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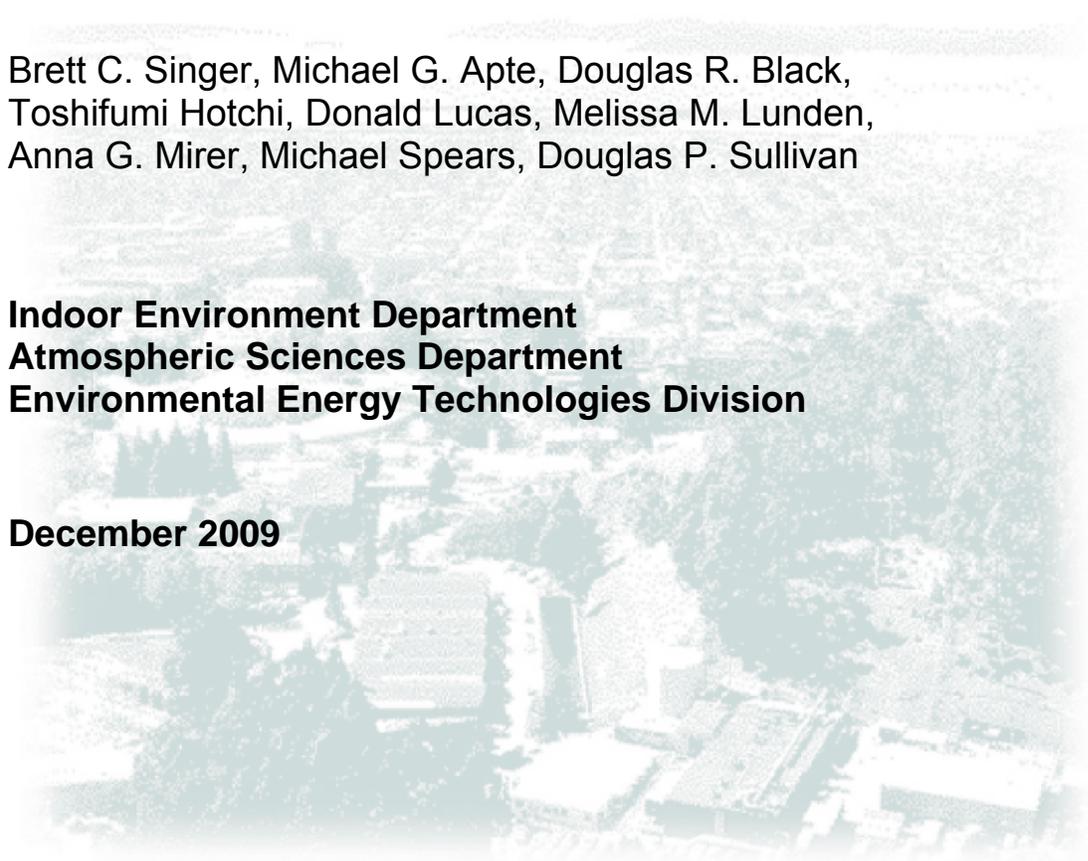
NATURAL GAS VARIABILITY IN CALIFORNIA: ENVIRONMENTAL IMPACTS AND DEVICE PERFORMANCE

EXPERIMENTAL EVALUATION OF POLLUTANT EMISSIONS FROM RESIDENTIAL APPLIANCES

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This report has been submitted to the California Energy Commission (CEC). It is anticipated that a version of the report – containing the same technical information but potentially differing in presentation based on changes made by CEC technical editors – will be published by the Energy Commission as report CEC-500-2009-099. Summary reports about individual burners are compiled as independent documents Appendices C-J; these documents will carry the same CEC report number and will be available through the CEC publication web site. The appendices may also be requested directly from the PI, Dr. Brett C. Singer at bcsinger@lbl.gov.

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Abstract

The effect of liquefied natural gas on pollutant emissions was evaluated experimentally with used and new appliances in the laboratory and with appliances installed in residences, targeting information gaps from previous studies. Burner selection targeted available technologies that are projected to comprise the majority of installed appliances over the next decade. Experiments were conducted on 13 cooktop sets, 12 ovens, 5 broiler burners, 5 storage water heaters, 4 forced air furnaces, 1 wall furnace, and 6 tankless water heaters. Air-free concentrations and fuel-based emission factors were determined for carbon monoxide, nitrogen oxides, nitrogen dioxide, and the number of (predominantly ultrafine) particles over complete burns—including transient effects (device warm-up and intermittent firing of burners) following ignition—and during more stable end-of-burn conditions. Formaldehyde was measured over multi-burn cycles. The baseline fuel was Northern California line gas with Wobbe number (a measure of fuel energy delivery rate) of 1320–1340; test fuels had Wobbe numbers of roughly 1390 and 1420, and in some cases 1360. No ignition or operational problems were observed during test fuel use. Baseline emissions varied widely across and within burner groups and with burner operational mode. Statistically significant emissions changes were observed for some pollutants on some burners.

Keywords: Carbon monoxide, formaldehyde, indoor air quality, liquefied natural gas, nitrogen dioxide, nitrogen oxides, particle number, pollutant exposures, ultrafine particles

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Executive Summary

Introduction

Anticipating an increasing use of liquefied natural gas in California, the California Energy Commission requested research to assess the potential impacts of this change. Liquefied natural gas typically contains more energy per unit volume compared to the natural gas that has been distributed in California. This difference has the potential to affect the performance and pollutant emissions of existing natural gas equipment. Lawrence Berkeley National Laboratory and the Gas Technology Institute are working in collaboration to assess these impacts. Lawrence Berkeley National Laboratory is focusing on residential appliances and air quality, while the Gas Technology Institute focuses on industrial burners. This report presents experimental results and analysis focusing on pollutant emissions from residential appliances.

Task Purpose and Objectives

The overall goal of the work presented in this interim report was to experimentally evaluate the effect of variations in natural gas composition and physical properties that is, gas quality, on residential appliance performance and pollutant emissions. The following specific objective and focus areas were selected to address gaps in the existing knowledge base:

- Quantify baseline emission rates of ultrafine particles (as indicated by particle number) and formaldehyde from common domestic appliances using natural gas currently distributed by Pacific Gas & Electric (PG&E) in Northern California.
- Measure the effect of gas quality variability on pollutant emissions from used appliances during operating cycles that start with ignition and include transient periods when the burner is not fully warmed.
- Measure emissions of carbon monoxide, nitrogen oxides, nitrogen dioxide, particle number, and formaldehyde.
- Investigate the effect of gas quality variability on performance and pollutant emission rates for emerging technology devices that have not been adequately examined in past studies.
- Investigate and quantify the effect of gas quality variability on performance and pollutant emission rates for common installed appliances.

Task Outcomes

Experiments were conducted on used appliances currently installed in residences and on used and new appliances in the laboratory. Appliances were operated through test cycles designed to capture key variations and transient features of actual use patterns. Appliances were operated with line-supplied natural gas from PG&E as a baseline fuel and with simulated LNG blends. Blends were formulated to achieve Wobbe numbers (a measure of energy delivery rate through a fixed orifice) of roughly 1420, 1390, and in later experiments, 1360 (as calculated from fuel heating value in British thermal units [Btu] per standard cubic foot). Pacific Gas & Electric line gas used in experiments typically was in the range of 1320–1340 Wobbe numbers. Two

variations each of the 1420 and 1390 Wobbe number fuels were used. Early lab experiments used site-mixed blends, whereas all field and many lab experiments used premixed cylinders.

The early 1420 Wobbe number blend was roughly 5.8% ethane, 3.0% propane, and 1.1% butanes with a balance of (90.1%) methane. The early 1390 Wobbe number fuel was the 1420 blend diluted with roughly 1.6% nitrogen. Premixed blends were 12% ethane, 1.6% propane, and 86.4% methane (1420 Wobbe number); 8.0% ethane and 92% methane (1390 Wobbe number); and 7.9% ethane, 1.9% nitrogen and 90.2% methane (1360 Wobbe number).

Experiments were conducted on thirteen sets of cooktop burners, twelve oven bottom burners, five dedicated “waist-high” broilers, five storage water heaters, four central forced air furnaces, one wall furnace, and six tankless (on-demand) water heaters. In all but one case, burners were evaluated with PG&E line gas and blends at 1390 and 1420 Wobbe number; many were additionally evaluated with the 1360 Wobbe number blend. Including method development and preliminary evaluations, over 250 experiments were conducted. Measurements of pollutant concentrations, carbon dioxide (CO₂), and oxygen levels in exhaust streams were used to calculate air-free concentrations; fuel properties were used to also calculate emission factors related to fuel energy consumption (for example, in units of nanogram of pollutant emitted per Joule of fuel energy). Results were obtained for carbon monoxide, nitrogen oxides, nitric oxide, nitrogen dioxide, the number of particles over individual burns, and for formaldehyde over multi-burn cycles. Size-resolved measurements showed that the vast majority of particles were < 100 nanometers in aerodynamic diameter; that is, they were ultrafine particles. Cooktops were operated with four burners at maximum firing rate. Broilers and storage water heaters were operated at a single setting and firing rate. Ovens were operated at three temperature settings and tankless water heaters were operated at three water flow rates. Two of the furnaces were operated at low and high firing rates.

In no case was basic burner operation (ignition and flame stability) observed to be compromised by use of the higher Wobbe number fuels.

Emissions of all pollutants varied widely across and within burner groups. Baseline emissions of carbon monoxide, nitrogen oxides, nitrogen dioxide and particle number varied with operating mode for oven-bottom and tankless water heater burners. The number of particles emitted was observed to be elevated in the first and sometimes the second experiment of the day in many cases. Bivariate (assuming one variable depends on only one other variable) and multivariate (assuming one variable depends on multiple other variables) linear models were employed to estimate the magnitude and statistical significance of fuel Wobbe number effects on emission rates independent of these factors. Formal statistical analyses were conducted to estimate the effect of fuel Wobbe number on each pollutant emission factor. The dependence of emissions on fuel Wobbe number was assumed to be linear and was calculated per 25 Wobbe number increase. These results can be scaled to estimate impacts for any level of Wobbe number increase up to the bounds of the experimental assessment; that is, to fuels with a Wobbe number of roughly 1420.

The tables provided at the end of this Executive Summary provide information about the burners evaluated and the number of experiments conducted at each fuel Wobbe level, as well as the measured pollutant emission rates with PG&E line gas, and the estimated percent change in emissions for a 50-unit increase in fuel Wobbe number. This increment represents the shift from fuels currently distributed in much of Northern and Southern California (with typical Wobbe number of roughly 1335) to the current regulated limit of 1385 Wobbe number. In the tables, the abbreviation “ns” indicates that no statistically significant trend was observed for a given pollutant on a given burner; lack of a discernible trend is independent of the magnitude of Wobbe number change.

These results should be considered in the context of potential impacts on air quality and human health. Since cooking appliances typically emit pollutants directly to indoor air, the focus is on pollutants which directly impact health (such as carbon monoxide, nitrogen dioxide, formaldehyde, and particle number concentration) and a hazard can result from any individual burner with high emissions that increase with an increase in fuel Wobbe number. Emissions of primary pollutants from all groups of burners present a potential ambient air quality concern to the extent that they contribute to overall levels of an area’s pollutants. Nitrogen oxides contribute to air-basin wide ozone and secondary aerosol formation. Since water heating and space heating comprise the majority of residential natural gas use and since emissions of nitrogen oxides do not vary widely by burner group, the impact of fuel changes on total nitrogen oxides from residential appliances will depend mostly on water heaters and furnaces.

Task Conclusions

Among cooking burners with substantial baseline carbon monoxide emissions (taken here as ≥ 100 nanograms per Joule), almost all had carbon monoxide increase at rates of 5–40 percent per 50 Wobbe number fuel change. For cooking burners having substantial baseline nitrogen dioxide emissions (taken here as ≥ 5 nanograms per Joule), roughly half had nitrogen dioxide emissions increase; the increase was in most cases on the order of 20 percent or less for a 50 Wobbe number increase in fuel. Only one of the cooking burners with the highest emissions of formaldehyde (≥ 1 nanograms per Joule) had emissions increase with fuel Wobbe number. Particle number emission rates from cooking burners varied much more with operating conditions (including recent use history) than with fuel Wobbe number. The impact of cooking burner pollutant emission changes on pollutant exposures in California homes are being assessed in another project task.

Among the vented burners, primary pollutant emissions from tankless water heaters appear to be the most sensitive to fuel Wobbe number. Two of the six tankless water heaters—including the one with highest baseline carbon monoxide—had carbon monoxide increase by about 110 percent, and a third had carbon monoxide increase by 22 percent per 50 Wobbe number fuel increase. Nitrogen dioxide was found to increase by 3–19 percent per 50 Wobbe number increase in five of six tankless water heaters and decrease by 3 percent in the sixth. Formaldehyde was estimated to decrease by 5–22 percent for a 50 Wobbe number change in five of six tankless water heaters. Two of the four central furnaces had carbon monoxide emissions decrease by 26 percent for a 50 Wobbe number fuel increase.

Consistent with past studies, nitrogen oxide emissions for most appliances were found to be marginally sensitive to changes in fuel Wobbe number. Mean nitrogen oxide was estimated to increase by 3–7 percent per 50 Wobbe number increase in three furnaces. The effect was even smaller for the storage water heaters tested. Tankless water heaters had lower nitrogen oxide on average relative to storage water heaters, but nitrogen oxide in these burners was much more sensitive to fuel Wobbe number. The outdoor air quality impacts of potential changes to fuel Wobbe number will be assessed in another project task.

One prominent finding that was not a focus of this study was the starkly different pollutant emissions of tankless and storage water heaters. Tankless units had emissions of carbon monoxide and formaldehyde that were orders of magnitude higher on average compared with storage water heaters. This finding suggests that a large shift to tankless technology (in the absence of controls on these emissions) could dramatically impact the baseline emission inventory for carbon monoxide and formaldehyde from natural gas water heating. A major increase in the population of tankless water heaters (with burner technology similar to that evaluated in this study) would also make the carbon monoxide and nitrogen oxide inventories for residential gas water heating much more sensitive to changes in gas quality.

Benefits to California

This research is helping to lay the groundwork for maintaining a safe and reliable natural gas supply in California. The proactive investigation of potential impacts of new supplies, including LNG, will allow California to better understand the impacts of gas quality on operability and pollutant emission levels for the existing population of appliances in the state. The results presented in this report will be used to assess potential impacts on indoor exposures associated with gas cooking burners and outdoor air quality, including ozone and secondary organic aerosol.

Table ES-1. Summary of experiments and results¹ for cooktop burners

ID Site ²	Burner description and ratings (kBtu/h)	Age	Fuels WN (n)	NO _x (ng/J)	CO (ng/J)	NO ₂ (ng/J)	HCHO (ng/J)	PN (10 ⁴ /J)
CT01 Lab	sealed; cast Al burner w/slots; cast iron cap; 9.1 (x3), 7	12	PG&E (2) 1390 (3) 1420 (5)	31.5 +3.2%	11 +27%	6.7 +14%	0.31 +35%	11 (1-490)
CT02 Lab	open; stamped Al w/slots; 9 (x4)	9	PG&E (4) 1390 (3) 1420 (3)	37.3 (ns)	29 +10%	8.5 +5.7%	0.55 (ns)	117 (29-460)
CT03 Lab	sealed; cast steel punched ports; 12 (x2), 9.2 (x2)	6	PG&E (2) 1390 (3) 1420 (2)	34.9 (ns)	231 +30%	12.1 +20%	1.00 +62%	265 (90-570)
CT04 Res4	sealed; cast Al burner w/slots; cast iron cap; 16, 12, 9.5, 5	2	PG&E 1420	47.3 (ns)	42 (ns)	10 (ns)	no data	310, 430*
CT05 Lab	open; stamped Al w/slots; 9 (x4)	5	PG&E 1390 1420	41.9 +4.5%	87 (ns)	11.2 (ns)	0.67 (ns)	1270 (610-9200)
CT06 Lab	sealed; cast Al burner w/slots; cast iron cap; 12, 9.5 (x2), 5	11	PG&E 1390 1420	38.5 +1.7%	13 +93%	5 (ns)	0.12 (ns)	320 (191-1080)
CT07 Lab	open; stamped Al w/slots; 9 (x4)	13	PG&E 1390 1420	34.2 (ns)	59 +16%	7.3 +12%	0.44 +37%	550 (380-2250)
CT08 Lab	sealed; cast iron, drilled ports; cast iron cap; 10 (x2), 6 (x2)	16	PG&E (2) 1390 1420	33.5 (ns)	7 +14%	6.7 (ns)	0.09 (ns)	305 (129-1640)
CT09 Lab	sealed; cast Al burner w/slots; cast iron cap; 9 (x4)	2	PG&E (2) 1390 1420	25 (ns)	823 +5.9%	17.7 (ns)	4.7 (ns)	197 (101-1110)
CT10 Lab	open; stamped Al w/slots; 9.5 (x4)	12	PG&E 1360, 1390 1420	36.2 (ns)	57 +26%	9.6 (ns)	1.15 -28%	34 (8-183)
CT11 Lab	sealed; cast Al burner w/slots; cast iron cap; 12, 9.5 (x2), 5	8	PG&E 1360, 1390 1420	29.6 +2.5%	107 +23%	7.6 +4.9%	0.31 (ns)	168 (68-1100)
CT12 Lab	Same as CT03; sealed; cast steel punched ports; 12 (x2), 9.2 (x2)	17	PG&E (2) 1360, 1390 1420	34.3 (ns)	123 +40%	10.2 +11%	0.81 (ns)	1380 (1100-5400)
CT13 Lab	sealed; cast Al burner w/slots; cast iron cap; 12, 9.5 (x3)	6	PG&E (2) 1360, 1390 1420	34.9 +1.5%	48 +54%	7.1 +11%	0.10 (ns)	205 (43-1180)

¹ For NO_x, CO, NO₂ and HCHO, first value in each cell is full burn emission rate with PG&E line gas. Percent change is for 50 Btu/scf increase in fuel WN adjusted for effect of oven temperature; changes shown only for p-values ≤ 0.15; p ≤ 0.05 in bold (broader limits for HCHO, see text of report). Low p-values indicate statistically significant results. Values shown for PN are the median and range of particle number counts for individual burns across all fuels.

² Res = residence, identified by number.

WN = Wobbe number, NO_x = nitrogen oxide, CO = carbon monoxide, NO₂ = nitrogen dioxide, HCHO = formaldehyde, PN = particle number, ns = not significant.

*Only two tests were run.

