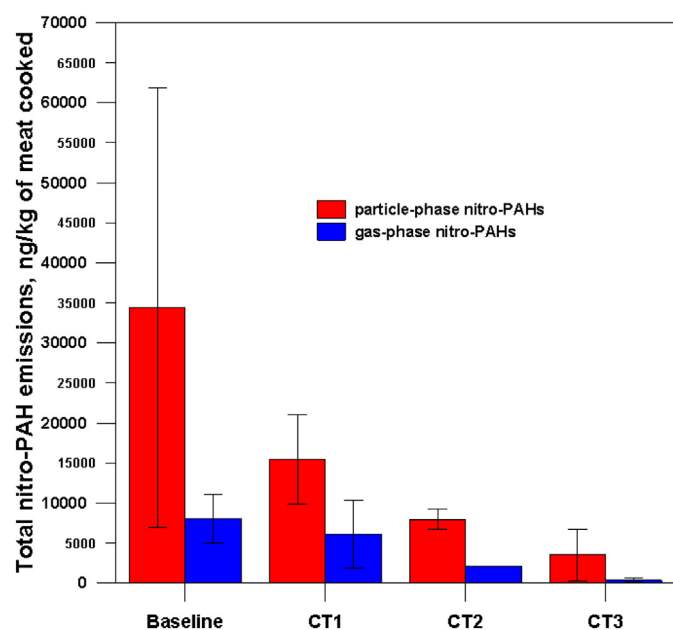


Fig. 3. Particle-phase and gas-phase nitrated PAH emissions, expressed in ng/kg of meat cooked, for the baseline testing and the three control technologies.

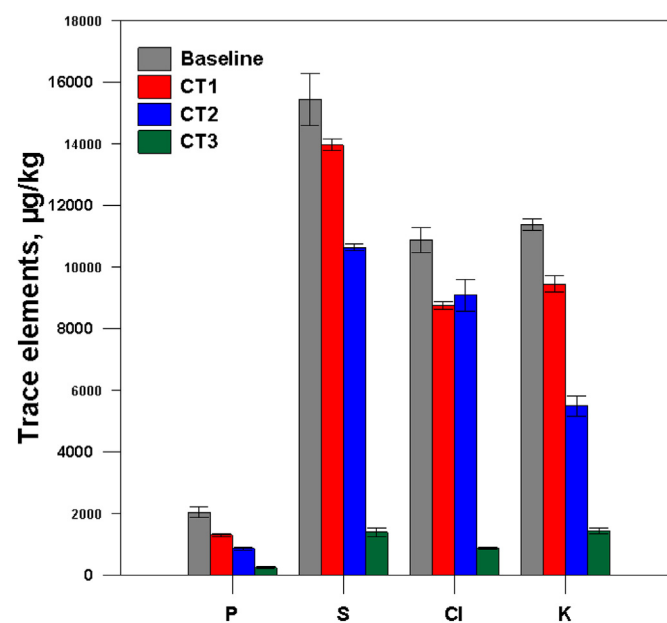


Fig. 4. Dominant trace elements, expressed in $\mu\text{g}/\text{kg}$ of meat cooked, for the baseline experiment and the three control technologies.

3.4. HAAs

HAAs are mutagenic and carcinogenic compounds and their formation through thermal stressing is the result of complex reactions that involve creatine/creatinine, free amino acids, and sugars through the Maillard reaction at temperatures between 150 °C and 250 °C (Viegas et al., 2012). Table 1 shows the gas- and particle-phase HAA emissions, with the gas-phase HAAs being in higher concentrations than those in the particle-phase samples. For the particle-phase HAAs, the dominant compounds were 2-amino-3,4,8-trimethylimidazo[4,5-f]quinoxaline (DiMeIQx) and 2-amino-1-methyl-6-phenylimidazo[4,5-b]pyridine (PhIP) emissions. A previous study also reported that PhIP is one of the most abundant HAA formed in cooked meat (Turesky, 2007). For the gas-phase HAAs, the most abundant compounds were PhIP and 2-amino-3-methylimidazo[4,5-f]quinoxaline (IQx). Overall, the use of control technologies results in large reductions in total HAA emission rates compared to the baseline testing, with the largest reductions observed for CT3. The reductions in total HAA emissions ranged from 67% to 90% for the particle-phase and from 68% to 94% for the gas-phase.