Table ES-2. Summary of experiments and results¹ for oven bottom burners, adjusted for effect of oven temperature

ID Site	Burner description and rating	Age	Fuels WN (n)	NO _x (ng/J)	CO (ng/J)	NO ₂ (ng/J)	HCHO (ng/J)	PN (10 ⁴ /J)
OV01 Lab	tube burner under bottom plate; hot surface ignition; 15.5 kBtu/h	12	PG&E (2) 1390 (2) 1420 (4)	35.9 (ns)	16 +37%	3.8 (ns)	0.49 (ns)	27-335 3-48
OV02 Lab	tube burner under bottom plate; pilot ignition; 18 kBtu/h	9	PG&E (3) 1390 (2) 1420 (2)	34.4 (ns)	99 +34%	7.5 +18%	0.38 +11%	75-191 395-6300
OV03 Lab	tube burner under raised bottom; hot surface ignition; 18 kBtu/h	6	PG&E (4) 1390 (2) 1420 (2)	36.3 (ns)	61 +93%	5.1 +17%	0.46 (ns)	18-530 11-122
OV05 Lab	tube burner under bottom plate; hot surface ignition; 18 kBtu/h	5	PG&E 1390 (2) 1420	31.4 -2.8%	163 +24%	13.9 (ns)	0.43 +23%	-4 to 25 81-285
OV06 Lab	tube burner under raised bottom; hot surface ignition; 16 kBtu/h	11	PG&E (2) 1390 (2) 1420	33.0 (ns)	124 +5%	8.1 (ns)	1.01 (ns)	13-144 12-145
OV07 Lab	tube burner under bottom plate; hot surface ignition; 18 kBtu/h	13	PG&E 1390 (2) 1420	31.8 -2.4%	156 +5.9%	6.1 +8.5%	0.57 (ns)	24-76 180-790
OV08 Lab	tube burner under raised bottom; hot surface ignition; 18 kBtu/h	16	PG&E 1360, 1390 1420	33.3 -3.9%	108 +30%	5.5 +11%	3.0 -21%	17-61 18-31
OV09 Lab	tube burner under bottom plate; hot surface ignition; 18 kBtu/h	2	PG&E 1360, 1390 1420	27.4 -7.3%	174 +19%	11.3 (ns)	0.6 (ns)	0-10 -1 to 275
OV10 Lab	tube burner under bottom plate; hot surface ignition; 18 kBtu/h	12	PG&E (2) 1360, 1390 1420	32.9 (ns)	58 +26%	4.4 +24%	0.32 (ns)	11-29 310-890
OV11 Lab	tube burner under bottom plate; hot surface ignition; 16 kBtu/h	8	PG&E 1360, 1390 1420	40.5 +2.3%	528 -14%	13.2 (ns)	5.5 (ns)	89-137 240-2750
OV12 Lab	tube burner under bottom plate; hot surface ignition; 16 kBtu/h	17	PG&E 1360, 1390 1420	34.5 -2.2%	36 +15%	5.6 +10%	0.25 (ns)	101-132 71-89
OV13 Lab	tube burner under bottom plate; hot surface ignition; 18 kBtu/h	6	PG&E (2) 1390 1420	39.7 -1.6%	70 +47%	6.3 +38%	0.33 +20%	0-107 -3 to 36

¹ For NO_x, CO, NO₂ and HCHO, first value in each cell is mean of full burn emission rates with PG&E line gas measured at 350°F, 425°F, and 500°F. Percent change is for 50 Btu/scf increase in fuel WN adjusted for effect of oven temperature; changes shown only for p-values ≤ 0.15; p ≤ 0.05 in bold (broader limits for HCHO, see text of report). Low p-values indicate statistically significant results. Values shown for PN are the ranges of particle number counts across all fuels for burns at 350°F and 500°F.

WN = Wobbe number, NO_x = nitrogen oxide, CO = carbon monoxide, NO₂ = nitrogen dioxide, HCHO = formaldehyde, PN = particle number, ns = not significant.

Table ES-3. Summary of experiments and results¹ for broiler burners

ID Site	Burner description and rating	Age	Fuels WN (n)	NO _x (ng/J)	CO (ng/J)	NO ₂ (ng/J)	HCHO (ng/J)	PN (10 ⁴ /J)
BR01 Lab	tube burner with spreader; hot surface ignition; 11 kBtu/h	12	PG&E 1390 1420 (4)	30.8 +7.6%	44 +45%	2.8 +47%	no data	44 (26-169)
BR02 Lab	same burner as OV02; 18 kBtu/h	9	PG&E (2) 1390 (2) 1420	30.3 (ns)	145 +17%	11.2 (ns)	no data	2550 (950-2650)
BR03 Lab	tube burner with spreader; hot surface ignition; 13 kBtu/h	6	PG&E (2) 1390 1420	31.7 (ns)	124 (ns)	13.0 -7.2%	no data	245 (138-590)
BR06 Lab	tube burner with spreader; hot surface ignition; 16 kBtu/h	11	PG&E 1390 1420 (2)	17.1 -1.4%	120 -5.1%	7.8 (ns)	0.93 +7.5%	67 (63-107)
BR12 Lab	tube burner with spreader; hot surface ignition; 13 kBtu/h	17	PG&E 1360, 1390 1420	36.8 +5.5%	29 +32%	5.7 +13%	0.13 +15%	295 (69-570)
BR13 Lab	tube burner with spreader; hot surface ignition; 14 kBtu/h	6	PG&E 1360, 1390 1420	30.1 -4.0%	178 +14%	12.6 (ns)	0.79 +20%	410 (245-1070)

¹ For NO_x, CO, NO₂ and HCHO, first value in each cell is full burn emission rate with PG&E line gas. Percent change is for 50 Btu/scf increase in fuel WN; changes shown only for p-values ≤ 0.15; p ≤ 0.05 in bold (broader limits for HCHO, see text of report). Low p-values indicate statistically significant results. Values shown for PN are the median and range of particle number counts for individual burns across all fuels.

WN = Wobbe number, NO_x = nitrogen oxide, CO = carbon monoxide, NO₂ = nitrogen dioxide, HCHO = formaldehyde, PN = particle number, ns = not significant.

Table ES-4. Summary of experiments and results¹ for central forced air and wall furnaces

ID Site ²	Burner description and rating	Age	Fuels WN (n)	NO _x (ng/J)	CO (ng/J)	NO ₂ (ng/J)	HCHO (ng/J)	PN (10 ⁴ /J)
CF01 Res2 (mix)	condensing 94% eff.; induced draft; direct vent; 60 kBtu/h	5	PG&E 1390 1420	33.6 +7.2%	3.8 (ns)	2.4 (ns)	no data	0.0 (-0.3 to 0.8)
CF02 Res4 (high)	non-cond. 82% eff.; induced draft; 80 kBtu/h	5	PG&E 1390 1420	27.1 (ns)	13.0 +21%	5.9 (ns)	no data	3.9, 4.9, 5.5*
CF02 Res4 (low)	non-cond. 81% eff.; induced draft; 80 kBtu/h	5	PG&E 1390 1420	26.2 (ns)	30.8 -6.2%	9.7 (ns)	no data	1.0, 1.5, 3.5*
CF03 Res7	non-cond. 81% eff.; induced draft; 69 kBtu/h	9	PG&E 1390 1420	22.3 +2.5%	19.4 -26%	5.1 (ns)	0.38 -34%	27 (16-46)
CF04 Res8	condensing 93% eff.; induced draft; direct vent; 100 kBtu/h	6	PG&E(2), 1390 1420	23.6 +5.5%	17.2 -26%	4.4 -14%	0.16 -24%	no data
WF01 Res1	Pilot; gravity direct vent; 72% eff.; 14 kBtu/h	4	PG&E 1390 1420	32.7 (ns)	<1 (ns)	0.6 (ns)	no data	12 (3.9-30)

¹ For NO_x, CO, NO₂ and HCHO, first value in each cell is full burn emission rate with PG&E line gas. Percent change is for 50 Btu/scf increase in fuel WN adjusted for effect of oven temperature; changes shown only for p-values ≤ 0.15; p ≤ 0.05 in bold (broader limits for HCHO, see text of report). Low p-values indicate statistically significant results. Values shown for PN are the median and range of particle number counts for individual burns across all fuels.

² Res = residence, identified by number. CF01 started at low then changed to high firing rate during 6 of 7 burns with valid data; full-burn rates include both types of operation. In each experiment, CF02 operated in low firing mode for first burn, high firing mode for second burn.

WN = Wobbe number, NO_x = nitrogen oxide, CO = carbon monoxide, NO₂ = nitrogen dioxide, HCHO = formaldehyde, PN = particle number, ns = not significant.

* Only two test runs were conducted.

Table ES-5. Summary of experiments and results¹ for storage water heaters

ID Site ²	Description and rating	Age	Fuels WN (n)	NO _x (ng/J)	CO (ng/J)	NO ₂ (ng/J)	HCHO (ng/J)	PN (10 ⁴ /J)
WH01 Lab-A	40 gal FVIR; pilot; natural draft; std. burner; 40 kBtu/h	new	PG&E 1390 1420	13.6 -2.5%	0.1 (ns)	0.30 -67%	no data	3.2 (1.0-8.4)
WH01 Lab-B	See above	-	PG&E 1420	26.3 (ns)	-0.7 -0.07	1.55 -1%	0.03 (ns)	23 (15-40)
WH02 Res2	40 gal, pre-FVIR; pilot; natural draft; std. burner; 40 kBtu/h	6	PG&E 1390 1420	31.9 +3.7%	-0.4 +0.2	2.22 (ns)	no data	0.3 (-1.3 to 2.6)
WH03 Res4	50 gal pre-FVIR; piloted; natural draft; std. burner; 40 kBtu/h	4	PG&E 1390 1420	24.0 (ns)	-1.0 +0.5	0.37 +65%	no data	4.7 (2.8-8.9)
WH04 Lab	40 gal induced draft; FVIR; spark igniter (no pilot); 40 kBtu/h	new	PG&E 1390 1420	29.0 +2.8%	2.0 -0.5	2.18 -21%	0.05 -14%	8.7 (4.7-14)
WH05 Res8	42 gal pre-FVIR; pilot; natural draft; std. burner; 34 kBtu/h	17	PG&E (2) 1390 1420	28.8 (ns)	0.4 +2.2	1.67 +24%	0.05 (ns)	22 (11-51)

¹ For NO_x, CO, NO₂ and HCHO, first value in each cell is full burn emission rate with PG&E line gas. Percent change is for 50 Btu/scf increase in fuel WN adjusted for effect of oven temperature; changes shown only for p-values ≤ 0.15; p ≤ 0.05 in bold (broader limits for HCHO, see text of report). Low p-values indicate statistically significant results. Values shown for PN are the median and range of particle number counts for individual burns across all fuels.

² Res = residence, identified by number. WH01 experiments repeated because of low NO_x results in first set. WN = Wobbe number, NO_x = nitrogen oxide, CO = carbon monoxide, NO₂ = nitrogen dioxide, HCHO = formaldehyde, PN = particle number, ns = not significant.

Table ES-6. Summary of experiments and results¹ for tankless water heaters, adjusted for effect of water flow rate

ID Site ²	Venting and burner range (kBtu/h) ³	Age	Fuels WN (n)	NO _x (ng/J)	CO (ng/J)	NO ₂ (ng/J)	HCHO (ng/J)	PN (10 ⁴ /J)
TW01 Lab	direct vent; 19-180	<1 ³	PG&E (2) 1390, 1420	24.0 +4.6%	50 -13%	8.9 +2.8%	1.5 -22%	0.8 (0.1-6.7)
TW02 Res5	ducted; 20-185	6	PG&E 1390, 1420	16.0 +45%	37 +109%	6.6 +19%	0.72 -16%	0.1 (-0.4-0.8)
TW03 Res6	direct vent; 37-165	3	PG&E (2) 1390, 1420	18.0 +3.0%	87 (ns)	6.1 +5.3%	2.4 -5.0%	0.1 (-0.6-14)
TW04 Res7	direct vent; 15-199	4	PG&E (2) 1390, 1420	9.0 +31%	19 +22%	4.0 +17%	0.25 -8.6%	3.1 (0.4-16)
TW05 Lab	direct vent & ducted; 19-199	new	PG&E(2) 1390, 1420	21.0 +7.2%	47 -1.3%	8.5 +5.8%	2.0 (ns)	11.4 (0.9-27)
TW06 Lab	direct vent & ducted; 25-180	new	PG&E (3) 1390 1420 (2)	31.0 +17%	434 +111%	7.9 -3.0%	0.24 -6.4%	1.0 (0.0-15)

¹ For NO_x, CO, NO₂ and HCHO, first value in each cell is mean full burn emission rate with PG&E line gas measured at 1, 2 and 3 or 4 gallons per minute. Percent change is for 50 Btu/scf increase in fuel WN adjusted for effect of water flow rate; changes shown only for p ≤ 0.15; p ≤ 0.05 in bold (broader limits for HCHO, see text of report). Low p-values indicate statistically significant results. Values shown for PN are the median and range of particle number counts for individual burns across all fuels.

² Res = residence, identified by number.

³ All TWs had ribbon burners with fan-assisted combustion. All but TW01 were certified to meet 40 ng/J NO_x std. TW01 purchased in 2001 and used for approximately 6 months in portable classroom, then stored at LBNL until used in this study.

WN = Wobbe number, NO_x = nitrogen oxide, CO = carbon monoxide, NO₂ = nitrogen dioxide, HCHO = formaldehyde, PN = particle number, ns = not significant.

1.0 Introduction

The California Energy Commission's Public Interest Natural Gas Research program has the charge to address significant natural gas issues in the State of California. One of the most important issues is the anticipated growth of new gas supplies—principally including liquefied natural gas (LNG) from Pacific Rim exporters—required to meet growing demand across the Western United States. These new fuels can differ in composition and have higher heating values and Wobbe numbers (energy content delivered through a fixed orifice) compared with recent historical supplies. These differences raise questions about the potential impacts of using LNG with the existing population of end-use equipment. Impacts of concern include safety, performance, service life, and air pollutant emissions.

Lawrence Berkeley National Laboratory (LBNL) and the Gas Technology Institute (GTI) are conducting research to support a broad examination of the potential air quality and end-use device performance impacts of LNG use in California. LBNL and GTI jointly developed a research plan that included experimental burner evaluations, statistical analysis and modeling of results, combustion modeling, outdoor air quality modeling, and indoor exposure modeling assessments. GTI focused on the experimental evaluation of industrial and commercial burners. LBNL focused on residential appliance burners and air quality impacts. This report describes the experimental study of pollutant emissions from residential appliances and the sensitivity of emission levels to fuel gas quality.

1.1. Summary of Existing Information

This section summarizes findings of an LBNL review of the available reports examining LNG interchangeability for residential appliances (Singer 2007). The vast majority of existing information focuses on safety and operability of so-called “legacy” appliances that use partially premixed burners.² The specific effects that have been most studied are ignition, flame stability (e.g., lifting), flame appearance (yellow tipping), carbon monoxide (CO) formation (a result of incomplete combustion), and soot formation. Device performance temperatures, energy or thermal efficiency, and formation of nitrogen oxides (NO_x) have been examined in a few studies. A wide variety of domestic appliances have been studied, including central furnaces, wall and floor furnaces, storage and on-demand water heaters, cooktops, ovens, clothing dryers, and other less common products. Commercial cooking equipment and boilers have been studied to a limited extent. Liquefied natural gas interchangeability evaluations generally have involved laboratory testing in which appliances are operated with (and when appropriate adjusted using) the natural gas historically used in an area, and then operated with “substitute” mixtures that simulate LNG blends. Test matrices usually include dilutions of the LNG mixtures with nitrogen, carbon dioxide (CO₂), or air. Testing has been conducted primarily using adaptations of standard procedures, such as the Z21 protocols of the American National

² In partially premixed burners, a fraction of the air required for complete combustion is mixed with gas prior to its release from the burner ports (the holes through which the mixture exits before it enters the flame area). This is the technology that has been and still is used in the vast majority of U.S. residential appliances. A common example is the standard cooktop burner.

Standards Institute (ANSI). Evaluation of exhaust pollutant concentrations resulting from gas quality variability has been reported almost exclusively for stabilized burner operation. The focus of many past studies has been on identifying locally acceptable gas quality limits for safe operation of installed appliances; the limits typically have been expressed in terms of heating value, Wobbe number, and sometimes composition—for example, the fractions of non-methane hydrocarbons and/or inert components (nitrogen, carbon dioxide). In some cases, limits have been developed based on industry standard interchangeability indices (refer to Singer 2007 and references therein for additional details). In cases pertaining to LNG introduction, concern typically has focused on how the installed appliance population that has been operating with domestic or continental natural gas will respond to the introduction of re-vaporized LNG that has higher heating value, higher Wobbe number, and higher concentrations of non-methane hydrocarbons (such as ethane, propane, and butanes).

The extent and severity of effects from distribution and use of LNG will depend on the properties of the delivered fuel. In light of recently approved tariff limits, it is expected that LNG supplies will be diluted with nitrogen to achieve a Wobbe number of ≤ 1385 British thermal units per standard cubic foot (Btu/scf) in California and ≤ 1400 Btu/scf in other parts of the United States. Results of previous studies (Singer 2007) suggest the following potential effects associated with distribution and use of LNG blends with Wobbe number as high as 1385–1400 Btu/scf:

- Problems with ignition or flame stability are highly unlikely for the vast majority of appliance burners; problems may result for burners that are already unstable due to poor adjustment, malfunction, and/or deterioration.
- The effect on energy/thermal efficiency is likely to be very small for most applications; the direction of change will vary among appliances.
- Performance problems may be encountered in specialized applications that are mostly associated with commercial use (e.g., timed processes like a chain-drive char-broiler).
- Output and performance temperatures (e.g., of furnace air) may increase in many cases without substantially affecting overall device performance.
- Exhaust CO concentrations will increase for some appliances; the largest increases will occur in appliances that are currently improperly adjusted or otherwise operating with low or insufficient amounts of combustion air.
- NO_x concentrations in exhaust gases may increase slightly for appliances with partially premixed burners and increase substantially for appliances with full or lean premix burners and no feedback control; full premix burners with advanced control of the fuel-air mixture may not be affected.

1.2. Gaps in Existing Information

This experimental study aimed to fill large gaps in the prior knowledge base. The first gap related to emissions of formaldehyde and ultrafine particles (*ultrafine* particles are those that have operational (aerodynamic or optical) diameters of < 100 nanometers (nm)). These pollutants are known to be emitted from natural gas appliances and are linked to significant health

impacts (ASTDR 1999; IARC 2006; Knol et al. 2009; Vinzents et al. 2005). The review identified no prior study that examined the impact of gas quality variability on emissions of these species. Some past studies have examined “soot” emissions. While soot is composed of ultrafine particles, the vast majority of applied soot research in this field has used metrics that focus on mass emissions of elemental carbonaceous material including black deposits on appliance components or air sampling media. The current study focused on particle number (PN) concentration since a shift in gas quality could lead to a very large increase in the number of particles emitted without producing a discernible change in mass emissions of elemental carbonaceous material. Preliminary range-finding experiments indicated substantial emission rates of formaldehyde and/or particles (indicated by particle number) from some appliances.

The second gap related to appliance and burner operational cycles. Past studies have reported gas quality effects on emissions during stabilized burner operation. However, it is well established that emissions of some pollutants can be much higher during transient operational modes (burner ignition, device warm-up, and intermittent firing of burners). Transient modes can comprise a substantial fraction of operational time and pollutant emission rates during these periods can be different than rates during stable operation. Preliminary range-finding experiments (and data presented later in this report) verified that both CO and PN can be much higher during transient operation relative to stable operation for some burners, whereas NO_x often increases as the burner reaches higher temperatures.

The third gap related to newer and emerging technologies. New standards and goals for energy efficiency and low emissions force changes to appliance designs and influence the market; these changes are indicated by the rapid rise in market share for on-demand water heaters and condensing furnaces, and efforts to incorporate low-NO_x burners into some residential appliances. Since LNG introduction will play out over the next one to two decades; the performance of emerging technologies is relevant.

The fourth major gap was in the study of installed, in-use appliances. There have been several substantial efforts to examine installed appliance performance, including some that have followed the introduction of new gas supplies. These efforts typically have included an evaluation of basic operational safety and in some cases CO emissions, yet there is little if any publicly available documentation from these field examinations. The authors are aware of no well-documented, publicly available study of gas quality variability effects on pollutant emissions from installed in-use appliances.

1.3. Objectives

The gaps described above translated to the objectives of the original experimental plan (Singer 2006):

- Quantify baseline emission rates of ultrafine particles and formaldehyde from common domestic appliances using current Northern California (Pacific Gas & Electric, PG&E) line gas.
- Measure the effect of gas quality variability on pollutant emission rates from a variety of used California residential appliances during operational cycles that include warm-up

(transient) periods; determine emission factors for carbon monoxide, nitrogen oxides, nitrogen dioxide, ultrafine particles, and formaldehyde.

- Investigate and quantify the effect of gas quality variability on performance and pollutant emission rates for emerging technology devices that have not been adequately examined in past studies.
- Investigate and quantify the effect of gas quality variability on performance and pollutant emission rates for common installed, in-use appliances.

2.0 Methods

2.1. Overview of Experimental Approach

The initial experimental plan (Singer 2006) for this study was developed following a review of available information on interchangeability of residential appliances, as summarized above. The study plan was designed to complement existing information and to fill important gaps in the current knowledge base. The plan evolved in response to experience gained during early experiments and unforeseen logistical challenges.

The basic approach was to quantify pollutant emissions from appliance burners as they were operated over defined cycles using line gas from PG&E and simulated LNG blends. Operating cycles were developed to capture features of typical operation. Pollutant emissions were quantified over the full period that the burner was operating (full-burn), to capture transient effects, and during a more stable period at the end of each burn. Simulated LNG blends were selected based on considerations of composition—i.e., the relative quantities of methane, ethane, propane, butane, and nitrogen (N₂)—and Wobbe number. Appliances were selected based on considerations of technology, age, use, and availability. Experiments were conducted in a laboratory at LBNL and in residences. Most of the evaluated appliances had seen regular use and many were tested in situ. Details are provided in the sections that follow.

2.1.1. Interchangeability Metrics

The primary measures of impact used in this study are exhaust concentrations and emission rates of the following air pollutants: carbon monoxide (CO), nitrogen oxides (NO_x), nitric oxide (NO), nitrogen dioxide (NO₂), ultrafine particles (UFP), and formaldehyde (HCHO). For this study nitrogen dioxide is estimated as the difference between NO_x and NO as measured by a chemiluminescence detector. Ultrafine particles are characterized by total particle number concentration (PN) with the assumption that the vast majority of particles in the exhaust are in the ultrafine mode (< 100 nm aerodynamic diameter); this assumption was confirmed for a subset of burners through size-resolved particle measurement. Pollutant concentrations measured in burner exhaust are normalized to reference conditions of dry air-free (0% oxygen, O₂) and 3% O₂ using measurements of O₂ and carbon dioxide (CO₂). Pollutant emission rates are normalized to fuel energy (e.g., nanograms of pollutant emitted per Joule [J] of fuel energy); these are calculated from the measured concentrations of pollutants and CO₂ and from fuel properties.

2.1.2. Fuel Gas Compositions

Both domestic natural gas and LNG vary in composition and energy content, expressed as either heating value or Wobbe number. The Wobbe number—equal to the higher heating value divided by square root of specific gravity—is a measure of the fuel energy supply rate for a burner with orifice fuel control and fixed air supply. Based on the review of past research, this metric is taken as the primary fuel variable for this study. Characteristics of the composition, including the relative concentrations of ethane, propane, butane, and inert components (nitrogen and CO₂) are secondary considerations.

The basic approach for this study was to evaluate each test burner with a core set of three fuels, including PG&E line gas plus two simulated LNG blends. PG&E line gas was treated as the baseline fuel against which potential LNG effects were compared. By recommendation of the California Energy Commission contract manager and the Project (technical) Advisory Committee (PAC), this study examined the interchangeability of LNG blends with Wobbe numbers that exceed the range expected in California in coming years. Test fuels were selected based on the current Wobbe limit of 1385 Btu/scf. In both field and laboratory experiments, the primary LNG test blends had Wobbe numbers of approximately 1385–1390 and 1415–1420 Btu/scf.

The fuel blends used for the core set of three experiments in residential and laboratory venues are shown in Table 1. For the first group of laboratory experiments, the lower Wobbe fuel was a nitrogen-diluted version of the higher Wobbe fuel (3A). For residential experiments the lower Wobbe fuel (1C) was achieved by shifting the relative amounts of non-methane hydrocarbons. Starting in early 2008, laboratory experiments were conducted with the same two simulated LNG blends that were being used in residential experiments (labeled as 1C and 3C). A fourth fuel (2C) was used in many of the cooking burner experiments that were added to support the indoor exposure modeling of Task 14. This fuel diluted 1C with 1.7% nitrogen to obtain a Wobbe number of 1359 Btu/scf. Fuel 2C was 90.4% methane, 7.9% ethane, and 1.7% nitrogen.

Table 1 shows the component and Wobbe number ranges for PG&E line gas samples collected during experiments at LBNL and residences in North Oakland and Berkeley in July through December 2007. Specific information about the fuel used in each experiment throughout the study is listed in the individual burner reports that are provided as appendices to this report.

The original research plan envisioned follow-up experiments with additional fuel mixtures for those burners showing substantial sensitivity across the initial set of test fuels. This study component had to be dropped in light of budget constraints following unanticipated costs related to setup for both laboratory and field experimental efforts. The focus instead was on the evaluation of the largest possible sample of appliances operated on the base three fuel mixtures.

Table 1. Properties of fuels used during experiments in July through December 2007

Location:	Lab/Field	Lab		Field, Lab ²	
Fuel ID:	PG&E	3A	3A + N ₂	3C	1C
Valid samples: ⁽¹⁾	16	19	12	6 ⁽³⁾	5 ⁽³⁾
Methane (%)	95.1 ± 1.5	90.2 ± 0.3	88.6 ± 0.2	86.5 ± 0.2	92.0 ± 0.1
Ethane (%)	2.65 ± 1.02	5.77 ± 0.13	5.62 ± 0.19	12.0 ± 0.2	8.04 ± 0.08
Propane (%)	0.44 ± 0.42	2.96 ± 0.10	2.87 ± 0.09	1.57 ± 0.02	-
Butanes & C5+ (%)	0.13 ± 0.11	1.09 ± 0.04	1.06 ± 0.03	-	-
Nitrogen (%)	0.85 ± 0.21	0.04 ± 0.09	1.80 ± 0.09	-	-
Carbon dioxide (%)	0.89 ± 0.18	-	-	-	-
Heating value (Btu/scf)	1023 ± 17	1123 ± 3	1102 ± 3	1125 ± 2	1071 ± 1
Wobbe number (Btu/scf)	1336 ± 10	1417 ± 2	1385 ± 3	1419 ± 1	1390 ± 1

¹ One or two samples were collected per experiment, but often only one was analyzed. Contamination (typically air leakage into bag) was determined by the presence of O₂ or excessive N₂. For example, N₂ was observed at levels of 0.25–0.28% in 3 of 22 samples for fuel 3A; these are excluded from the table.

² Fuels 1C and 3C were used in lab experiments starting in February 2008.

³ Roughly one-third of the fuel samples from the November 2007 field sampling effort were analyzed at PG&E several weeks after collection, and this group had a higher incidence of contamination.

2.1.3. Appliance Burner Selection

Appliance burners were selected for evaluation based on considerations of technology, age, availability and potential for significant indoor or outdoor air quality impacts. The review of existing information (Singer 2007) includes an appendix that provides an overview of residential appliance technologies.

Guidelines for burner selection were developed through consultation with the California Energy Commission contract manager and the project's technical advisory committee. This guidance directed a focus on mainstream technologies that are currently predominant, technologies that will continue to have large saturation fractions (be present in a large number of residences) over the next decade or more, and new technologies that have not been evaluated to a sufficient extent for fuel quality interchangeability. The guidance with respect to age was to balance the objective of evaluating used appliances with a caution to avoid units that are very likely to be retired within the next few years. This guidance recognized that as appliances age, they may be more sensitive to fuel quality change, but also sought to focus on appliances with a substantial amount of useful life remaining.

The residential natural gas burners with the largest potential air quality impacts are those associated with cooking appliances, water heaters, and furnaces. Cooking appliances are important because they typically vent directly to the living space where a much smaller mass of emitted pollutant can lead to high concentrations, owing to limited dilution volume and where emitted pollutants are much more likely (relative to pollutants emitted outdoors) to be inhaled by people (Bennett et al. 2002). Water heaters and furnaces are more relevant for outdoor air quality because they account for the vast majority of natural gas used in domestic appliances.

Storage (tank) water heaters still vastly predominate in saturation and new sales, but sales of tankless water heaters are increasing sharply, in part related to energy efficiency considerations. Central forced air furnaces account for the overwhelming majority of natural gas use for home heating. A more extensive discussion of appliance technology selection was submitted for review by the advisory committee at the start of this experimental work; this memorandum is available upon request.

Used appliances tested in the laboratory were identified via a free online message board (sfbay.craigslist.org). Sellers were contacted by e-mail or telephone to ascertain a basic history (used regularly or not), and to confirm that the appliance was in good working order. Before purchase, appliances were inspected for obvious signs of mistreatment or tampering. Appliances were purchased for the asking price using project funds. One cooking range was purchased from a used appliance store; all other used appliances were purchased from individuals. New appliances tested in the laboratory were “off the shelf” production units purchased from retail or business to business vendors. Tankless water heater TW01 was purchased by LBNL several years before the current study began. It was used for less than one year in a study of energy and indoor environmental quality in portable classrooms, then stored at LBNL until it was tested in this study.

Installed appliances were identified through colleagues in the Environmental Energy Technologies Division at LBNL. Access was granted without any offer of incentive. Scoping visits were made to homes containing appliances that fit within the technology and age targets. During the visits, the feasibility of testing was determined based on the physical configuration of the appliance within the home and the homeowner’s schedule.

2.1.4. Field and Laboratory Experiments

Experiments were conducted both in residences and in the laboratory in an effort to achieve the objectives identified above within the constraints and opportunities associated with each venue. Considerations included both operational issues and the availability of suitable test specimens. A key consideration was the objective of testing installed or in-use burners whenever possible.

Residential experiments are operationally more challenging but they offer the key scientific benefit of in-situ evaluation of appliances currently in use. There is a dearth of such information in the research record, and it is the most intuitively relevant to residential natural gas customers. The most significant challenges identified with conducting experiments in residences were the time and space requirements for equipment setup. These challenges were overcome through construction of a highly portable instrumentation cart and development of operational protocols that allowed setup, experiments, and clean-up within a single eight- to ten-hour day (see details in later sections). The residential test program was well suited for many but not all of the target appliances and technologies. Individual appliances were identified for all target technologies for furnaces and several each for storage and tankless water heaters.

Laboratory experimentation was a necessary and valuable complement to the field effort. The laboratory was used extensively in the method development stage and for evaluation of some

burners and technologies that could not be accomplished in the field. All but one of the cooking burners was evaluated in the lab. This strategy was initially motivated by the recognition that ovens had to be pre-cleaned before experimental evaluation to minimize emissions of particles associated with food residue volatilization. An investigation of online classifieds indicated that cooking appliances featuring the most common contemporary technologies and features are routinely discarded and offered for sale when kitchens are remodeled. The rationale for change may be stylistic or based on features, i.e., on factors unrelated to specific concerns about degraded performance. Online classifieds provided a suitable pool from which to procure specimens that met the standards of being used but still having substantial useful life remaining. The single cooktop tested in a residence showed the additional and very significant challenge associated with working in a finished space—where floors, cabinets, and other surfaces can be scratched—as compared to the garages, utility rooms, and crawl spaces that typically house furnaces and water heaters. The laboratory configuration also was used for extensive replicate testing of several cooking burners and for testing of specific appliances and technologies for which residential installations were not identified.

2.2. Experimental Equipment and Analytical Methods

2.2.1. Overview of Experimental Equipment

The major components of the experimental apparatus used in this study included the following:

- Fuel gas supply and monitoring
- Instrumentation to measure combustion products and pollutants
- Dilution system for aerosol sampling
- Exhaust sample collection and conditioning
- Instrumentation to measure appliance operation and sampling conditions
- Data acquisition system
- Fuel composition analysis
- Formaldehyde sampling and analysis

These components are described in the subsections that follow.

The initial research plan was developed with the goal of obtaining results as quickly as possible. To facilitate this, separate experimental systems were designed and constructed to allow for field and laboratory experiments to be conducted on a parallel schedule by two research teams. The sampling program was in actuality implemented sequentially with a single core research team. This change was made in an attempt to maintain technical consistency and lower costs while addressing an array of unforeseen logistical challenges related to both field and laboratory components of the study.

2.2.2. Fuel Gas Supply and Monitoring

PG&E line gas was used as the baseline test fuel for both field and laboratory experiments, and two different approaches were used to supply simulated LNG blends. In early laboratory experiments, constituent gases were mixed on site to provide a supply stream of the target

blend. Simulated LNG blends used in all field experiments and later laboratory experiments were purchased as mixtures supplied in 150 cubic foot cylinders from Scott Specialty Gas (Longmont, Colorado). The compositions of premixed LNG fuels are shown in Table 1. The component gases used to create simulated LNG mixtures on site were provided by the local Airgas distributor, with the details shown in Table 2.

Table 2. Constituent gases used to create simulated LNG blends for laboratory experiments

Constituent	Grade ¹	Purity (%)	Cylinder size (Qty)
Methane	UHP	99.97	200 (200 ft ³)
Ethane	CP	99.0	80 (10 lbs)
Propane	Research	99.9	LP5
n-Butane	CP	99.0	LP5 (17 lbs)
Nitrogen	UHP	99.97	200 (230 ft ³)

¹ UHP = ultra high purity; CP = Chemically pure.

The laboratory mixing system used a series of needle valves that were preset prior to an experiment to provide the appropriate flow of each constituent gas; total flow was set in excess of that required by the burner being tested. The flow rate of each gas was monitored using the sensors of inline mass flow controllers that were set to full open position. Needle valves were used in place of the mass flow controllers to avoid transient variations that can result when gas flow starts with burner ignition.

Because the measurement of emissions during transient burner operation was a focus of this study it was important to provide a consistent fuel supply during and just after burner ignition. The component gas streams were mixed via a manifold into a stainless steel transfer line (1/2" outside diameter [OD], 3/8" inside diameter [ID]; approximate length of 8 meters [m]) terminating at a tee. One branch of the tee connected to a backpressure regulator (EB2SC3-HF, Insight Process Solutions, insightprocess.com) that vented excess gas as required to maintain a set-point pressure in the supply line; the other branch from the tee led to the appliance, as described below. The backpressure regulator was set to maintain a supply pressure of about 7 in. H₂O.

In the system described above, the methane cylinder regulator was heated either intermittently or continuously to counteract expansion cooling of the fuel; this was not an issue for the other constituents that are provided at much lower gas flow rates. Heating was initially accomplished using a strip of resistance heat wrap. Starting in December 2007 this was replaced with a hair dryer that typically was operated on the low setting (700 watts [W]).

From the backpressure tee, the mixed fuel supply line connected via another tee to the supply system for the appliance; the other side of this tee was connected to the PG&E distribution network. Ball valves allowed fuel to be supplied either from the mixing system or the PG&E distribution system. Downstream of this tee, fuel flowed through a factory-calibrated temperature-compensating dry gas meter (American Meter AC250-TC) and a dry test meter (Singer DTM-115) en route to the appliance. The gas meter used was equipped with a pulse counter (Product RD AMRC-10P, Riotronics, riotronics.com) that resolves 10 counts per

revolution of the 1 cubic foot (ft³) dial (1 counter per 0.1 ft³ of fuel used). Most of the transfer lines were 3/4-inch steel; the final connection was made with a flexible stainless steel connector sized for the appliance. Fuel flow rate was calculated using the data acquired from the pulse counter and also from timing the fuel flow rate during burner operation; the latter was accomplished using the appropriate test meter dial (1-L, 1/4-foot or 1/2-foot) and a stopwatch.

Field experiments used the line gas supplied to the residence as the baseline fuel. Prior to the start of experiments the AC250-TC dry gas meter with pulse counter was installed between the local shut-off (ball) valve and the appliance. Simulated LNG (fuels 1C and 3C) were supplied from the compressed gas cylinders described above. A low-pressure regulator reduced the fuel supply pressure from approximately 10 pounds per square inch (psi) (the outlet pressure from the second stage of the cylinder regulator) to match the supply pressure observed in the residence, which sometimes differed a bit from the standard 7 in. H₂O. The low-pressure regulator was connected to both the cylinder regulator and the gas meter using flexible stainless steel lines sized for the appliance burner. A hair dryer at 700 W setting was used to warm the single cylinder regulator during field experiments. As in the laboratory, fuel flow rate was quantified both by analysis of pulse counter data and by clocking the rotation of the meter dial using a stopwatch. Pre-mixed (cylinder) fuel was used for laboratory experiments starting in early 2008. The use of fuel 2C started in January 2009.

2.2.3. Instrumentation to Measure Combustion Products and Pollutants

Instrumentation used for time-resolved measurements of gaseous analytes is listed in Table 3 ; aerosol instrumentation is listed in Table 4. Each table includes a list of primary instrumentation that was used for the majority of experiments and alternate instrumentation that was used on a more limited basis (mostly during the preliminary phase as described below). The history of this equipment is as follows. The original study plan envisioned separate systems for field and lab work that would allow for parallel implementation to achieve an accelerated completion of the experimental program; the listed equipment was initially organized into these two systems.

Based on the experience of preliminary experiments in both the laboratory and residential field sites, it was decided that the experimental program should instead proceed with a single set of analytical instrumentation operated by a single team of researchers. For each analyte or set of analytes, the instrument determined to be the most robust, stable, and or most conducive to field sampling was selected as primary. For example, the Thermo 42i NO_x analyzer reaches operating temperature much faster than the Teledyne-API NO_x analyzer. The Horiba PG-250 combustion gas analyzer was used for its capability to measure NO or NO_x (allowing NO to be used to measure dilution ratios in the dilution sampler) and for a more stable baseline for the CO channel. The PP Systems EGM-4 and B&K 1302 were unavailable for some periods when they were deployed for a field study of range hood effectiveness. On these days, ambient CO₂ measurements were collected using either a Q-Trak, or starting in 2009, a Fuji ZFP9-AB21 analyzer. The scanning mobility particle spectrometer (SMPS) system described in Table 4 is shared by several groups; it was used as available for laboratory experiments.

The primary analytical instrumentation listed in the tables below was mounted on a pair of stackable carts with wheels (Figure 1). The small footprint of the cart allowed for use of the

equipment with minimal floor space requirements. Many electrical, communications, and plumbing connections were maintained on the two carts during transport, allowing for the quick installation and start-up that was required for field experiments.

The instruments were linked to a computer with LabView data acquisition software (National Instruments, www.ni.com) that provided a real-time observation interface, control of sampling time resolution, and coordination of sampling intervals among the instruments. The standard data acquisition interval was 10 seconds.

The specific instrument configurations, ranges, and calibration levels used for individual experiments are described in individual burner reports which are provided in the appendices.

Exhaust sample collection and treatment for aerosol and gaseous analytes, including appliance specific variations, are described in the subsections that follow.

Schematics of selected sampling configurations are provided in a following subsection; the configurations used in specific experiments are provided in the individual burner reports in the appendices. Figure 1 (below) shows the field cart with primary instrumentation installed in a residence.

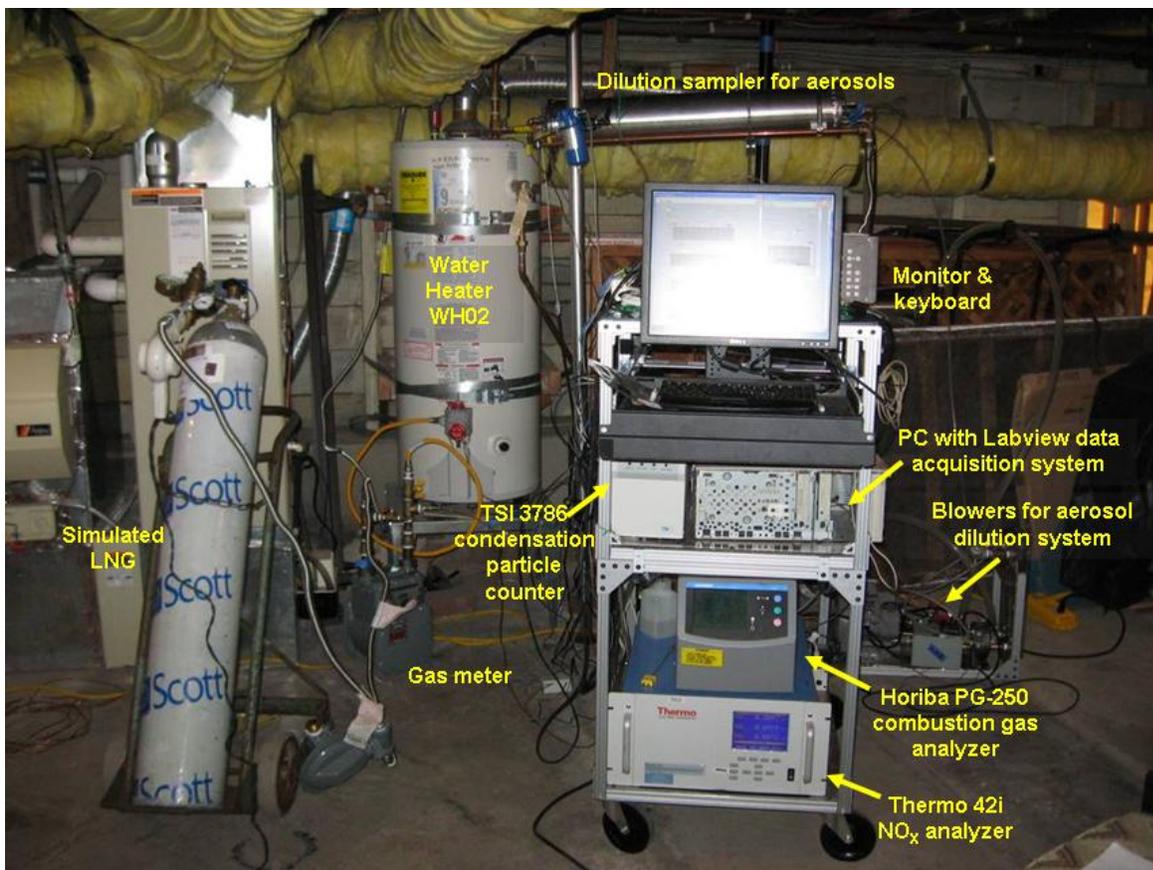


Figure 1. Instrumentation cart installed for experiments with storage water heater.