3.5. Oxidative stress and electrophilic properties

The DTT based redox activity or prooxidant content of the particle- and gas-phase components of cooking aerosols from the baseline and the three control technologies is shown in Fig. 5(a). The particle-phase components of PM showed a decline trend in redox activity compared to the baseline testing. For the particle-phase samples, CT1 exhibited similar redox activity to the baseline, whereas CT2 and CT3 showed statistically significant decreases in redox activity relative to the baseline testing on the order of 58% and 97%, respectively. The prooxidant content of the gas-phase samples was lower than that for the particle-phase samples. This finding is in agreement with a previous study conducted on ambient air samples (Eiguren-Fernandez et al., 2015). The results reported here suggest that charbroiled cooking aerosols contain more redox-active constituents in the particle-phase than the gas-phase of cooking emissions. In particular, the higher redox activity in the particle-phase could reflect the presence of redox active metals and organic compounds such as quinones and humic like substances (Ghio et al., 2012). All three control technologies resulted in statistically significant reductions in DTT activity in the gas-phase compared to the baseline testing, with CT3 showing the lowest redox activity in the semi-volatile fraction of the emissions. The role of metal ions in the DTT-based redox activity was also determined by comparing DTT activity in the presence and absence of DTPA, a metal chelator that binds Cu and Fe and blocks their redox activity (Fig. 5b). In the presence of DTPA, the baseline testing was 100% inhibited by DTPA, which indicates that all of the measured prooxidant activity was due to metals. CT1, CT2, and CT3 retained about 17%, 15%, and 24%, respectively, of the total prooxidant activity. These findings suggest that even though the DTT

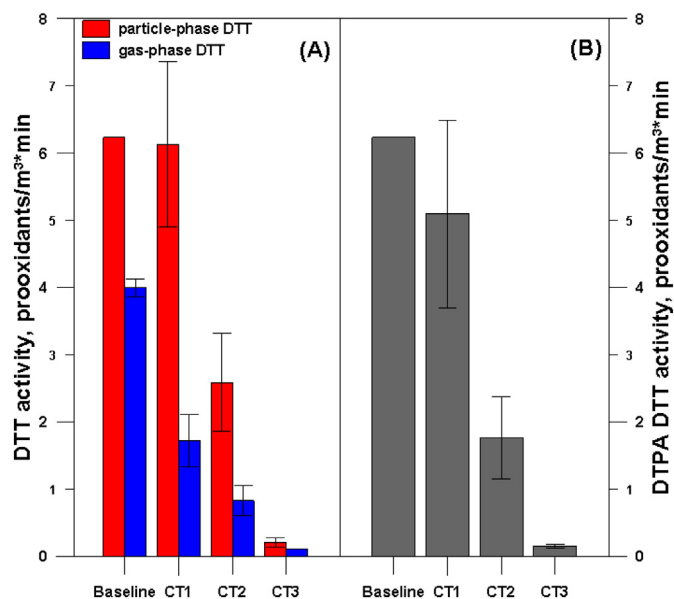


Fig. 5. (a–b): Particle-phase and gas-phase DTT activity (A) and redox activity in the presence of the metal chelator DTPA for the baseline testing and the three control technologies.

activity was decreased by the addition of the metal chelator for the control technologies, other PM compounds than metals contributed to the overall redox activity of cooking PM.

The electrophile content of the samples was determined by GAPDH inhibitory actions. As shown in Fig. 6, the semi-volatile components generally exhibited higher electrophile content than the PM, showing that most of the cooking PM constituents with electrophilic capacity are associated with the semi-volatile phase. This result was particularly evident for the baseline samples, which showed higher concentration of electrophiles than all the samples. It is theorized that semi-volatile compounds including quinones and α,β -unsaturated carbonyl compounds

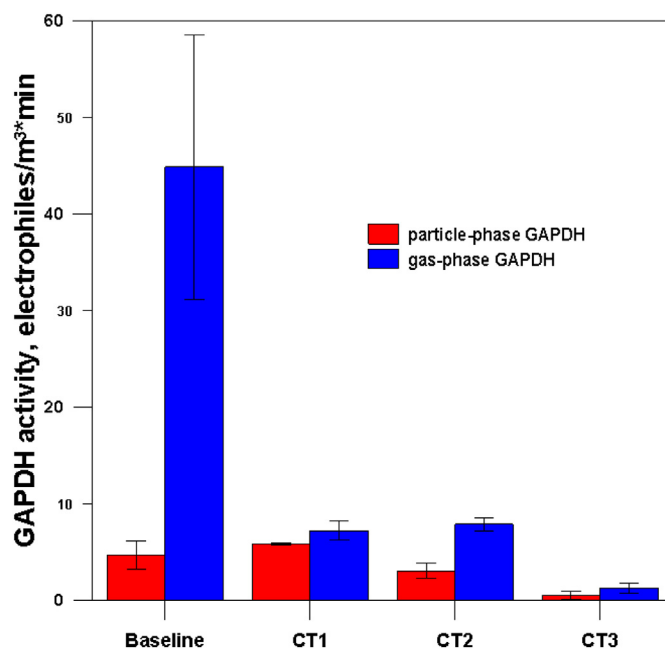


Fig. 6. Electrophilic content of the particle-phase and gas-phase components of cooking aerosol for the baseline testing and the three control technologies.

Table 1

HAAs emission rates, expressed in ng/kg of meat cooked, for the baseline testing and the three control technologies.

HAAs	Baseline	CT1	CT2	CT3
Particle-phase				
4,8-DiMeIQx	493 ± 454.6	64.6 ± 1.5	25.7 ± 10.2	5.997
PhIP	ND	93.4 ± 26.5	41.6 ± 1.1	44 ± 15.5
MeAaC	3.903	4.347	1.795	0.8 ± 0.1
IQx	5.443	5.383	2.3 ± 0.02	0.161
Gas-phase				
4,8-DiMeIQx	33.1 ± 30.6	13.5 ± 0.3	7.8 ± 3.1	1.1 ± 1.1
PhIP	1024 ± 22	355.8 ± 2.9	162.3 ± 0.1	33.5 ± 0.3
IQx	224.5 ± 224.5	81.1 ± 81.1	341.2 ± 2.9	7.6 ± 7.6
AaC	ND	1703.4 ± 1015.7	ND	29.4 ± 29.4

ND: below the detection limit.

reacted with the thiol groups of GAPDH. The gas-phase electrophile content showed statistically significant reductions on the order of 84%, 82%, and 97%, respectively, for CT1, CT2, and CT3 compared to the baseline testing. Statistically significant reductions in electrophilic activity for the particle-phase samples were observed for CT2 (34%) and CT 3 (88%) compared to the baseline testing.

4. Conclusions

Commercial meat charbroiling is the greatest source of PM and VOC emissions in California (South Coast Air Quality Management District (SCAQMD), 2016). Although public may not be aware of the adverse air quality and health effects of cooking operations, this study showed that underfired charbroiled meat cooking operations will produce high concentrations of toxic pollutants including PAH and nitro-PAH emissions, which the exposure to these species may induce a number of health effects. In addition, cooking emissions will produce organic acids and other polar compounds known to be precursors for SOA formation in urban areas. Overall, the toxicity of cooking aerosol reduced with the use of aftertreatment control technologies. Simple filtration technologies did not result in large emissions and toxicity benefits compared to the baseline experiment. More complex technologies, such as aerosol grease removers based on the boundary layer momentum transfer theory and electrostatic precipitators followed by a carbon activated bed, proved to be significantly more efficient in reducing most harmful pollutants and the potency of cooking aerosol.

Acknowledgments

The authors thank Mr. William A. Welch of the University of California, Riverside for his contribution to set up the experimental procedures and install the control technologies. We acknowledge funding from the South Coast Air Quality Management District (SCAQMD) under contract 12174.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.03.318>.