Table 3. Instrumentation for Gaseous Analytes

Equipment ¹	Sample Location	Analytes ²	Method Principle ³	Analytical Range(s)	Linearity/Drift ⁴
PRIMARY INSTRUMENTATION					
Horiba PG-250	direct or dilute exhaust	CO ₂	NDIR	0–5% to 0–20%	1% of full scale
		O ₂	paramagnetism	0–5% to 0–25%	
		CO	NDIR	0–200 ppm to 0–5000 ppm	
		NO or NO _x	chemiluminescence	0–25 ppm to 0–2500 ppm	
Thermo 42i	dilute exhaust or dilution sampler	NO, NO _x ; NO ₂	chemiluminescence	0–0.05 ppm to 0–100 ppm	1% of full scale*
PPSystems EGM-4	ambient	CO ₂	NDIR	5000 ppm	less than 1% of span conc.
ALTERNATE INSTRUMENTATION (SEE TEXT)					
California Analytical 600-series (model 602P)	direct or dilute exhaust	CO ₂	NDIR	0–1.5%, 0–15%	1% of full scale
		O ₂	paramagnetism	0–25%	
		CO	NDIR	0–1000 ppm, 0–1%	
Teledyne-API 200E	dilute exhaust or dilution sampler	NO, NO _x ; NO ₂	chemiluminescence	0–0.05 ppm to 0–20 ppm	1% of full scale
Bruel & Kjaer 1312 ⁵	field dilution sampler; ambient	CO ₂	photoacoustic infrared absorbance	Calibrate at 250–2500 ppm	repeatability 1% of reading
TSI Q-Trak Model 8554	ambient	CO ₂	NDIR	5000 ppm	3% or 50 ppm
Fuji ZFP9-AB21	ambient	CO ₂	NDIR	2000 ppm selected	1% repeatability

Note: ppm = parts per million

¹ Horiba Environmental and Process Instruments, Irvine, California (environ.hii.horiba.com); California Analytical Instrumentation (gasanalyzers.com); Teledyne-API, San Diego, California (Teledyne-api.com); Thermo Fisher Scientific, Waltham, Massachusetts (thermo.com); TSI Instruments, Shoreview, Minnesota (tsi.com); Waters Corporation, Milford, Massachusetts (waters.com).

² CO₂ = carbon dioxide; O₂ = oxygen; CO = carbon monoxide; NO = nitric oxide; NO_x = nitrogen oxides; NO₂ = nitrogen dioxide. NO₂ is estimated as the difference between NO_x and NO measurements. PG-250 can be configured to measure either NO or NO_x.

³ NDIR = non-dispersive infrared.

⁴ Indicators of accuracy; span drift is typically provided for a 24-hour period. If values for linearity and drift differ, larger value is presented. *The Thermo 42i performed much better than the 1% linearity / drift quoted in product literature.

⁵ Bruel & Kjaer is now Innova. The B&K 1312 is similar to the Innova 1412, which is distributed and serviced in the United States by California Analytical Instrumentation (gasanalyzers.com).

Table 4. Instrumentation for Aerosols (Particles)

Equipment ¹	Analyte	Method Principle ²	Min. size (D ₅₀) ³	Maximum Concentration	Accuracy
PRIMARY INSTRUMENTATION					
TSI 3786 ultrafine CPC	total PN, # cm ⁻³	grow particles w/H ₂ O, count w/laser	2.5 nm	10 ⁵ cm ⁻³ single particle mode	±12%
TSI 3550 nanoparticle surface area monitor	surface area of particles (SA) depositing in lung alveolar region ⁴	diffusion charging	10 nm	10 ⁵ μm ² cm ⁻³	±20% at 20–200 μm ² cm ⁻³
Lasair 1003 optical particle counter (OPC)	number conc. of particles 0.1-2.0 μm diameter	laser counting	0.1 μm	1.4 × 10 ⁴ cm ⁻³	<10% ⁵
ALTERNATE INSTRUMENTATION (See Text)					
TSI 3022A CPC	total particle number conc. (PN), # cm ⁻³	grow particles w/butanol, count w/laser	7 nm	10 ⁷ cm ⁻³	±12% to 5×10 ⁵ cm ⁻³ ; ±20% at >5×10 ⁵ cm ⁻³
TSI SMPS: 3071A classifier, 3025A ultrafine CPC	PN resolved by size (aerodynamic diameter)	Sort using electrostatic classifier, count with CPC	3 nm	10 ⁵ cm ⁻³	±10%

¹ TSI Instruments, Shoreview, Minnesota (tsi.com). CPC = condensation particle counter. SMPS = Scanning mobility particle spectrometer.

² Detailed information provided in product literature.

³ D₅₀ is the particle diameter (in nanometers) at which 50% of the particles are detected.

⁴ Monitor has settings available for tracheobronchial (TB) or alveolar (A) regions; specifications are provided for the alveolar option which is being used in this study.

2.2.4. Dilution System for Aerosol Sampling

An important consideration when sampling aerosols from combustion systems is that the exhaust be cooled to a reasonable temperature for the sampling instrumentation. The particles resulting from combustion are produced directly in the flame and by condensation of combustion by-products as they cool. To properly characterize both types of particles, it is also important to dilute the exhaust in a way that mimics the dilution experienced in the atmosphere. A common approach to sampling these combustion aerosols—especially at high concentrations—is to use a dilution sampling system that mixes a small flow of exhaust gas with a much larger flow of pre-cleaned dilution air. A dilution sampling system was constructed following the general design of Lipsky and Robinson (Lipsky and Robinson 2005).

A schematic of the dilution sampling system is shown in Figure 2. In this system, inlet and outlet flows are controlled and balanced to create a slight vacuum that draws sample air through a heated inlet. In laboratory experiments, supply air was provided at pressure by the building compressed air system, and dilution tube exhaust flow was provided by a vacuum pump. In field applications both supply and exhaust air flows were generated by ring compressors. Both systems can achieve dilution ratios of approximately 10–200. Dilution ratios

for the appliance experiments were typically in the range of 15–30. The dilution ratio can be determined by a calibration that relates sample flow measurements to the vacuum in the system (for a given sample inlet). Alternately, dilution ratio can be measured directly by measuring the concentration of an analyte in the primary exhaust stream (from which the dilution system draws its sample) and from the diluted air stream.

In this study, dilution ratios were determined by measurement of NO or NO_x for the following reasons: (1) background concentrations were low relative to combustion exhaust in both ambient and dilution air, and (2) the chemiluminescence analyzers used to measure NO and NO_x operate accurately over a large dynamic range.

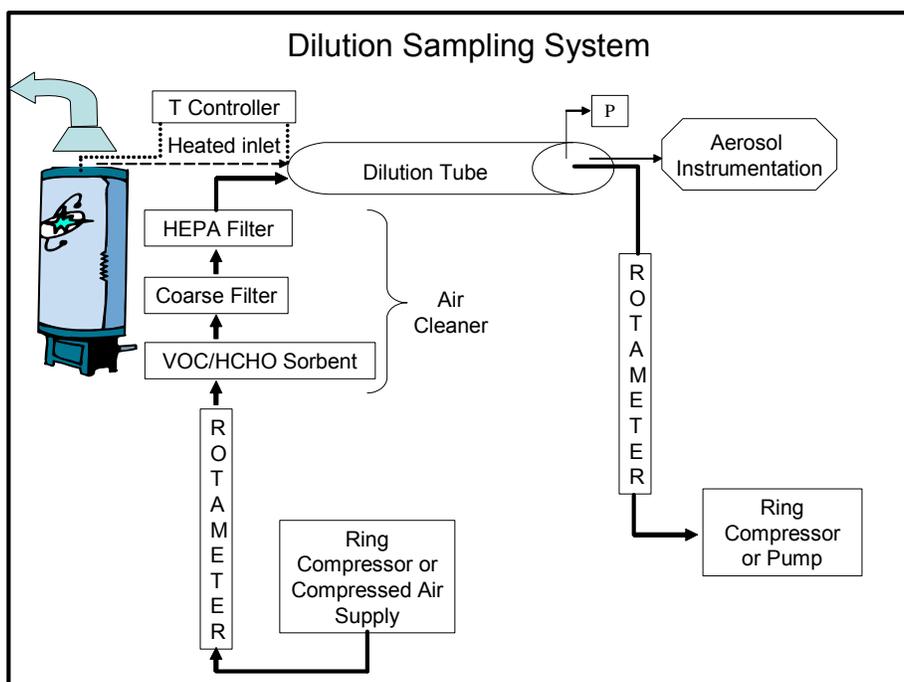


Figure 2. Dilution sampling system configured for direct exhaust sampling

Additional operational details of the dilution sampling system follow. Supply air passes through a container of sorbent media (Purafil SP Blend, Purafil, Inc., Doraville, Georgia) to remove formaldehyde and other volatile organic compounds, through a coarse filter to remove dust (including any suspended sorbent media), and finally through a high efficiency particulate air (HEPA) filter to remove fine and ultrafine particles. Supply and exhaust flow rates are monitored with rotameters, and the flows are controlled using the rotameter needle valves. The sample inlet is a 1/8" OD stainless steel tube that is slipped through a silicon stopper into the dilution sampler. The inlet is wrapped with a 1" wide by 25" long, 125 amp, 120 volt, flexible silicone heater (Product ID 010250C1-0001F, Watlow, Winona, Minnesota) with an overlay of insulation. The heater is powered with a controller (Series 988 Temperature/Process Controller, Watlow, Winona, Minnesota) that can be operated in either automatic or manual mode. The automatic configuration includes a proportional feedback controller that attempts to match a

response signal (from a thermocouple placed under the heater at the downstream end of the inlet tube) to a lead signal (from a thermocouple inserted into the combustion exhaust stream, alongside the inlet opening). The manual configuration provides a fractional voltage of 0%–100%. This system was used in both automatic and manual modes. When used in manual mode, the required setting was determined by monitoring of exhaust temperatures during a range finding run of the burner being tested or from previous experience. Sampling from the dilution tube is accomplished via four bulkhead unions with 1/4" Swagelok fittings.

The inlet heater described above was installed in November 2007, after a lower-power heater in use prior to this date was determined to be non-functional. In laboratory experiments conducted prior to this change, the aerosol inlet was heated solely by exhaust gases; this configuration was used for evaluation of the following burners: CT02, CT03, OV02, OV03, and WH01.³

The dilution tube is a 92 centimeter (cm) long by 14.6 cm (ID) stainless steel tube with end caps that are clamped then sealed with Teflon and metal duct tape. On the inlet side clean dilution air is provided through nominal 1/2" copper pipe connected to a multiport discharge upstream of a mixing baffle (see Figure 3). The sample (e.g., from the appliance exhaust) enters through a 50.5 cm by 3.2 millimeter (mm) (1/8 in.) OD (1.6 mm ID) stainless steel tube that projects through the middle of the end cap and discharges into the turbulent flow of dilution air.

³ Details of these burners are shown in tables 10, 11, and 13.



Figure 3. Dilution sampler inlet configuration

Front view shows clean dilution air supply (copper pipe) and inlet sample tube (thin, curved stainless steel tube) wrapped with heater. Dark circles on copper pipe behind end cap are supply ports for dilution air in tube. Photo at right shows turbulence-inducing baffles and outlet of sample tube.

The diluted sample is drawn from the outlet end of the tube through four bulkhead union ports, as shown in Figure 4. The copper tube shown at the center is connected to the exhaust blower fan. Other tubes are connected to analytical instrumentation. The copper tube in the upper left quadrant is clean dilution air supply.



Figure 4. Outlet of dilution sampling system

2.2.5. Exhaust Sample Collection and Conditioning

The sampling train by which combustion exhaust was monitored by the instrumentation described above was flexible, to accommodate a variety of residential appliance burners. The primary dichotomy was between burners for which combustion products are vented through a constrained duct (furnaces and water heaters) versus those exhausting to open spaces (cooktops and ovens). To accommodate this dichotomy, the sampling system was configured to measure either direct or dilute exhaust streams. The actual configurations used for each burner are described in the burner reports.

The first configuration was designed for concentrated exhaust streams such as the central flue of a storage water heater or the flue of a forced air furnace. In this configuration, O_2 , CO_2 , CO , and NO or NO_x (with the Horiba PG-250) were measured by the combustion gas analyzer sampling directly from the concentrated exhaust stream. This type of sampling used an engineered water removal system, the components of which are described in Table 5 below. The inlet to the dilution system for aerosols sampled from this same exhaust stream. In this configuration, particle concentrations and resolved nitrogen oxides (NO_x and NO ; NO_2 by difference) were measured in the dilution sampler. The ratio of NO (or NO_x) measured in the dilution sampler to NO (or NO_x) measured in the direct exhaust stream provided a direct measurement of the dilution ratio in the system. Several of the tankless water heaters had a defined exhaust port but no flue; these were fitted with a short length of duct to provide a confined exhaust stream. A schematic of the direct exhaust sampling configuration is shown in Figure 5. The nanoparticle surface area monitor shown in this schematic was not available for laboratory interchangeability experiments conducted before November 2007, nor after March 2008. This analyzer is configured to report the surface area of particles that would deposit in the lung

alveoli of a person inhaling the sample aerosol. The SMPS was used for some lab experiments during February through May 2008 and for most of the cooking burner experiments conducted December 2008 through April 2009.

Table 5. Water removal system for direct exhaust sampling (field and lab)

Device / Purpose	Product Details ¹	Locations
Water drop out: condense water as sampling stream cools from exhaust temperature to close to ambient	Filter housing for water removal, Parker Model HN2S-6DSJ, (Specialty Process Equipment)	Outlet of stainless steel sampling line in direct exhaust stream
Drying of gas sampling stream to ambient relative humidity (RH)	ME110 36" air dryers from Permapure LLC	Downstream of water condenser, upstream of exhaust gas analyzer

¹ Permapure LLC: Tom's River, New Jersey (permapure.com); Parker Hannifin Corporation, Oxford, Michigan (parker.com), distributed by Specialty Process Equipment: Union City, California, (specialtyprocess.com).

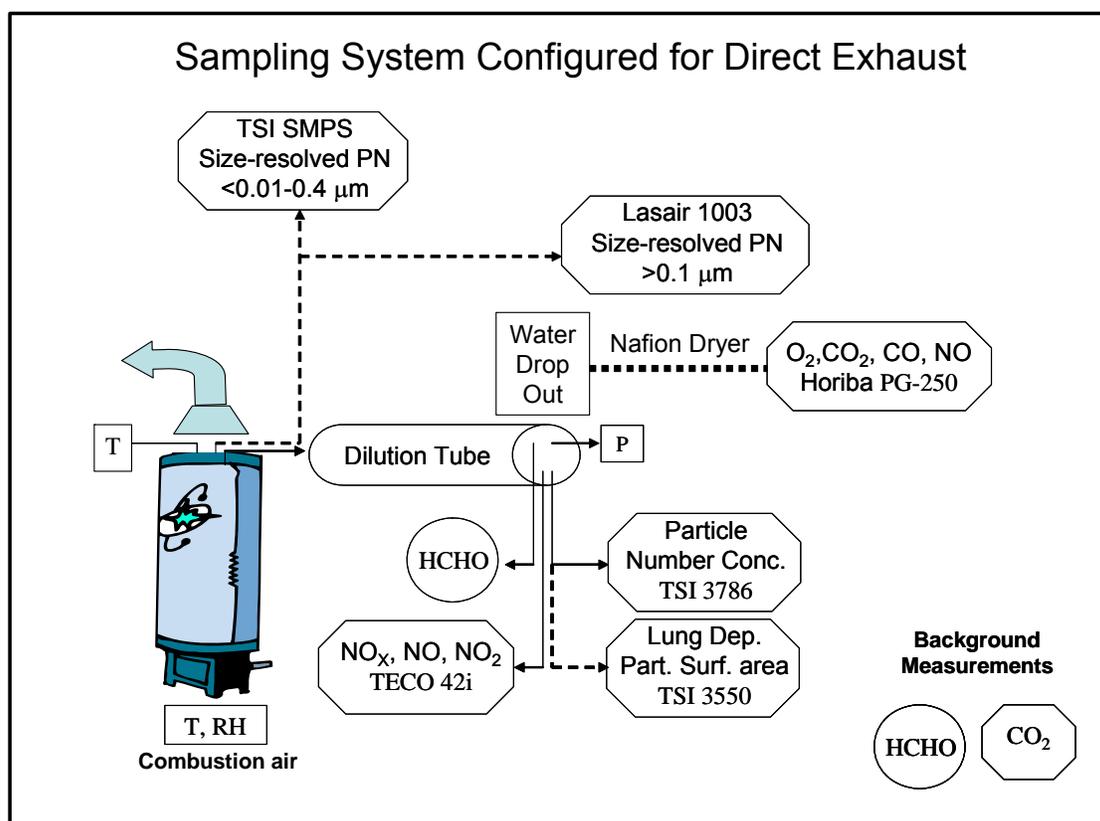


Figure 5. Sampling system configured for measurement of direct exhaust from water heater

Particles, NO_x , and HCHO are measured via the dilution sampling system. The dilution ratio is calculated from measurements of NO in the dilution sampler and manifold. Abbreviations for analytes and instruments are defined in Tables 3 and 4. Dashed lines to instruments indicate measurements that have been made for only a subset of burner experiments; actual configurations are shown in individual burner reports. The SMPS was used exclusively in lab experiments. The Lasair typically is not used in conjunction with SMPS.

The second general configuration was for appliances with open flames and no directed exhaust stream. Exhaust from these burners was captured by a hood connected via flexible ducting to a variable-speed blower to control the overall airflow rate. A schematic of this system is shown

below in Figure 6. The blower speed was set to achieve analyte concentrations that were sufficiently high for accurate measurement while ensuring sufficient excess (dilution) air to avoid water condensation in the sampling system. Based on typical indoor temperature and humidity conditions in the laboratory (in Berkeley, California), a dilute exhaust CO₂ level of 0.6% was sufficient to maintain a sampling stream well below the dew point. The temperature and relative humidity of the sampling stream were measured continuously in the glass sampling manifold. Flow to the glass sampling manifold was provided in excess of the needs of the samplers using an auxiliary pump; the total flow was varied as needed to maintain a manifold vacuum of 1 in. H₂O. Formaldehyde samples also were collected via this glass manifold. The hood configuration was used to collect and sample exhaust from cooktop, oven, and broiler burners through May 2008. The dilution sampler was used together with the hood collection system to provide a larger dynamic range for particle number concentration measurements with a much lower and more consistent baseline. The TSI 3550 monitor was used for only some experiments. The SMPS was used in selected lab experiments starting in February 2008.

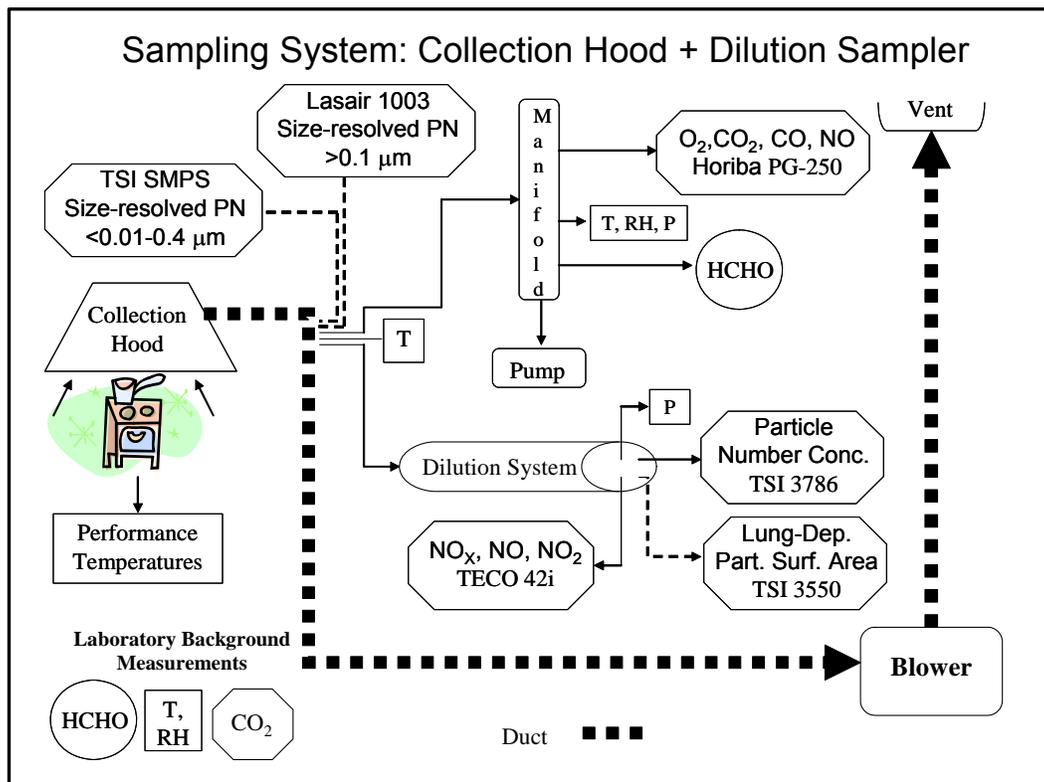


Figure 6. Sampling system configured for measurement of cooking burner via collection hood

Particles and NO_x were measured via the dilution sampling system. The dilution ratio was calculated from measurements of NO in the dilution sampler and manifold. Abbreviations for analytes and instruments are defined in Tables 3 and 4. Dashed lines to instruments indicate measurements that have been made for only a subset of burner experiments; actual configurations are shown in individual burner reports. The SMPS was used exclusively in lab experiments. The Lasair typically is not used in conjunction with SMPS.

A variation of this setup was used for cooking burner experiments conducted December 2008 through April 2009; a schematic of the configuration is provided in each of the individual burner reports (which are compiled in appendices to this report). An exhaust collection hood was custom designed and constructed to be utilized on cooktops installed in residential kitchens. It was constructed of polished stainless steel sheets fastened with rivets and supported by a framework of aluminum angle members. The hood was supported by poles clamped at the four corners; short poles are used for mounting over counters, and longer poles extend to the floor. The hood was 36" wide and 26" deep. The hood featured an open back designed to fit around the raised rear control panel common to freestanding ranges and a front-to-back sloping top panel designed to fit under an above-the-stove cabinet, range hood, or microwave. Installation was aided with hinged side panels and a removable front panel (all 8" tall). Exhaust air was pulled through a 6" flexible duct connected to the 16" high rigid section of the front panel.

Figure 7 shows the hood installed over CT04. A different hood configuration was used for preliminary laboratory experiments; the hood shown below was used starting in August 2007.



Figure 7. Collection hood installed over island cooktop

The back of the hood is open to accommodate the raised rear structure of stand-alone ranges; a strip of aluminum foil was placed over this open rear section for experiments with CT06 to create a more uniform bottom perimeter. The flexible exhaust duct is connected to a blower that exhausted to the outdoors. Also shown are the instrument cart at left and the dilution tube for aerosol sampling at the top of the photo.

2.2.6. Instrumentation to Measure Appliance Operation and Sampling Conditions

The equipment used to measure other parameters is listed in Table 6. Details about specific equipment configurations are provided in the individual burner reports.

Table 6. Instrumentation for aerometric and other measurements

Measured Quantity	Location(s)	Device(s) ¹
Fuel pressure	Inlet to appliance regulator Outlet of appliance regulator	Magnehelic gauge; Model 264 transducer (Setra)
Fuel volume and flow rate	Fuel flow to appliance during burner operation	AC-250-TC T-compensating dry gas meter with 1- and 1/4-ft dials (American Meter); flow rate timed by stopwatch
Fuel flow rate	Fuel flow to appliance during burner operation	Pulse counter for AC-250-TC, 10 counts per rev (Riotronics)
Fuel volume and flow rate ²	Upstream of appliance (lab only)	Singer DTM-115 calibrated with AC-250-TC
Dilution sampler vacuum	Dilution tube	Magnehelic gauge (early expts); Setra Model 264 transducer
Gas sampling manifold vacuum	Gas sampling manifold	Magnehelic gauge
Temperature, air	Ambient (combustion air), gas sampling manifold	Precision NTC thermistor (APT)
Relative humidity	Ambient (combustion air), gas sampling manifold	Thermostet polymer based capacitance RH sensor (APT)
Temperature, exhaust	Exhaust flue of furnace, tankless or storage WH, etc.	Thermocouple (K), screw-mount, Omega KQSS-18E-12
Temperature, oven	Oven interior, oven, and broiler burners	Thermocouple (K), screw-mount, Omega XCIB-K-4-2-3
Temperature, exhaust sample, cooking burners	In duct leading from collection hood, at exhaust sample point	Thermocouple (K), probe, Omega KQSS-18E-12
Temperature, water	Water inside pots, cooktop experiments	Thermocouple (K), probe, Omega KQSS-18E-12

¹ APT: Automated Performance Testing System, Energy Conservatory, Minneapolis, Minnesota (energyconservatory.com); Setra: Boxborough, Massachusetts (setra.com); Riotronics: Englewood, Colorado (riotronics.com); American Meter (americanmeter.com); obtained via Miners & Pisani, San Leandro, California; Omega Engineering, Stamford, Connecticut (omega.com)

² An additional meter was in place and sometimes used for lab experiments.

2.2.7. Fuel Composition Analysis

Fuel composition was determined at LBNL using the gas chromatographic method described below. Fuel properties were calculated for the measured composition using the American Gas Association (AGA) Interchangeability Program, Version 3.1.

Fuel samples were analyzed using an SRI gas chromatograph (Model 8610 A, www.srigc.com) equipped with electron capture (ECD) and flame ionization (FID) detectors.

Fuel samples were collected in 1-L Cali-5-Bond (www.calibrated.com/bags.htm) gas sampling bags that were evacuated prior to sample collection. The bags have a luer fitting (with spring sealer) that is connected to a luer connector with a ball valve installed on the dry gas meter. For each sample, the bag was filled with fuel, then pressed by hand to empty and filled again

several times before filling a final time. The bags were stored at room temperature until analysis. Samples were almost always analyzed within one week of collection and typically within one to two days. The sample was introduced to the gas chromatograph (GC) by connecting the bag to the inlet, then using a syringe to pull 30-millileter (mL) of sample from bag through a 1-mL sample loop. The GC was configured for analysis by thermal conductivity detection (TCD) using a set of columns and operating parameters recommended by SRI in an online manual (www.srigc.com/MG1man.pdf). Methane, ethane, propane, nitrogen, and carbon dioxide were analyzed by TCD response. A flame ionization detector was installed in parallel and used to quantify butanes and larger hydrocarbons when present in substantial quantities.

The GC was calibrated for carbon dioxide and hydrocarbons (methane, ethane, propane, butanes) using blends of a low-methane natural gas mixture (G6, Scott Specialty, Longmont, Colorado) and ultra-high purity (99.999% pure) methane (Airgas) ranging from 100% G6 to 100% methane. The G6 mixture contained 71.2% methane, 10.4% ethane, 8.96% propane, 1.01% n-butane, 1.00% iso-butane, and 0.52% carbon dioxide. Calibration mixtures for nitrogen were produced by mixing UHP nitrogen (Airgas) with UHP methane to achieve levels of nitrogen up to 9% by volume. Mixtures were produced by pumping pure standards into five-layer gas sampling bags (Cali-5-Bond, Calibrated Instruments Inc, calibrated.com) at a measured flow rate for a measured time interval. Flow rate was measured using a DryCal DC-Lite primary flow meter (Bios International, biosint.com).

Quantitative analysis of the GC peaks was performed using Peak Simple software (SRI Instruments, Torrance, California). Methane, ethane, propane, CO₂, and N₂ were quantified using the TCD chromatogram; butanes and higher hydrocarbons were quantified using the FID chromatogram.

Fuel composition determined at LBNL was compared against the composition measured by online gas chromatographs in PG&E's distribution system. Based on the close agreement of these results, gas composition analysis was discontinued at LBNL. Composition of line gas used in the last set of experiments—conducted in December 2008 through April 2009—was provided by PG&E.

2.2.8. Aldehyde Sampling and Analysis

Formaldehyde and acetaldehyde emission rates were determined from time-integrated samples collected on XPosure Aldehyde sampler (Waters Corp., product WAT047205, waters.com). The samplers contain a silica substrate coated with dinitrophenylhydrazine (DNPH) that reacts with aldehydes in the sample to form derivates that are extracted with 2 mL acetonitrile. Extracts were analyzed by HPLC (Agilent 1200 Series, agilent.com) with UV diode-array detection at 360 nm, following American Society of Testing and Materials (ASTM) Method Number D 5197. Derivative concentrations were determined by comparison to calibration mixtures. Following sample collection, cartridges were stored in a freezer until extraction, and extracts were again stored until analysis.

Aldehyde samples were collected from the exhaust stream and from room or laboratory air. The background air concentration was used in the calculation of a formaldehyde emission rate, as

described in Section 2.4.. Exhaust samples were collected from the gas sampling manifold for cooking appliance burners (Figure 5) and from the dilution system for burners having ducted exhaust systems (Figure 6). A single aldehyde sampling period was designated for each experiment. The aldehyde sample(s) typically were stopped between longer discrete burns (e.g., between the two 15-minute cooktop burns) and sampled continuously for appliances operating with a series of short burns (e.g., ovens). In each case, the actual sampling times were used to calculate average exhaust CO₂ as required for the formaldehyde emission rate calculation.

Aldehyde sample flow rates were initially controlled by critical orifices with fixed flows of 1–1.1 L/min. The precise flow rate for each orifice was determined in June 2007 prior to the start of experiments, and the flow rates were found to be consistent over repeated sampling. Initially, three orifices were installed for the laboratory system, and two others were installed on the field cart. This arrangement was used for experiments through L039 and F010 in the lab and field series (refer to tables of experiments in Section 3.1.2). In mid-October 2007, one of the critical orifices from the laboratory system was moved to the field cart and aldehyde samples for lab experiments were henceforth collected using the orifices installed on the field cart. This arrangement was in place for experiments L040–L062 and F011–F027 (refer to tables of experiments in Section 3.1.2).

Flow rates were not verified, as planned, during each experiment. It was discovered in early February 2008 that the flow rates of two of three orifices on the field cart were significantly below the expected values. Aldehyde measurements including very limited numbers of co-located samples were reviewed in an attempt to discern the start and extent of flow irregularities. Unfortunately, the available information is insufficient to allow useful bounds to be placed on the aldehyde data for this period. These data are not being included in the final dataset and are not presented in this summary report or the individual burner reports.

Starting with experiments L063 and F028 (refer to tables of experiments in Section 3.1.2), the aldehyde sampling system was modified to use peristaltic pumps instead of critical orifices, and flow rates were measured during each sampling event. Aldehyde data from this point forward are presented later in this report and in the individual burner reports.

2.3. Experimental Protocols

2.3.1. Overview of Experimental Protocols

This section describes the operational protocols employed for the experimental evaluation of fuel interchangeability for residential natural gas appliances. The operational elements included the following:

- Appliance installation and configuration
- Pre-cleaning of cooking appliances for laboratory experiments
- Installation of analytical instrumentation
- Calibration of gas analyzers
- Fuel supply and fuel switching

- Burner operating protocols (including pre-conditioning)

2.3.2. Appliance Installation

Residential experiments were conducted on furnaces, storage water heaters, tankless water heaters, and one cooktop; these were all tested as installed. No attempts were made to adjust the burner for optimum performance on the baseline PG&E line gas. (This is somewhat of an academic point since most modern appliances are designed to operate at factory set-points; adjustments to airflow, and thus air-fuel mixing ratio, are not made). The installation was modified temporarily to allow connection of a gas meter between the local shut-off valve and the appliance. A pressure sensor was connected to the burner side of the appliance pressure regulator when this was accessible; generally this was done for water heaters and furnaces but not for cooking appliances. Following this step, burner control switches were returned to operational positions and pilot burners were lit as necessary.

Laboratory experiments were conducted on cooking appliances, storage water heaters, and tankless water heaters. The laboratory test bay was constructed to accommodate simultaneous installation of one to two appliances at a time. The exhaust collection hood was installed above each range. The test bay included a water supply system that controlled both supply flow and temperature (for water heaters). Outflow water was routed to a laboratory sink. The storage water heater flue included a four-foot straight vertical riser that dumps into a vent connected to the laboratory exhaust air system. Non-ducted tankless water heaters were fitted with a short section of duct to create a well-mixed and defined exhaust stream. Photographs of sampling configurations are provided in the individual burner reports.

2.3.3. Cleaning of Cooking Appliances

Cooking appliances were cleaned prior to experimental evaluation to ensure that any observed pollutant formation was associated with fuel combustion and not the result of volatilization and/or oxidation of spilled food residues. Preliminary experiments with ovens containing such residues showed that particle emission rates (as indicated by measured number concentrations) were especially sensitive to such residues. Following cleaning, exhaust particle concentrations from the first two ovens tested were much lower than they had been before cleaning; particle emissions also were much more consistent following the cleaning procedure described below.

Ranges were cleaned as follows. First, all accessible areas of the cooktop, drip pans, oven compartment, and broiler or storage area underneath the oven burner were vacuumed. The cooktop surface, grills and any drip pans were then cleaned with a concentrated glycol-ether based degreaser and kitchen sponge. The degreaser was applied liberally and left to soak for five minutes, followed by light scrubbing and finally rinsing with water-soaked paper towels. All surfaces were then dried with paper towels. Ovens were additionally cleaned by heating to the highest available temperature setting for a period of at least 3 hours. The self-clean setting was used if available; this setting ignited both oven and waist-high (broiler) burners to achieve higher temperatures. For ovens without the self-clean setting, the highest temperature setting typically was 550°F. After an oven cooled, all interior surfaces were wiped repeatedly with wet and then dry paper towels until all dislodgeable residues (highly oxidized organics and char) had been removed. Following this procedure, the oven was heated one additional time before

experiments were started to ensure that any deposits associated with cleaning were volatilized before the interchangeability experiments began. If more than a few weeks elapsed since the last use of an oven or broiler, the oven compartment was wiped with a wet paper towel and then dried before conducting any new experiments. The correct placement of sealed burner covers and the oven bottom plate (which is often connected to the spreader above the oven bottom burner) was checked before the start of an experiment.

2.3.4. Installation of Analytical Instrumentation

The analytical equipment described above was used for both laboratory and field (residential) experiments. Laboratory installations typically were installed and left in place for several days or longer as experiments were completed and data analyzed for a given appliance. A single installation was used for experiments with all burners on a cooking range.

For most appliances tested in situ at residences, equipment setup and removal had to be completed in a single day. In some cases equipment was left in place overnight or stored at the residence overnight. With two researchers working together, equipment installation generally was completed in 1.5 to 2 hours and removal was accomplished in 1 to 1.5 hours.

Setup for vented appliances (furnaces and water heaters) generally proceeded in the following manner. The stackable equipment carts were moved into place alongside the appliance. Electrical and communications connections between the carts were made. Analyzers were started so they could warm to required operating temperatures during the remaining installation tasks. Sampling lines for the combustion analyzer and aerosol dilution tube were inserted into the flue. The dilution tube and air purification unit (filter and sorbent containers) were mounted and the aerosol sampling line was placed firmly into the tube. The purification unit was connected to the supply blower and the dilution tube was connected to the exhaust blower. The gaseous sample line was connected to the combustion analyzer via the water removal system. A thermocouple was installed alongside the gas and aerosol sampling lines. The dilution blowers were then powered on.

Once this system was in place, the appliance was operated through a range-finding run. This guided the setting of instrument ranges and the temperature required for the dilution tube inlet (when using the manual setting approach). Following the range-finding run, fuel flow to the appliance was stopped at the local shut-off valve, and the gas meter with counter was installed. The gas meter, temperature and relative humidity probes, and pressure sensors (for line and manifold pressure) were installed during instrument calibration.

2.3.5. Calibrations

Gas analyzers were calibrated on each day in which experiments were conducted. Certified calibration gases (Table 7) were mixed with ultra-zero air or ultra high purity (UHP, 99.999%) nitrogen to achieve a range of concentrations for daily span checks. Instruments were calibrated using either a dynamic dilution flow system or from bags containing gas mixtures of specified concentrations. In the laboratory, a dilution calibrator containing two mass flow controllers mixed clean diluent (generally UHP N₂) at 1–10 L min⁻¹ with concentrated calibration gas at 10–100 mL min⁻¹ to achieve dilutions of 10–1000. This system was used primarily to create mixtures

for laboratory calibrations at levels relevant to cooking burner experiments. For cooking appliance experiments (that utilized the collection hood), the following calibration levels were commonly used: CO₂ at 0.77%, CO at 50 parts per million (ppm), and NO_x and NO at 5.0 ppm; these levels were created from the cylinders containing 100% CO₂, 5010 ppm CO, and 501 ppm NO_x as NO.

Table 7. Calibration gases used for LNG interchangeability experiments

Analyte	Conc.	Rated Precision	Balance	Supplier	Direct	Dilution Calibrator	Gas Divider
CO ₂	100%	-	-	Airgas		X	
CO ₂	10%	±2%	Air	Airgas	X		X
CO ₂	2532 ppm ¹	±2%	N ₂	Airgas	X		X
O ₂	16.04%	±1%	N ₂	Scott-Marrin			X
CO	5010 ppmv	±1%	N ₂	Scott-Marrin		X	X
CO	350 ppmv	not avail.	N ₂	Matheson	X		X
CO	40 ppmv	not avail.	N ₂	Scott Specialty	X		
NO	501 ppmv	±1%	N ₂	Scott-Marrin		X	X
NO	20.2 ppmv	±1%	N ₂	Scott Specialty	X		
NO	2.5 ppmv ²	±1%	N ₂	Airgas	X		
NO ₂	462 ppmv	±1%	N ₂	Scott-Marrin		X	

¹ Supplier original analysis rated this mixture as 2356 ppm ±2%. However, a cross-check (of 20% of this mix in nitrogen) against two other cylinders with recently validated (and cross-validated) concentrations in the range of 400–500 ppm CO₂ indicates that the cylinder concentration is approximately 2532 ppm.

² The supplier's analysis rated this as 2.4 ppm nitrogen oxides, 2.34 ppm NO. A comparison against a 5 ppm mixture generated by a 100x dilution of the 501 ppm NO cylinder consistently gave the reading of 2.5 ppm for this mixture.

Calibration mixtures also were created in bags using a gas divider that allows 10% to 90% dilution of calibration gas with air or nitrogen. Two types of bags were used: Cali-5-Bond (calibrated.com/bags) and SKC Series 232 Tedlar bags (skcinc.com/prod/232-01). Bag size was selected to provide a sufficient quantity of gas to allow multiple field calibrations.

Table 7 indicates how each of the calibration gases was used. The specific instrument ranges and calibration levels used for each set of experiments are provided in the individual burner reports. In February 2008, the calibration cylinders of CO and NO at varying levels were inter-compared using the gas divider and calibration dilution system to produce mixtures within similar ranges.