References

- Abdullahi, K., Delgado-Saborit, J.M., Harrison, R.M., 2013. Emissions and indoor concentration of particulate matter and its specific chemical components from cooking: a review. *Atmos. Environ.* 71, 260–294.
- Allan, J.D., Williams, P.I., Morgan, W.T., Martin, C.L., Flynn, M.J., Lee, J., Nemitz, E., Phillips, G.J., Gallagher, M.W., Coe, H., 2010. Contributions from transport, solid fuel burning and cooking to primary organic aerosols in two UK cities. *Atmos. Chem. Phys.* 10, 647–668.
- Buonanno, G., Morawska, L., Stabile, L., 2009. Particle emission factors during cooking activities. *Atmos. Environ.* 43, 3235–3242.
- Chen, Y., Ho, K.F., Ho, S.S.H., Ho, W.K., Lee, S.C., Yu, J.Z., Sit, E.H.L., 2007. Gaseous and particulate polycyclic aromatic hydrocarbons (PAHs) emissions from commercial restaurants in Hong Kong. *J. Environ. Monit.* 9, 402–409.
- Cheng, Y., Li, S.M., Leithead, A., Brickell, P.C., Leitch, W.R., 2004. Characterizations of cispinic acid and n-fatty acids on fine aerosols in the lower Fraser Valley during Pacific 2001 Air Quality Study. *Atmos. Environ.* 38, 5789–5800.
- Chiang, T.A., Pei-Fen, W., Ying, L.S., Wang, L.F., Ko, Y.C., 1999. Mutagenicity and aromatic amine content of fumes from heated cooking oils produced in Taiwan. *Food Chem. Toxicol.* 37, 125–134.
- Cho, A.K., Sioutas, C., Miguel, A.H., Kumagai, Y., Schmitz, D.A., Singh, M., Eiguren-Fernandez, A., Froines, J.R., 2005. Redox activity of airborne particulate matter at different sites in the Los Angeles Basin. *Environ. Res.* 99, 40–47.
- Commins, B.T., 1969. Formation of polycyclic aromatic hydrocarbons during pyrolysis and combustion of hydrocarbons. *Atmos. Environ.* 3, 565–572.
- Cross, A.J., Sinha, R., 2004. Meat-related mutagens/carcinogens in the etiology of colorectal cancer. *Environ. Mol. Mutagen.* 44, 44–55.
- Durant, J.L., Busby, W.F., Lafleur, A.L., Penman, B.W., Crespi, C.L., 1996. Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols. *Mutation Research/Genetic Toxicology* 371, 123–157.
- Eiguren-Fernandez, A., Di Stefano, E., Schmitz, D.A., Lefol Nani Guarieiro, A., Salinas, E.M., Nasser, E., Froines, J., Cho, A.K., 2015. Chemical reactivities of ambient air samples in three Southern California communities. *J. Air Waste Manage. Assoc.* 65, 266–273.
- Elmore, J.S., Warren, H.E., Mottram, D.S., Scollan, N.D., Enser, M., Richardson, R.I., Wood, J.D.A., 2004. Comparison of the aroma volatiles and fatty acid compositions of grilled beef muscle from Aberdeen Angus and Holstein-Friesian steers fed diets based on silage or concentrates. *Meat Sci.* 68, 27–33.
- Fine, P.M., Chakrabarti, B., Krudysz, M., Schauer, J.J., Sioutas, C., 2004. Diurnal variations of individual organic compound constituents of ultrafine and accumulation mode particulate matter in the Los Angeles Basin. *Environ. Sci. Technol.* 38, 1296–1304.
- Ghio, A.J., Carraway, M.S., Madden, M.C., 2012. Composition of air pollution particles and oxidative stress in cells, tissues, and living systems. *J. Toxicol. Environ. Health B Crit Rev* (1), 1–21.
- Gysel, N., Welch, W.A., Chen, C.L., Dixit, P., Cocker III, D.R., Karavalakis, G., 2018. Particulate matter emissions and gaseous air toxic pollutants from commercial meat cooking operations. *J. Environ. Sci.* 65, 162–170.
- He, L.Y., Hu, M., Huang, X.F., Yu, B.D., Zhang, Y.H., Liu, D.Q., 2004. Measurement of emissions of fine particulate organic matter from Chinese cooking. *Atmos. Environ.* 38, 6557–6564.
- Hildemann, L.M., Markowski, G.R., Cass, G.R., 1991. Chemical composition of emissions from urban sources of fine organic aerosol. *Environ. Sci. Technol.* 25, 744–759.
- Knecht, A.L., Goodale, B.C., Truong, L., Simonich, M.T., Swanson, A.J., Matzke, M.M., Anderson, K.A., Waters, K.M., Tanguary, R.L., 2013. Comparative developmental toxicity of environmentally relevant oxygenated PAHs. *Toxicol. Appl. Pharmacol.* 271, 266–275.
- Kumagai, Y., Koide, S., Taguchi, K., Endo, A., Nakai, Y., Yoshikawa, T., Shimojo, N., 2002. Oxidation of proximal protein sulfhydryls by phenanthraquinone, a component of diesel exhaust particles. *Chem. Res. Toxicol.* 15, 483–489.