2.3.6. Burner Operating Cycles

Burner experimental operating cycles (described in Table 8 below) were developed with the objective of capturing key features of realistic use patterns with a total cycle time that would allow completion of three to four experiments—with setup and calibration—in a single day. Appliances generally were operated through multiple burns, each following a designated cooling period. With the exception of some variations in early experiments, cooktop, waist-high (broiler), and storage water heater burners were operated through two 15-minute burns that were intended to serve as replicates. The central furnace protocol included one shorter (10-minute) and one longer (20-minute) burn to capture potentially different operating conditions; of specific interest were the two firing rates for burners having this capacity. Ovens were operated at three set-point temperatures (350°F, 425°F, and 500°F, corresponding to 177°C,

218°C, and 260°C), representing common temperatures used for cooking. At each temperature setting, the ovens were operated through one ramp burn (to reach the setting) and at least two additional burns to maintain temperature. Tankless water heaters were operated at three different flow rates intended to cover the vast majority of typical use. The standard flow rates were 1, 2, and 4 gallons per minute (gpm), with 8-minute burns following 10-minute cooling periods. Prior to the start of formal experiments, burners usually were operated through a series of short range-finding burns to determine appropriate instrument ranges and calibration levels. When fuels were switched, burners were fired for short periods to purge the previous fuel from external and internal transfer lines. Purge burns for oven and broiler burners typically were accomplished using the cooktop (without pots) of the freestanding range. Purge burns were timed to use at least 2 ft³ of fuel. While operating protocols were revised during and following the early experiments with each type of burner, care was taken to use consistent protocols for each set of experiments with a given burner.

Table 8. Burner operating procedures for interchangeability experiments

Burner	Operation
Cooktop	On each of 4 corner burners place 5-L stainless steel pot containing 4-L H ₂ O. Burn 1: fire all burners at highest setting for 15 min. Remove and cool pots, then refill. Allow burner to cool for 15 min (cooling varied in early experiments). Burn 2: fire all burners at highest setting for 15 min. "End-of-burn" is last 5 min.
Oven Bottom Burner	Start with oven interior surfaces at room temperature (cool to touch). Operate without load and with door closed. Set oven to "bake" (as required) at 350°F for initial burn to achieve set-point plus 2 or more burns to maintain temperature. Reset to 425°F for ramp plus 2 or more maintenance burns, then repeat at 500°F. Calculate pollutant emissions metrics for first burn at each temperature setting; "end-of-burn" is last 1 min of each burn. Aldehydes sampled over entire cycle.
Broiler (Waist-High Burner)	Start with oven interior surfaces at room temperature (cool to touch). Operate without load and with door closed. Set to "broil" and/or 550°F (depending on configuration) for 15 min (Burn 1). Allow oven to cool then repeat (Burn 2). BR02 and BR03 experiments had single 30-min burn.
Storage Water Heater	Allow burner to cool at least 15 min following purge or other preparatory burn. Set burner control to stand-by or "pilot." Draw 10 gal (or 20% of tank volume for units exceeding 50-gal capacity) of water to establish temperature deficit in tank. Set burner control to "on" to initiate burn. Allow burner to fire as needed to achieve temperature set-point or for 15 min (Burn 1). Set control to stand-by or pilot. Pre-draw water then start Burn 2 15 min after end of Burn 1. In early experiments, burner control was always on and burn was initiated by tank temperature decrease with water draw. Cooling time between burns was 8 min for WH01; 9-20 min for WH02.
Central or Wall Furnace	Operate burner by raising thermostat setting to initiate burn and lowering setting to stop burn. Allow burner to cool for 20 min following range-finding or purge burn, then operate for 20 min (Burn 1). Allow burner to cool for 10 min then operate for 10 min (Burn 2). For CF01, Burn 1 was 19 min following 20 min burner cooling period; Burn 2 was 9 min following 10 min cooling period.
Tankless Water Heater	Allow burner to cool 10 min following purge burn. Draw water at specified rates to initiate burner operation. 8-min burns following 10-min cooling periods. Standard cycle was 1, 2, and 4 gallon per minute (gpm) water draws. TW02 had draws of 1, 2, 2, 4 gpm. TW03 maximum draw was 3 gpm.

2.4. Data Reduction and Calculation of Metrics

2.4.1. Primary Data, Data Reduction, and Data Archives

Broadly, the data obtained from an experiment included the following:

- Fuel composition obtained by analysis of collected fuel sample(s)
- Fuel supply parameters including supply pressure, appliance manifold pressure (when accessible), and volumetric fuel use rates
- Ambient and combustion air temperature (T) and relative humidity (RH)
- Sampling system conditions, including exhaust air T at the point of pollutant sampling, dilution tube vacuum, and T and RH in the gas sampling manifold for experiments using the collection hood
- Time-resolved concentrations of exhaust constituents (O₂, CO₂, CO, NO, NO_x, NO₂, and PN) measured during periods of burner operation and background periods
- Time-integrated concentrations of formaldehyde and acetaldehyde in exhaust and background air

- Performance temperatures for cooking appliances

Data on particle size distributions were collected in a subset of experiments using either the Lasair or SMPS. These data have a more coarse time resolution based on the scan time of the instrument.

With the exception of aldehyde samples and gas composition, all data noted above were averaged over 10-second intervals. Raw data were saved by the Labview system as comma-delimited text files.

For each experiment, individual data files were imported and organized into a single worksheet in Microsoft Excel. Each data interval comprises one row of the worksheet. Custom macros were created to analyze the data and produce results as described below. The worksheet for each experiment includes the time resolved data, fuel properties, calculated mean and standard deviation of measured parameters over each burn and for the background period, and calculated results (emission factors, air-free concentrations, etc.). Each set of experiments conducted on a given burner are compiled into a single workbook; multiple workbooks exist for a few burners on which separate series of experiments were conducted at distinct times, i.e., separated by weeks to months. These two sets of files represent the primary data archives for the project.

The sections which follow describe the calculations performed on the primary data to obtain the results that are presented later in this report and in the individual burner reports.

2.4.2. Fuel Properties

The measured fuel composition was input to the American Gas Association (AGA) Interchangeability Program, Version 3.1 to obtain fuel properties, including higher heating value and Wobbe number. Two additional fuel parameters that are needed for calculation of pollutant emission rates are the theoretical (complete combustion) air-free dry exhaust CO₂ mole fraction and the molar production of CO₂ per megajoule (MJ) of fuel energy. The calculation and use of these parameters is described below in the subsection on pollutant concentrations at reference conditions.

2.4.3. Fuel Supply Parameters

Mean fuel supply and appliance manifold pressures and fuel use rates (cubic foot per minute, ft³ min⁻¹) were calculated for each individual burn for most appliances, and the first burn at each new temperature setting for ovens. Appliance manifold pressure was not obtained for all appliances, principally due to the lack of a suitable access port. In at least one cooking range, the gas regulator was used to facilitate the addition of a pressure tap inline. Fuel use rate was calculated as the sum of volumetric fuel counts (at 0.1 ft³ intervals) divided by the time over which the fuel volume data were collected.

2.4.4. Ambient and Combustion Air Conditions

Temperature and relative humidity of the combustion supply air generally were consistent through the course of an experiment; they were averaged over periods that varied by burner.

2.4.5. Sampling System Conditions

Sampling system conditions—including the exhaust air T at the point of pollutant sampling, the dilution tube vacuum, and T and RH in the gas sampling manifold for experiments using the collection hood—were averaged over each entire burn and over a short period at the end of each burn. The ratio of dilution to sample air in the dilution sampling system was calculated over both the entire period of each burn and for a shorter period at the burn. This calculation used the background-corrected NO or NO_x values measured in both the primary exhaust stream and in the dilution system. The end-of-burn calculation was for most burners indicative of stable, fully-warmed burner operation; the calculation was made over a 5 minute period for burns longer than 10 minute duration. For ovens, the calculation was made over the final 1 minute of operation during the first burn to reach each temperature setting.

2.4.6. Pollutant Emission Metrics

Pollutant concentrations were averaged over varying periods to calculate concentrations at reference conditions (air-free and 3% O₂) and emission rates. These calculations were made for a short period at the end-of-burner operation and for the entire period of each burn for most pollutants. Formaldehyde emission rates were calculated for the period of sampling (typically including all burns); this calculation required the average exhaust CO₂ measured over the same period. Pollutant concentrations thus were averaged over the periods described above and for one or two background periods to account for any pollutants contained in combustion air. Background air CO₂ was measured throughout an experiment with a separate analyzer, i.e., not the combustion exhaust analyzer.

2.4.7. Pollutant Concentrations Normalized to Reference Conditions

Pollutant concentrations were calculated for the reference conditions of air-free (0% O₂) and at 3% O₂ over the following periods:

- Entire period of each individual burn excluding temperature maintenance burns for ovens
- Final 5 minutes of each burn of 10 minutes or longer duration
- Final 1 minute of the initial burn at each oven T setting

The adjustment to air-free concentrations can be done using either the measured O₂ or the measured CO₂ and calculated theoretical dry CO₂ to adjust other analytes to dry-air free conditions. Both approaches should provide approximately the same answer. Results can differ based on imprecision in the measurements of O₂ and CO₂. The CO₂-based calculations were used as the primary estimate of air-free concentrations for all analytes. NO_x results also were calculated at the reference condition of 3% O₂ (O₂-based calculation).

The air-free concentration C_i of pollutant i was calculated using the measured O₂ concentration as

$$C_i(@ 0\% O_2) = (C_{i,msd} - C_{i,bkg}) \left[\frac{20.95}{20.95 - O_{2,msd}(\%)} \right] DR \quad (1)$$

where $C_{i,msd}$ is the concentration of i , $O_{2,msd}$ is the concentration of O_2 (both measured over the period of interest), $C_{i,bkg}$ is the background concentration of pollutant i , and DR is the dilution ratio. For analytes sampled at the same location as O_2 , DR = 1. For analytes measured in the dilution sampling system, DR is the measured ratio of NO or NO_x in the primary exhaust sample stream and in the dilution system.

Concentrations at 3% O_2 were calculated using Equation 2 below:

$$C_i(@ 3\% O_2) = (C_{i,msd} - C_{i,bkg}) \left[\frac{20.95 - 3}{20.95 - O_{2,msd}(\%)} \right] DR \quad (2)$$

Air-free concentrations can also be calculated using the measured values of CO_2 ; this approach first requires calculation of the theoretical air-free exhaust CO_2 concentration.

The theoretical value of air-free exhaust CO_2 can be calculated from the composition as follows:

$$\text{Theoretical } CO_2 \text{ (air - free)} = \frac{\sum n_i [CO_2]_i}{\sum n_i N_{total,i}} \quad (3)$$

where n_i are the mole fractions of i fuel components, $[CO_2]_i$ are the moles of exhaust CO_2 produced per mole of i in the fuel, and $N_{total,i}$ are the total moles of exhaust gas per mole of i in the fuel (assuming complete combustion). Air-free CO_2 can be expressed on a wet or dry basis (H_2O included or excluded from products). The PG-250 analyzer that was used to collect CO_2 has an internal water removal system to remove the humidity that was present in dilute sampling. A more substantial water-removal system was used when sampling direct exhaust streams. Thus, the analytes measured with the PG-250 (CO_2 , CO, NO) should always be considered on a dry basis.

The Thermo 42i NO_x analyzer sampled from a dilute stream with no water removal. The concentrations of NO, NO₂, and NO_x from this analyzer can be adjusted to a dry basis using the measured humidity, converted to a mole fraction in air. Alternately, the NO_x values can be presented without adjustment; these differ by approximately 2%–4% from the values on a dry basis. The discrepancy between wet and dry exhaust NO_x values should be consistent for all experiments with a given appliance and sampling configuration. Table 9 provides values for $[CO_2]_i$ and $N_{total,i}$ for the major fuel components.

Table 9. Calculation of exhaust CO_2 production from natural gas components

Component	Balanced Equation	$[CO_2]_i$	$N_{total,i}$ (dry)	$N_{total,i}$ (wet)
Methane (CH_4)	$CH_4 + 2(O_2+3.78N_2) \rightarrow CO_2 + 2H_2O + 2(3.78)N_2$	1	8.56	10.56
Ethane (C_2H_6)	$C_2H_6 + 3.5(O_2+3.78N_2) \rightarrow 2CO_2 + 3H_2O + 3.5(3.78)N_2$	2	15.23	18.23
Propane (C_3H_8)	$C_3H_8 + 5(O_2+3.78N_2) \rightarrow 3CO_2 + 4H_2O + 5(3.78)N_2$	3	21.90	25.90
Butane (C_4H_{10})	$C_4H_{10} + 6.5(O_2+3.78N_2) \rightarrow 4CO_2 + 5H_2O + 6.5(3.78)N_2$	4	28.57	33.57
Pentane (C_5H_{12})	$C_5H_{12} + 8(O_2+3.78N_2) \rightarrow 5CO_2 + 6H_2O + 6.5(3.78)N_2$	5	35.24	41.24
CO_2	$CO_2 \rightarrow CO_2$	1	1	1
N_2	$N_2 \rightarrow N_2$	0	1	1

Pollutant measurements can be adjusted to air-free values using the ratio of measured to theoretical (calculated) air-free CO₂.

$$C_i(\text{air} - \text{free}) = (C_{i,\text{msd}} - C_{i,\text{bkg}}) \left[\frac{CO_2(\text{air} - \text{free})}{CO_{2,\text{msd}} - CO_{2,\text{bkg}}} \right] DR \quad (4)$$

where CO_{2,bkg} is the value measured in the combustion supply air (generally around 500 ppm or 0.05%) and C_{i,bkg} is the background value of species *i* measured before and after burner operation (generally insignificant compared with C_{i,msd}), and DR is the dilution ratio. For analytes sampled directly with CO₂, DR = 1. For analytes measured in the dilution sampling system, DR was the measured value for this system. Background CO₂ was generally much smaller than sample CO₂ in direct exhaust sampling (CO₂ = 4%–10%), but it can be substantial with respect to the primary exhaust stream CO₂ values of 0.3%–0.6% measured for cooking burners and other experiments using the collection hood.

2.4.8. Pollutant Emission Rates Normalized to Fuel Energy

Emission rates were normalized to fuel energy to account for variations in energy density associated with fuel composition changes. The calculation is presented in Equation 5, which includes both the input terms and the required unit conversions:

$$E_i \left[\frac{\mu\text{g}}{\text{KJ}} \right] = \frac{\left(\frac{10^{-6} \text{ mol } i}{\text{mol air}} \right)}{\left(\frac{10^{-2} \text{ mol CO}_2}{\text{mol air}} \right)} \left(\frac{\text{mol CO}_2}{\text{MJ fuel}} \right) \left(\frac{\text{g } i}{\text{mol } i} \right) \left(\frac{\text{MJ}}{10^3 \text{ KJ}} \right) \left(\frac{10^6 \mu\text{g}}{\text{g}} \right) DR \quad (5)$$

The first term on the right-hand side of the equation is the ratio of background-corrected (or air-free) concentration of analyte *i* (in ppm) to the concentration of CO₂ (in percent). The second term on the right-hand side is calculated based on fuel composition, as shown below in equations 9–11. The third term on the right-hand side is the molecular mass of the analyte. The fourth and fifth terms are unit conversions. Dilution ratio enters as above: for pollutants sampled alongside exhaust CO₂ a value of 1 is used; for pollutants sampled in the dilution system, the value is calculated using the ratio of NO or NO_x measured in both direct and dilute exhaust streams. This equation is written for the case of near-complete combustion; it can be more generically formulated to consider exhaust carbon—including both CO and CO₂—rather than carbon dioxide alone. The distinction is important only in cases of very high CO emissions, on the order of thousands of parts per million.

Rearranging Equation 5 yields the following equation:

$$E_i \left[\frac{\mu\text{g}}{\text{KJ}} \right] = (10^{-1}) \frac{C_{i,\text{AIR-FREE}} [\text{ppm}]}{\text{Theor. CO}_2 [\%]} \left(\frac{\text{mol CO}_2}{\text{MJ fuel}} \right) M_i (DR) \quad (6)$$

For illustration, consider experiments using a natural gas with 95.8% methane, 2.14% ethane, 0.29% propane, 0.10% butanes, 0.85% N₂, and 0.84% CO₂; this fuel has a Wobbe number of 1333 Btu/scf, a theoretical CO₂ dry exhaust fraction of 0.1183, and 1.11 moles (mol) CO₂ per MJ

of fuel energy. Inserting these values into Equation 6 above, and considering the case of CO (molecular mass of 28 grams per mole [g/mol]) sampled directly (DR = 1) yields the following:

$$E_i \left[\frac{\mu\text{g}}{\text{KJ}} \right] = (10^{-1}) \frac{C_{i,AIR-FREE} [\text{ppm}]}{11.83} (1.11)(28)(1) = (0.262) (C_{i,AIR-FREE} [\text{ppm}]) \quad (6a)$$

For this fuel, a dry air-free concentration of 1000 ppm corresponds to a CO emission rate of 262 ng/J.

For particle number or surface area, the concentrations were normalized to an air volume (cm³); this required an additional conversion factor as shown below:

$$E_i \left[\frac{\# \text{ or } \mu\text{m}^2}{\text{KJ}} \right] = \frac{\left(\frac{\# \text{ or } \mu\text{m}^2}{\text{cm}^3 \text{ air}} \right) \left(\frac{\text{cm}^3 \text{ air}}{\text{mol air}} \right)}{\left(\frac{10^{-2} \text{ mol CO}_2}{\text{mol air}} \right)} \left(\frac{\text{mol CO}_2}{\text{MJ fuel}} \right) \left(\frac{\text{MJ}}{10^3 \text{ KJ}} \right) DR \quad (7)$$

At the reference conditions of 60°F and 14.73 pounds per square inch absolute (psia), the volume of 1 mole of air is 23.6 L or 23,600 cm³.

Rearranging yields the Equation 8:

$$E_i \left[\frac{\# \text{ or } \mu\text{m}^2}{\text{KJ}} \right] = (23.6 \times 10^2) \frac{C_{i,AIR-FREE} \left[\frac{\# \text{ or } \mu\text{m}^2}{\text{cm}^3} \right]}{\text{Theor. CO}_2 [\%]} \left(\frac{\text{mol CO}_2}{\text{MJ fuel}} \right) DR \quad (8)$$

As an example to relate CO₂ production to fuel energy, the calculation is first presented for 100% methane. Each mole of CH₄ produces 1 mole of CO₂ in exhaust. The heat of combustion of methane is 37.7 MJ/m³. At reference conditions of 60°F and 14.73 psia, one mole occupies 23.6 L or 0.0236 m³. This leads to the following calculation:

$$H_{CO_2,CH_4} = \left(\frac{1 \text{ mol CO}_2}{\text{mol CH}_4} \right) \left(\frac{\text{mol CH}_4}{0.0236 \text{ m}^3} \right) \left(\frac{\text{m}^3 \text{ CH}_4}{37.7 \text{ MJ}} \right) = \frac{1.12 \text{ mol CO}_2}{\text{MJ CH}_4 \text{ energy}} \quad (9)$$

Similar calculations can be made for each hydrocarbon component *i* of the fuel. Generally:

$$H_{CO_2,i} = \left(\frac{\text{mol CO}_2}{\text{mol } i} \right) \left(\frac{\text{mol } i}{0.0236 \text{ m}^3} \right) \left(\frac{\text{m}^3 \text{ } i}{\text{MJ}} \right) \quad (10)$$

where the final term is the inverse of the higher heating value.

For a given set of $H_{CO_2,i}$ (moles produced per megajoule of energy in fuel component *i*) for *i* fuel components, the composite value can be calculated as follows:

$$H_{CO_2,Fuel_4} = \sum_i y_i H_{CO_2,i} \quad (11)$$

Emission rates normalized to fuel energy were calculated for the discrete periods described above (entire burn and short period at end of each burn to capture warmed burner conditions). The calculation used the average pollutant concentrations measured over the defined period.

2.4.9. Aldehyde Emission Rates Normalized to Fuel Energy

This section demonstrates the calculation of formaldehyde and acetaldehyde emission rates. The objective was to calculate the mass (μg) of formaldehyde (HCHO) or acetaldehyde emitted per quantity of fuel energy used (MJ); the logic of the calculation is demonstrated for formaldehyde:

$$\frac{\mu\text{g HCHO}}{\text{MJ fuel energy}} = \left(\frac{\text{mol HCHO}}{\text{mol CO}_2} \right) \left(\frac{\text{mol CO}_2}{\text{MJ fuel energy}} \right) \left(\frac{\mu\text{g HCHO}}{\text{mol HCHO}} \right) \quad (12)$$

The first term on the right-hand side of the equation is the relative concentration of HCHO to CO_2 in the exhaust stream. CO_2 is measured in the primary exhaust stream (direct in flue or from outlet of collection hood). Formaldehyde is measured alongside CO_2 in the sampling manifold for the collection hood exhaust stream and measured in the dilution system for appliances with concentrated exhaust. The calculation of formaldehyde is complicated by the need to account for removal of HCHO in the dilution air for dilution system sampling and the consideration that the formaldehyde sample may include periods when the burner was not operating.

2.4.10. Formaldehyde Measured in the Dilution Sampling System

Presented first is the more complicated situation in which HCHO was measured in the dilution sampling system. To calculate the HCHO concentration in the primary exhaust stream where CO_2 is measured, the calculation considers contributions to the HCHO measured in the dilution system. The description starts with a mass balance for HCHO in the dilution stream:

Mass of HCHO in dilution tube =
 mass contributed by combustion (when burner on) +
 mass in excess combustion air +
 mass from room air pulled into sample line when burner off +
 mass from dilution air (fraction that passes through Purafil sorbent).

The first three terms represent contributions via the sample inlet. The generic calculation considers the time-averaged concentration of formaldehyde in the sample flow into the dilution system (C_{sample}), which results from the three contributions listed. In Equation 13, Q_{sample} is the flow rate through the sample inlet. $C_{\text{dil,air}}$ is the concentration of HCHO in dilution air, which is equal to $(1-\eta) \cdot C_{\text{ambient}}$ where η is the removal efficiency of HCHO in the supply air conditioning system.

$$C_{tube} = \frac{C_{sample} Q_{sample} + C_{dil.air} Q_{dil.air}}{Q_{sample} + Q_{dil.air}} = \frac{C_{sample} Q_{sample}}{Q_{sample} + Q_{dil.air}} + \frac{C_{dil.air} Q_{dil.air}}{Q_{sample} + Q_{dil.air}} \quad (13)$$

The flow terms can be expressed in terms of the measured dilution ratio (DR), which is equal to the total flow over the sample flow (Q_T / Q_{sample}) where $Q_T = Q_{sample} + Q_{dil.air}$. DR was calculated from the ratio of NO or NO_x concentrations measured in the direct exhaust and in the dilution tube. $Q_{dil.air}$ was measured with the rotameter reading on the clean air supply to the dilution system.

Equation 13 can be restated using the measured dilution ratio, as follows:

$$C_{tube} = \frac{C_{sample}}{DR} + C_{dil.air} \left(1 - \frac{1}{DR} \right) \quad (14)$$

Equation 14 may be rearranged to get the following:

$$C_{sample} = (DR)C_{tube} - (1 - \eta)(DR - 1)C_{ambient} \quad (15)$$

Equation 15 may be simplified with the approximation that the last parenthetical term is close to 1. For a value of DR = 15 (generally the smallest value used), the error in the adjustment for dilution air is only 7%. Since the concentration in dilution air is generally very low, this approximation contributes very little bias to the overall result.

Using the approximation that $Q_{dil.air}/(Q_{sample}+Q_{dil.air})$ is close to one, Equation 15 can be rearranged as follows:

$$C_{sample} = (C_{tube} - (1 - \eta)C_{ambient})DR \quad (16)$$

The equations above apply when the dilution air is being drawn from the room or other ambient source. In laboratory experiments, the dilution air was drawn from the on-site compressed air supply. The HCHO concentration in this supply air was measured periodically; it was twice found to be below the detection limit. With the HCHO contribution in conditioned dilution air at a level much lower than in the sample air, then the equation simplifies further to the following:

$$C_{sample} = C_{tube} DR \quad (17)$$

HCHO in the sample flow to the dilution system came from two sources: production related to combustion (C_{exh}) and formaldehyde entering with combustion air (excess air plus air entering sample line when burner is off). When combustion air was drawn from outside (at a residence), the concentration of HCHO in the combustion air may have differed from the sample collected alongside the dilution system intake ($C_{ambient}$). Typically, separate samples were not collected to quantify HCHO outside; instead the concentration measured alongside the burner $C_{ambient}$ was taken as an upper bound estimate on this value. Note that C_{exh} is the average contribution from combustion to the air entering the sample inlet of the dilution system; not the concentration in pure exhaust (since all of the burners tested had excess air in the flue). The average exhaust concentration was calculated as follows:

$$C_{exh} = C_{sample} - C_{ambient} \quad (18)$$

Here C_{exh} is the time-averaged contribution to the exhaust stream from combustion; this term was divided by the time-averaged combustion contribution of CO_2 in the exhaust stream over the period of HCHO sampling. The ratio of HCHO to CO_2 concentrations yields the first term on the right side of Equation 12, shown below in more detail:

$$\left[\frac{\text{moles HCHO}}{\text{moles } CO_2} \right] = \frac{C_{exh(HCHO)} \left[\frac{\text{moles HCHO}}{\text{moles air}} \right]}{\left(CO_{2,exh} - CO_{2,bkg} \right) \left[\frac{\text{moles } CO_2}{\text{moles air}} \right]} \quad (19)$$

Here the CO_2 concentration is adjusted by subtracting the amount entering in combustion and excess air. The adjustment was small when there was little excess air, but increased with the amount of time sampled with the burner off and with the excess air level. The adjustment for ambient air typically was about 500 ppm or 0.05%; that is, a small fraction of exhaust CO_2 in the range of 6%–8%. Fuel gas may have CO_2 at up to the 1% by volume level. Considering the stoichiometry of approximately 10 volumes of air needed to combust 1 volume of fuel, this translates to an upper limit of about 0.1% in the exhaust. Excess air reduces this contribution.

2.4.11. Formaldehyde Measured With CO_2 in Direct Exhaust

Since no dilution system is involved, the calculation started with Equation 18 and used the HCHO concentrations measured in the gas sample manifold and the ambient (combustion) air.

The mass balance proceeds as follows:

Mass of HCHO in sample = mass contributed by flame when burner on + mass from room air.

The calculation proceeds from here in a similar manner as above.

2.5. Statistical Analysis Procedures

2.5.1. Results Database

To facilitate analysis, a results database was created by reading selected experimental variables, summary data, and calculated results from the individual burner worksheets described above. Experimental variables include those such as the date, experiment number, burner ID, fuel ID, and fuel properties. Summary data include the ambient and sampling system temperature and relative humidity, fuel supply pressure, dilution system vacuum, analyte concentrations during designated background period and during each experimental period, and relevant appliance operational temperatures (e.g., in oven or pots for cooktop experiments). Calculated results include all of the end-of-burn and full-burn air-free concentrations and emission rates. The database is organized around the individual burn (i.e., on period of burner operation) as the primary unit of analysis. Valid data are available for at least two burns in most experiments on cooktops, broilers, water heaters, and furnaces; and three burns were specified in the protocols for ovens and tankless water heaters.

2.5.2. Statistical Analysis Methods

This subsection describes the statistical methods used to analyze the experimental results. Analysis was focused on the objective of evaluating the effect of fuel variability on the operation and air pollutant emissions of residential natural gas appliances. Experimental protocols were developed to approximate realistic appliance use patterns, specifically including transient operation. As a result of the relatively long duration of an individual experiment to evaluate a given burner being operated on a given fuel, the number of fuel variations that could be evaluated was limited to just a few per burner. The primary fuel variable was the Wobbe number (WN) and most burners were operated with three fuels, including PG&E line gas (WN mostly in the range of 1330–1340 Btu/scf), a mid-Wobbe fuel in the range of about 1380–1390, and a high Wobbe fuel in the range of about 1415–1425. The analyzed outcomes (results) of each experiment were the calculated pollutant emission rates.

Differences in measured emission rates with a given burner using different fuels can result from the fuel, from unintentional variability in some other experimental parameter, or from imprecision in the experimental methods used to measure emission rates. Pollutant emission rates may vary in a repeatable fashion based on operational variables such as the amount of primary air provided (if adjustable), combustion air humidity, or the fuel Wobbe number. These controlling variables may have varying impacts by pollutant and by appliance burner. Emissions also may vary with fuel in a way that appears less repeatable due to other factors that are not well characterized (e.g., the amount of dust or grime that has accumulated on a burner).

In addition to variability in the actual emission rate based on experimental conditions, there will be some uncertainty in both the accuracy and the precision of the measurement. *Accuracy* describes the degree to which a sufficiently large ensemble of measurements will yield a mean estimate that is the correct or true value. It derives from the traceability of calibration gases, the calibration procedures by which these gases are utilized, the linearity of response for an analytical instrument, and the degree to which the analytical instrument maintains a consistent response over time (following calibration). *Precision* refers to the closeness of any given measurement to the mean value that would be obtained from an ensemble of measurements (whether or not the mean value is accurate). It is affected by the analytical instrumentation's resolution and magnitude of fluctuation and the number of measurements used to derive an estimate of the measured value, assuming stable or repeatable operation of the test specimen.

The main objective of the experiments conducted for this study was to determine if pollutant emission rates of residential natural gas appliances vary with (are affected by) variability in fuel composition and properties. For this purpose, the key issues were (1) the variability of emission rates for repeat experimental implementations of a given combination of burner and fuel (recognizing that some known variables such as ambient conditions are not controlled and other unspecified factors may affect emissions), (2) the variability of emission rates as a function of the fuel properties (i.e., a change in emissions resulting from a change in fuel), and (3) the relative accuracy and precision of the experimentally determined emission rates. The rigorous determination of each factor is challenging in practice and requires either a complete

understanding and accounting for all of the important variables or a substantial amount of experimental replication.

The most straightforward way to assess whether emission factors obtained during experiments using different fuels indicate an effect of fuel on emissions is to conduct a sufficient number of replicate experiments to generate an ensemble of results at each condition. However, given the methods used, it was impractical to routinely obtain data for more than two or three burns per experiment. It was assumed that uncertainties associated with analytical instrument performance were independent of the burner being tested but could depend on the absolute level of emissions being measured (e.g., higher relative uncertainties for lower absolute values and for exhaust concentrations that are closer to background). It was further assumed that the method uncertainties should be similar for all burners of a given type (since all were tested with the same protocol). With these assumptions, replicate experiments were conducted for a subset of conditions and replicates were pooled by burner group to assess the repeatability of a result. The calculation of a metric to quantify experimental repeatability is described below.

The following points are also relevant to the consideration of uncertainty.

- The primary instruments used to measure gaseous analytes are rated to drift less than 1% over a 24-hour period, to have 1% precision at full scale, and to remain within 1% deviation from linearity. Thus, for concentrations substantially above background levels (or the noise level of the instrument, whichever is larger), the instruments are capable of discerning differences of a few percent or less for same day experiments. For experiments occurring on different days, there can be additional uncertainty associated with imprecision in the on-site dilution of calibration gases. Both the dynamic calibrator used in early experiments and the gas divider used in later experiments are precise to within 2% or better.
- Aerosol instrument responses were not adjusted throughout the experimental program. Rated accuracy of particle counts (e.g., in units of number of particles per cubic centimeter) is on the order of 10%–20%; repeatability and the ability to discern actual differences between experiments conducted with different fuels could be better than this. With some burners, variations observed in PN emissions from experiments or replicate burns with the same fuel were larger than variations between fuels; these results suggest that minor variations in operation or other factors (e.g., recent operational history) can have large effects on ultrafine particle formation.
- Comparison of experiments conducted on different days should consider variability associated with changes in environmental conditions (air temperature and humidity) and potentially other factors (e.g., accumulation of dust on burners).
- Calculated concentrations at reference conditions (air free or 3% O₂) and emission rates depend on the measured concentrations of the analyte of interest and on either CO₂ or O₂. Uncertainties of both measurements contribute to the overall uncertainty of the result. Comparison of results obtained with O₂ and CO₂ corrections to reference conditions can provide a more robust analysis. Cooktop experiments involve small

relative decrements in O₂ relative to background; thus CO₂-based analysis is preferred. For vented burners, both CO₂ and O₂ should provide robust and valid results.

The following paragraphs summarize the statistical analyses conducted. The first analysis assessed the uncertainty associated with individual experimental results. This is an important element in assessing whether an apparent difference between conditions (fuels) is a result of methodological imprecision or a true variation resulting from the change of fuel. Next, bivariate linear regression analysis was conducted to quantify the relationships between emission factors and fuel Wobbe number, and to determine the statistical significance or robustness of these relationships for each individual burner. For ovens and tankless water heaters multivariate analysis was used to assess the effect of fuel Wobbe number adjusted for variations caused by burner operation. Additional multivariate analysis was conducted to evaluate the effect of fuel WN on particle number (PN) emission rates, adjusted for the effect of experiment order. These analyses are described in more detail below.

The initial work plan envisioned a comprehensive statistical analysis by burner group. The plan was to use either generalized estimating equations (GEE) or a mixed effects (ME) model to estimate an effect of fuel Wobbe number on emissions for each burner group. Preliminary exploratory analyses were conducted. The GEE approach was found to be unsuitable for most pollutant-burner group combinations because the bivariate results indicate widely varying response functions for individual burners within each group; GEE is designed to tease out an assumed common response function of all the individual subjects within the group. The mixed effects approach is suitable to obtain an overall group effect given differential individual responses. However, the final dataset was deemed to be too sparse for robust implementation of this approach. Effort was instead focused on more extensive multivariate analysis of individual burner results, e.g., to assess effects of burner operation and experiment order for PN.

Statistical analyses were performed with SAS software version 9.1.3 as described in the following subsections.

Univariate Analysis. The database was analyzed to calculate mean values and data counts (n) for key metrics including air-free exhaust concentrations and emission factors by condition (combination of burner, fuel, and burner operation). One set of output from this analysis is presented as the mean air-free pollutant concentrations over full-burn and end-of-burn periods. These results, discussed at length in Section 3.2.2, provide insight into the magnitude and direction of the effect of transient burner operation.

Repeatability Analysis. Experimental repeatability (an indicator of uncertainty) was assessed by analysis of replicate burns by burner group. Replicates were defined as pertaining to the same burner, fuel group, and operating condition. Cooktops, broilers, and water heaters were operated similarly during all burns for a given burner, generally with two burns per experiment; thus for most of these burners there was at least one set of two replicates (duplicates). If a replicate experiment was conducted (e.g., a second experiment with one of the three primary test fuels), that provided four replicates for the condition. Ovens were operated at three different temperatures in each experiment; thus, oven replicate burns are available only

for those burners for which a replicate experiment was conducted. Most tankless water heaters were operated at three different flow rates with a full replicate experiment (replicates on each of the three conditions) for at least one fuel (typically PG&E). TW02 was operated at 1, 2, 2, and 4 gallons of water per minute (gpm) with each of the three primary fuels, providing replicates at 2 gpm within each experiment. The two furnace burns, while of different duration, provide replicates in those cases in which the firing rate (condition) was the same for both burns.

For each set of replicates, a relative deviation, d_{rel} was calculated for each pollutant metric as follows. For duplicates, d_{rel} was the absolute value of the difference divided by the mean of the metrics (results) for the two burns. When three or more replicate burns were available, d_{rel} was the relative standard deviation (standard deviation divided by the mean). A repeatability metric was then calculated for each burner group as the mean of the relative deviations and relative standard deviations. As noted above, the repeatability metrics were calculated by burner group (and pollutant metric) based on the assumption that experimental errors are a function of the experimental configuration—which was largely constant for all burners within a group. Relative deviations were calculated for all replicate burns occurring on the same day, then for all replicate burns occurring any day. In recognition that precision at low concentration levels can be dominated by instrument noise, the repeatability assessment excluded conditions which produced very low levels of CO (< 20 ng/J), NO₂ (< 4 ng/J) or PN (< 10⁵/J).

Bivariate Regression Analysis. The effect of fuel Wobbe number on emissions was evaluated first through bivariate linear regression. This statistical test determines both a linear trend line and assesses the degree to which the central trend could result from chance as opposed to a true relationship. This analysis was conducted using “Proc Reg” in SAS . The primary result is the best fit linear relationship, which is expressed as a change in the metric per increase of 25 Btu/scf in the fuel Wobbe number. This slope allows estimation of the effect of fuels other than those tested, but is intended only for interpolation (i.e., for fuels having Wobbe numbers below about 1420 Btu/scf). Another key result is the p-value, which indicates the likelihood that a calculated trend is due to chance; lower p-values indicate a more robust association. This report refers to relationships with $p < 0.05$ as being “statistically significant” and refers to trends with somewhat higher p-values as being “likely” or “probable.” Other results include the correlation coefficient, the best fit y-intercept, and 95% confidence intervals around the fitted slope. The statistical model produces the same set of results for the calculated y-intercept; however, since this number has no physical significance (it is meaningless to consider a fuel with $WN=0$), these results are not presented. The confidence interval indicates the uncertainty of the estimate, specifically identifying levels at which there is < 5% chance that the true value is above or beyond these values (referred to as the *95% confidence interval*).

Bivariate regression was conducted by burner and separately for each burner operating mode. For cooktops, broilers, and water heaters all burns were included in a single analysis for each burner. For ovens, the analysis was done at each of the three temperature settings. Fits were obtained for tankless water heaters at each of three flow rates. And for two of four central furnaces, the analysis was conducted for both low and high rates.

Multivariate Regression Analysis. Multivariate regression analysis was conducted for ovens and tankless water heaters (TW) to assess the effect of fuel Wobbe number on pollutant emissions, adjusting for burner condition. Multivariate analysis allows simultaneous consideration of multiple independent variables that can independently and in concert affect the value of a dependent variable. In this analysis, pollutant metrics are the dependent variables of interest. Wobbe number was treated as a continuous variable with linear impact on emissions. Oven temperature setting and TW flow rate were each treated as Class⁴ (categorical) variables. This analysis was required because the temperature setting and flow rate were observed to affect emissions from ovens and TWs respectively. Results of the multivariate analysis provide an equation that can be used to predict emissions for any fuel WN for each of the classes (settings) of oven temperature or TW flow rate. The key results are the linear regression parameters related to fuel WN (see previous section for description of these parameters). Multivariate analysis was conducted using “Proc Genmod” in SAS.

Multivariate analysis was also used to analyze particle number emission data in light of the observation that PN emissions were strongly affected by the order of experiment for cooktops, broilers, and possibly other burners. Disentangling a potential dependence on fuel WN from an experiment order effect was complicated by the fact that a majority of burners were tested first with PG&E, and in some cases the fuels progressed in order of increasing WN. There were, however, several cases in which PG&E line gas was used in both the first and last experiments of the day, and other cases in which another fuel was used first. Additionally, there were several cooktops and broilers for which a large suite of experiments were conducted, providing sufficient data for the multivariate analysis. Experiment order was treated as a class variable with three values: first experiment of day, second experiment of day, and all other experiments. The analysis assessed the significance of experiment order and provided an estimate of WN effect on PN emissions corrected for experiment order.

⁴ SAS uses the Class statement to create a set of indicator (or “dummy”) variables from one categorical variable with more than two levels. It re-codes the categorical variable into a set of n-1 orthogonal binary variables where n is the number of categories in the original variable.

3.0 Results and Discussion

This section first provides descriptions of the burners evaluated and lists of the experiments that were conducted in both the laboratory and on-site at residences. Selected summary results (pollutant emission factors) are then presented and discussed. Finally, summary results of the statistical analyses are presented and discussed. Much additional information, including experimental notes, pictures of burners and flames, plots of primary data, and additional results are included in a series of individual burner reports provided as appendices.

The presentation of results reflects the fact that extensive analysis was conducted following what was thought at the time to be the completion of experiments in May 2008. A preliminary version of this report including figures and tables was prepared at that time. The report was expanded to report on experiments and results for the additional cooking burners evaluated in support of the indoor exposure modeling. The data included in any given analysis is noted in the text.