- Kreyling, W.G., Semmler-Behnke, M., Moller, W., 2006. Health implications of nanoparticles. *J. Nanopart. Res.* 8, 543–562.
- Lelieveld, J., Evans, J.S., Fnais, M., Giannadaki, D., Pozzer, A., 2015. The contribution of outdoor air pollution sources to premature mortality on a global scale. *Nature* 525, 367–371.
- Lewtas, J., 2007. Air pollution combustion emissions: characterization of causative agents and mechanisms associated with cancer, reproductive, and cardiovascular effects. *Mutat. Res.* 636, 95–133.
- Li, C.T., Lin, Y.C., Lee, W.J., Tsai, P.J., 2003a. Emission of polycyclic aromatic hydrocarbons and their carcinogenic potencies from cooking sources to the urban atmosphere. *Environ. Health Perspect.* 111, 483–487.
- Li, N., Sioutas, C., Cho, A., Schmitz, D., Misra, C., Sempf, J., Wang, M.Y., Oberley, T., Froines, J., Nel, A., 2003b. Ultrafine particulate pollutants induce oxidative stress and mitochondrial damage. *Environ. Health Perspect.* 111, 455–460.
- Li, N., Bhattacharya, P., Karavalakis, G., Williams, K., Gysel, N., Rivera-Rios, N., 2014. Emissions from commercial-grade charbroiling meat operations induce oxidative stress and inflammatory responses in human bronchial epithelial cells. *Toxicol. Rep.* 1, 802–811.
- Lijinsky, W., 1991. The formation and occurrence of polynuclear aromatic hydrocarbons associated with food. *Mutation Research/Genetic Toxicology* 259, 251–261.
- McDonald, J.D., Zielinska, B., Fujita, E.M., Sagebiel, J.C., Chow, J.C., Watson, J.G., 2003. Emissions from charbroiling and grilling of chicken and beef. *J. Air Waste Manage. Assoc.* 53, 185–194.
- Miet, K., Le Menach, K., Flaud, P.M., Budzinski, H., Villenave, E., 2009. Heterogeneous reactivity of pyrene and 1-nitropyrene with NO₂: kinetics, product yields and mechanism. *Atmos. Environ.* 43, 837–843.
- Mohr, C., Huffman, J.A., Cubison, M.J., Aiken, A.C., Docherty, K.S., Kimmel, J.R., Ulbrich, I.M., Hannigan, M., Jimenez, J.L., 2009. Characterization of primary organic aerosol emissions from meat cooking, trash burning, and motor vehicles with high-resolution aerosol mass spectrometry and comparison with ambient and chamber observations. *Environ. Sci. Technol.* 43, 2443–2449.
- Mohr, C., DeCarlo, P.F., Heringa, M.F., Chirico R Slowik, J.G., Richter, R., Reche, C., Alastuey, A., Querol, X., Seco, R., Penuelas, J., Jimenez, J.L., Crippa, M., Zimmermann, R., Baltensperger, U., Prevot, A.S.H., 2012. Identification and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer data. *Atmos. Chem. Phys.* 12, 1649–1665.
- Netto, L.E., Stadtman, E.R., 1996. The iron-catalyzed oxidation of dithiothreitol is a biphasic process: hydrogen peroxide is involved in the initiation of a free radical chain of reactions. *Arch. Biochem. Biophys.* 333, 233–242.
- Ni, W., McNaughton, L., LeMaster, D.M., Sinha, R., Turesky, R.J., 2008. Quantification of 13 heterocyclic aromatic amines in cooked beef, pork, and chicken by liquid chromatography-electrospray ionization/tandem mass spectrometry. *J. Agric. Food Chem.* 56, 68–78.
- Nolte, C.G., Schauer, J.J., Cass, G.R., Simoneit, B.R.T., 1999. Highly polar organic compounds present in meat smoke. *Environ. Sci. Technol.* 33, 3313–3316.
- Pei, B., Cui, H., Liu, H., Yan, N., 2016. Chemical characteristics of fine particulate matter emitted from commercial cooking. *Front. Environ. Sci. Eng.* 10, 559–568.
- Phillips, D.H., 1999. Polycyclic aromatic hydrocarbons in the diet. *Mutation Research/Genetic Toxicology and Environmental Mutagenesis* 443, 139–147.
- Robinson, A.L., Subramanian, R., Donahue, N.M., Bernardo-Bricker, A., Rogge, W.F., 2006. Source apportionment of molecular markers and organic aerosol. 3. Food cooking emissions. *Environ. Sci. Technol.* 40, 7820–7827.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., 1991. Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations. *Environ. Sci. Technol.* 2, 1112–1125.
- Rose, M., Holland, J., Dowding, A., Petch, S.R.G., White, S., Fernandes, A., Mortimer, D., 2015. Investigation into the formation of PAHs in foods prepared in the home to determine the effects of frying, grilling, barbecuing, toasting and roasting. *Food Chem. Toxicol.* 78, 1–9.

- Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmos. Environ.* 30, 3837–3855.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 1999. Measurement of emissions from air pollution sources. 1. C1–C29 organic compounds from meat charbroiling. *Environ. Sci. Technol.* 33, 1566–1577.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2002. Measurement of emissions from air pollution sources. 4. C1–C27 organic compounds from cooking with seed oils. *Environ. Sci. Technol.* 36, 567–575.
- Shinyashiki, M., Rodriguez, C.E., Di Stefano, E.W., Sioutas, C., Delfino, R.J., Kumagai, Y., Froines, J.R., Cho, A.K., 2008. On the interaction between glyceraldehyde-3-phosphate dehydrogenase and airborne particles: evidence for electrophilic species. *Atmos. Environ.* 42, 517–529.
- Sinha, R., 2002. An epidemiologic approach to studying heterocyclic amines. *Mutat. Res.* 506–507, 197–204.
- Sinha, R., Rothman, N., Brown, E.D., Salmon, C.P., Knize, M.G., Swanson, C.S., Rossi, S.C., Mark, S.D., Levander, O.A., Felton, J.S., 1995. High concentrations of the carcinogen 2-amino-1-methyl-6-phenylimidazo[4,5-b]pyridine (PhIP) occur in chicken but are dependent on the cooking method. *Cancer Res.* 55, 4516–4519.
- Sioutas, C., Delfino, R.J., Singh, M., 2005. Exposure assessment for atmospheric ultrafine particles (UFPs) and implications in epidemiologic research. *Environ. Health Perspect.* 113, 947–955.
- South Coast Air Quality Management District (SCAQMD), 2016. AQMP White Paper. September 2015. <http://www.aqmd.gov/docs/default-source/Agendas/aqmp/white-paper-working-groups/wp-pm-draftfinal.pdf?sfvrsn=4>.
- Sun, Y.L., Zhang, Q., Schwab, J.J., Demerjian, K.L., Chen, W.N., Bae, M.S., Hung, H.M., Hogrefe, O., Frank, B., Rattigan, O.V., Lin, Y.C., 2011. Characterization of the sources and processes of organic and inorganic aerosols in New York City with a high-resolution time-of-flight aerosol mass spectrometer. *Atmos. Chem. Phys.* 11, 1581–1602.
- Turesky, R.J., 2007. Formation and biochemistry of carcinogenic heterocyclic aromatic amines in cooked meats. *Toxicol. Lett.* 168, 219–227.
- Viegas, O., Novo, P., Pinto, E., Pinho, O., Ferreira, I.M.P.L.V.O., 2012. Effect of charcoal types and grilling conditions on formation of heterocyclic aromatic amines (HAs) and polycyclic aromatic hydrocarbons (PAHs) in grilled muscle foods. *Food Chem. Toxicol.* 50, 2128–2134.
- Wang, G., Cheng, S., Wei, W., Wen, W., Wang, X., Yao, S., 2015. Chemical characteristics of fine particles emitted from different Chinese cooking styles. *Aerosol Air Qual. Res.* 15, 2357–2366.
- Williams, B.J., Goldstein, A.H., Kreisberg, N.M., Hering, S.V., Worsnop, D.R., Ulbrich, I.M., Docherty, K.S., Jimenez, J.L., 2010. Major components of atmospheric organic aerosol in southern California as determined by hourly measurements of source marker compounds. *Atmos. Chem. Phys.* 10, 11577–11603.
- Zhang, Q., Gangupomu, R.H., Ramirez, D., Zhu, Y., 2010. Measurement of ultrafine particles and other air pollutants emitted by cooking activities. *Int. J. Environ. Res. Public Health* 7, 1744–1759.
- Zhao, Y., Hu, M., Slanina, S., Zhang, Y., 2007a. The molecular distribution of fine particulate organic matter emitted from Western-style fast food cooking. *Atmos. Environ.* 41, 8163–8171.
- Zhao, Y., Hu, M., Slanina, S., Zhang, Y., 2007b. Chemical compositions of fine particulate organic matter emitted from Chinese cooking. *Environ. Sci. Technol.* 41, 99–105.