3.1. Summary of Experiments

3.1.1. Burners Evaluated

The tables which follow provide summary information about the appliances and burners evaluated in this experimental study. Key aspects or components of the technology are summarized. Additional information about the appliances and burners is provided in the individual burner reports.

Through May 2008, experiments were conducted on a total of 31 appliance burners, including six cooktops (Table 10), six oven bottom burners (Table 11), three waist-high broiler burners (Table 11), five storage water heaters (Table 12), four central forced air furnaces and one wall furnace (Table 13), and six tankless water heaters (Table 14). BR02 and OV02 are the same burner; the different IDs are used to indicate that this burner was tested with both oven and broiler protocols. All burners except CT04 were evaluated with at least three fuels including PG&E line gas, a fuel with WN in the range of 1380–1390, and a higher WN fuel in the range of 1415–1425 Btu/scf.

Experiments were conducted in December 2008 through April 2009 to evaluate additional cooking burners, including seven cooktops, six oven bottom burners, and two waist-high broiler burners. During this same period repeat experiments were conducted to obtain aldehyde emission factors for OV02 and CT02.

Table 10 provides information about the cooktop burner sets that were evaluated. Except for CT04, which was evaluated as installed in a residence, all cooking appliances were procured specifically for these experiments and installed and tested in a laboratory at LBNL. All but CT11 were procured from individual sellers; the range with CT11 was purchased from a used appliance retailer.

Table 10. Cooktop burner sets evaluated experimentally for fuel interchangeability

ID	Technology ¹	Year New	Manufacturer	Rating (kBtu/h)	Fuels Evaluated ²
CT01	sealed; cast Al burner w/slots; cast iron cap; EI	1995	Amana (Raytheon)	9.1 (x3), 7	PG&E(2), 1C, 3A+N ₂ (2), 3A(5)
CT02	open; stamped Al w/slots; pilot ignition	1998	Frigidaire (Electrolux)	9 (x4)	PG&E(3), 3A+N ₂ (2), 3A(2); PG&E, 1C, 3C
CT03	sealed; cast steel punched ports; EI	2001	Jenn Air (Maytag)	12 (x2), 9.2 (x2)	PG&E, 1B, 3A+N ₂ , 3A; PG&E, 1C, 3C
CT04	sealed; cast Al burner w/slots; cast iron cap; EI	2006	Frigidaire (Electrolux)	16, 12, 9.5, 5	PG&E, 3C
CT05	open; stamped Al w/slots; EI	2003	Frigidaire (Electrolux)	9 (x4)	PG&E, 1C, 3C
CT06	sealed; cast Al burner w/slots; cast iron cap; EI	1997	General Electric	12, 5, 9.5 (x2)	PG&E, 1C, 3C
CT07	open; stamped Al w/slots; EI	1995	General Electric	9 (x4)	PG&E, 1C, 3C
CT08	sealed; cast iron, drilled ports; cast iron cap; EI	1992	General Electric	10 (x2), 6 (x2)	PG&E(2), 1C, 3C
CT09	sealed; cast Al burner w/slots; cast iron cap; EI	2007	Kenmore (Electrolux)	9 (x4)	PG&E(2), 1C, 3C
CT10	open; stamped Al w/slots; EI	1997	General Electric	9.5 (x4)	PG&E, 2C,1C, 3C
CT11	sealed; cast Al burner w/slots; cast iron cap; EI	2001	General Electric	12, 5, 9.5 (x2)	PG&E, 2C,1C, 3C
CT12	Same as CT03; sealed; cast steel punched ports; EI	1992	Maytag	12 (x2), 9.2 (x2)	PG&E(2), 2C,1C, 3C
CT13	sealed; cast Al burner w/slots; cast iron cap; EI	2003	Frigidaire (Electrolux)	12, 9.5 (x3)	PG&E(2), 2C,1C, 3C

¹EI = electronic ignition. ²One experiment per fuel, except as indicated in parentheses.

Table 11. Oven and broiler burners evaluated experimentally for fuel interchangeability

ID	Technology ¹	Year New	Manufacturer	Rating (kBtu/h)	Fuels Evaluated ²
OV01	Tube burner under bottom plate; EI	1995	Amana (Raytheon)	15.5	PG&E(2), 1C, 3A+N ₂ (2), 3A(4)
OV02	Tube burner under bottom plate; pilot ignition	1998	Frigidaire (Electrolux)	18	PG&E, 3A+N ₂ , 3A; PG&E(2), 1C, 3C
OV03	Tube burner under raised bottom plate; EI	2001	Jenn Air (Maytag)	18	PG&E(2), 3A+N ₂ , 3A; PG&E(2), 1C, 3C
OV05	Tube burner under bottom plate; EI	2003	Frigidaire (Electrolux)	18	PG&E, 1C(2), 3C
OV06	Tube burner under raised bottom plate; EI	1997	General Electric	16	PG&E(2), 1C(2), 3C
OV07	Tube burner under bottom plate; EI	1995	General Electric	18	PG&E, 1C(2), 3C
OV08	Tube burner under raised bottom plate; EI	1992	General Electric	18	PG&E, 2C, 1C, 3C
OV09	Tube burner under bottom plate; EI	2007	Kenmore (Electrolux)	18	PG&E, 2C, 1C, 3C
OV10	Tube burner under bottom plate; EI	1997	General Electric	18	PG&E(2), 2C, 1C, 3C
OV11	Tube burner under bottom plate; EI	2001	General Electric	16	PG&E, 2C, 1C, 3C
OV12	Tube burner under bottom plate; EI	1992	Maytag	16	PG&E, 2C, 1C, 3C
OV13	Tube burner under bottom plate; EI	2003	Frigidaire (Electrolux)	18	PG&E(2), 1C, 3C
BR01	Tube burner with spreader; EI	1995	Amana (Raytheon)	11	PG&E, 3A+N ₂ , 3A(4)
BR02	Same burner as OV02	1998	Frigidaire (Electrolux)	18	PG&E(2), 3A+N ₂ (2), 3A
BR03	Tube burner with spreader; EI	2001	Jenn-Air (Maytag)	13	PG&E(2), 3A+N ₂ , 3A
BR06	Tube burner with spreader; EI	1997	General Electric	16	PG&E, 1C, 3C(2)
BR12	Tube burner with spreader; EI	1992	Maytag	13	PG&E, 2C, 1C, 3C
BR13	Tube burner with spreader; EI	2003	Frigidaire (Electrolux)	14	PG&E, 2C, 1C, 3C

¹ EI = electronic ignition. ² One experiment per fuel, except as indicated in parentheses.

Table 12. Central and wall evaluated experimentally for fuel interchangeability

ID	Technology ¹	Year New	Manufacturer & Model	Rating (kBtu/h)	Fuels Evaluated ²
CF01	Modern condensing FAF; 94% eff.; two-stage burner; induced draft; direct vent	2002	Carrier WeatherMaker Infinity HE	60	PG&E, 1C, 3C
CF02	Modern, non-condensing FAF; 82% eff.; two-stage burner; induced draft	2002	Carrier WeatherMaker 8000VS	80	PG&E, 1C, 3C
CF03	Modern, non-condensing FAF; 81% eff.; single-stage burner; induced draft	1999	Bryant	69	PG&E, 1C, 3C
CF04	Modern condensing FAF; 93% eff.; single-stage burner; induced draft	2002	Bryant Plus-90	100	PG&E(2), 1C, 3C
WF01	Pilot; gravity direct vent; 72% eff.	2003	Williams	14	PG&E, 1C, 3C

¹FAF = forced air furnace. ²One experiment per fuel, except as indicated in parentheses.

Table 13. Storage water heaters evaluated experimentally for fuel interchangeability

ID	Technology ¹	Age	Manufacturer & Model	Rating (kBtu/h)	Fuels Evaluated ²
WH01	FVIR; pilot; natural draft; conventional burner; 40 gal	New	American Proline Flame Guard	40	PG&E, 3A+N ₂ , 3A PG&E, 3C
WH02	Pre-FVIR; pilot; natural draft; conventional burner; 40 gal	6	GE Profile SmartWater	40	PG&E, 1C, 3C
WH03	Pre-FVIR; piloted; natural draft; conventional burner; 50 gal	4	Rheem Professional 50	40	PG&E, 1C, 3C
WH04	Induced draft; FVIR; spark igniter (no pilot); 40 gal	New	American PowerFlex Direct	42	PG&E, 1C, 3C
WH05	Pre-FVIR (older legacy unit); pilot; natural draft; conventional burner	17	American	34	PG&E(2), 1C, 3C

¹FVIR = flammable vapor ignition resistant. ²One experiment per fuel, except as indicated in parentheses.

Table 14. Tankless water heaters evaluated experimentally for fuel interchangeability

ID	Technology	Age	Manufacturer & Model	Rating (kBtu/h)	Fuels Evaluated ²
TW01	Ribbon burner, fan-assisted, direct vent	<1 ¹	Rinnai Continuum 2424	19–180	PG&E(2), 1C, 3C
TW02	Ribbon burner, fan-assisted, direct vent; ducted; certified to 40 ng/J NO _x std.	6	Takagi Flash TK-2	20–185	PG&E, 1C, 3C
TW03	Ribbon burner, fan-assisted, direct vent; certified to 40 ng/J NO _x std.	3	Controlled Energy Aquastar 240-FX (Takagi TK-1)	37–165	PG&E(2), 1C, 3C
TW04	Ribbon burner, fan-assisted, direct vent; certified to 40 ng/J NO _x std.	4	Rinnai Continuum 2532	15–199	PG&E(2), 1C, 3C
TW05	Ribbon burner, fan-assisted, direct vent; ducted; certified to 40 ng/J NO _x std.	New	Rheem RTG-74PVN-2	19–199	PG&E(2), 1C, 3C
TW06	Ribbon burner, fan-assisted, direct vent; ducted; certified to 40 ng/J NO _x std.	New	Noritz N0631-S	25–180	PG&E(2), 1C, 3C; PG&E, 3C

¹ Unit purchased in 2001 and used for approximately six months in portable classroom, then stored at LBNL until used in this study. ²One experiment per fuel, except as indicated in parentheses.

3.1.2. Experiments

Experiments were conducted over a series of intensive periods generally alternating between laboratory and residential sites. This section provides an overview of the intensive periods and notes important changes in equipment, procedures, and practices that occurred over time. Valid experiments are listed in a series of tables, organized by intensive period.

The first phase of experiments had three purposes: (1) full deployment of equipment and methods intended to gain experience with both lab and field configurations, to evaluate feasibility for wider implementation, and to identify problems before the start of interchangeability experiments, (2) range-finding for analyte exhaust concentrations and pollutant emission levels, especially for formaldehyde and ultrafine particles—for which limited data previously existed, and (3) screening of appliances for inclusion in subsequent interchangeability testing. Fully separate analytical systems were used in the first groups of field and laboratory experiments. The field cart was outfitted with the California Analytical 602P combustion gas analyzer (O₂, CO₂, CO), Teledyne 200E NO_x analyzer, and TSI 3022A CPC. Dilution ratios for aerosol determination were calculated by comparing CO₂ levels measured in the direct exhaust to those measured in the dilution sampling system. The laboratory configuration used the Horiba PG-250 combustion gas analyzer (O₂, CO₂, CO, and NO or NO_x), Thermo 42i NO_x analyzer, and TSI 3786 water-based CPC to measure particle number concentrations. With the lab system, dilution ratios for aerosols and NO_x were calculated by ratio of NO measured by the Horiba analyzer in the direct sampling stream compared to the NO measured by the Thermo analyzer in the dilution sampling system.

The first set of laboratory experiments (L001–L007, L008–L011, Table 15) were conducted on three used cooking ranges that were purchased for this study, plus a tankless water heater (TW01) that had been used in an LBNL study of portable classroom air quality and energy efficiency. The ranges included three cooktops (CT01–CT03), three oven bottom burners (OV01–

OV03) and two waist-high broiler burners (BR01, BR03). The first set of field experiments (F001–F010) were conducted on nine appliance burners in three residences; included were three storage water heaters, two forced air furnaces, one wall furnace, one cooktop, one pool heater and one storage water heater. All of the experiments used PG&E line gas. Unlike subsequent campaigns, the initial field and lab experiments were interwoven through June and July of 2007. All of the burners tested in the initial lab experiments and three of those tested in the field (WH02, CF01, and WF01) were evaluated in subsequent interchangeability experiments. As the last part of this series, a group of “FL” experiments was conducted in the laboratory; both field and laboratory instrumentation was used in various configurations with CT03, OV03, and BR03 burners. Raw data from all of these preliminary experiments were processed and reviewed by visual inspection but not fully processed to calculate emission rates for inclusion in the final database of results.

Table 15. Preliminary experiments (PG&E line gas)

Expt	Date	Location	Burner Description and Age (y) ¹
L001	06/20/07	LBNL	CT01
L002	06/26/07	LBNL	OV01
L003	06/27/07	LBNL	OV01
L004	06/27/07	LBNL	BR01
L005	06/29/07	LBNL	CT02
L006	06/29/07	LBNL	CT02
L007	06/29/07	LBNL	OV02
L008	07/03/07	LBNL	OV03
L009	07/05/07	LBNL	CT03
L010	07/05/07	LBNL	BR03
L011	07/06/07	LBNL	TW01
F001	06/13/07	Res1	Storage WH: legacy tech, >15 y
F002	06/14/07	Res1	
F003	06/20/07	Res1	WF01
F004	06/21/07	Res1	Rinnai 2532 TW: Ribbon burner, direct vent, fan-assist, 15-199 kBtu/h, 2 y
F005	07/17/07	Res2	WH02
F006	07/19/07	Res2	CF01
F007	07/24/07	Res3	Cooktop (Thermador): sealed burners, 40 kBtu/h total, 6 y
F008	07/25/07	Res3	Storage WH (GE): legacy tech., 40 kBtu/h, <2 y
F009	07/26/07	Res3	Forced air furnace (Carrier): non-condensing, 74 kBtu/h, 12 y
F010	07/26/07	Res3	Pool heater (Raypak): conventional tech., 181 kBtu/h, 6 y

¹ Refer to tables in Subsection 3.1.1 for descriptions of numbered burners.

The second intensive period included laboratory experiments in which used cooking appliance burners (CT02, OV02, CT03, OV03, and BR03, Table 16) and a new storage water heater (WH01) were evaluated with PG&E line gas and two additional fuels (3A and 3A diluted with N₂) that were mixed on-site from component gases. The cooking burner experiments (L013–L039) were conducted during August–September 2007 and the water heater was evaluated October 30–November 2 (L041–L043).

Prior to the third group—field experiments F011–F027 (Table 17)—there was a decision to change the original plan for parallel field and laboratory deployments and a single set of analytical equipment was configured for use in both lab and field settings. Toward this end, the Horiba combustion gas analyzer and Thermo NO_x analyzer were installed on the field sampling cart. This configuration was used at three residences to evaluate six burners, including three that had been first tested as part of the range-finding series (as noted above) and three appliances at a residence that had not been visited previously (CT04, WH03, and CF02). These were the first experiments to use premixed simulated LNG compositions 1C and 3C, which were taken to the field in compressed gas cylinders. A number of operational problems were encountered during these experiments, as described in the individual burner reports. This intensive field campaign occurred over the period of November 20–30, 2007.

Table 16. Second intensive group of experiments: conducted at LBNL

Expt ID ¹	Date	Burner ID	Fuel ID	HHV (Btu/scf)	Wobbe (Btu/scf)	Notes
L013	08/17/07	CT03	PG&E	1011	1329	All data ok
L014	08/17/07	CT03	1B	1067	1386	All data ok
L015	09/04/07	OV03	PG&E	1013	1332	PN sampled direct; NO _x data missing from start of B1
L016	09/04/07	OV03	3A	1122	1417	PN sampled direct
L017	09/04/07	OV03	3A+N2	1103	1385	PN sampled direct
L018	09/05/07	BR03	PG&E	1013	1332	One 30-min burn
L019	09/05/07	BR03	3A	1125	1419	One 30-min burn
L020	09/05/07	BR03	3A+N2	1105	1387	One 30-min burn
L021	09/06/07	CT03	3A	1123	1417	B1: hood flow low at start; data look OK
L022	09/06/07	CT03	3A+N2	1102	1386	All data ok
L024	09/13/07	CT02	PG&E	1012	1329	Manifold RH high
L026	09/14/07	CT02	3A	1122	1417	Manifold RH high
L027	09/14/07	CT02	3A+N2	1103	1386	Manifold RH high
L028	09/14/07	CT02	PG&E	1017	1334	Manifold RH high
L029	09/18/07	CT02	PG&E	1028	1342	All data ok
L030	09/18/07	CT02	3A	1124	1418	All data ok
L031	09/20/07	CT02	3A+N2	1104	1386	All data ok
L032	09/20/07	OV02	3A+N2	1101	1384	All data ok
L033	09/20/07	OV02	3A	1123	1417	All data ok
L034	09/20/07	OV02	PG&E	1068	1362	All data ok
L035	09/20/07	BR02	PG&E	1068	1362	Single 30-min burn; PN data bad
L036	09/21/07	BR02	PG&E	1045	1348	One 30-min burn
L037	09/21/07	BR02	3A	1125	1418	One 30-min burn
L038	09/27/07	BR02	3A+N2	1104	1387	One 30-min burn; hood air flow high and PG250 concentrations low, but data look ok
L039	09/27/07	BR02	3A+N2	1104	1387	One 30-min burn; repeat of L038 with lower hood air flow
L041	10/30/07	WH01	PG&E	1045	1348	PG250 NO too low; NO _x , NO, NO ₂ , and PN questionable based on dilution ratio calc.
L042	11/01/07	WH01	3A	1117	1414	PG250 NO too low; NO _x , NO, NO ₂ , and PN questionable based on dilution ratio calc.
L043	11/01/07	WH01	3A+N2	1095	1379	PG250 NO too low; NO _x , NO, NO ₂ , and PN questionable based on dilution ratio calc.

¹Missing experiment numbers: L023, OV03 operated in convection mode; L025, OV03 cleaning cycle; L040, WH01 with flue damper; not included as valid experiments in this dataset.
HHV = higher heating value

Table 17. Third intensive group of experiments: residential field sites

Expt ID	Date	Burner ID	Fuel ID	HHV (Btu/scf)	Wobbe (Btu/scf)	Location & Notes
F011	11/20/07	CF01	PG&E	1046	1348	Res2; All data ok; note low, high firing rate
F012	11/20/07	CF01	1C	1071	1390	Res2; All data ok; note low, high firing rate
F013	11/20/07	CF01	3C	1125	1419	Res2; All data ok; note low, high firing rate CPC (PN) offline for B1
F014	11/21/07	WH02	PG&E	1009	1322	Res2; All data ok
F015	11/21/07	WH02	1C	1071	1390	Res2; All data ok
F016	11/21/07	WH02	3C	1125	1419	Res2; All data ok
F017	11/26/07	CT04	PG&E	1015	1330	Res4; PN bad for B1; fuel flow data bad; Lasair data ¹
F018	11/26/07	CT04	3C	1125	1419	Res4; fuel flow data bad; Lasair data ¹
F019	11/28/07	CF02	PG&E	1020	1337	Res4; All data ok; Lasair data ¹
F020	11/28/07	CF02	3C	1125	1419	Res4; All data ok; Lasair data ¹
F021	11/28/07	CF02	1C	1071	1390	Res4; All data ok; Lasair data ¹
F022	11/29/07	WH03	PG&E	1016	1333	Res4; TECO NO _x offline for first half of B1; Lasair data ¹
F023	11/29/07	WH03	3C	1125	1419	Res4; All data ok; Lasair data ¹
F024	11/29/07	WH03	1C	1071	1390	Res4; All data ok; Lasair data ¹
F025	11/30/07	WF01	PG&E	1016	1333	Res1; All data ok; Lasair data ¹
F026	11/30/07	WF01	3C	1125	1419	Res1; All data ok; Lasair data ¹
F027	11/30/07	WF01	1C	1071	1390	Res1; All data ok; Lasair data ¹

¹ Lasair provides size-resolved particle number concentrations for aerodynamic diameters of 0.1 to > 2 micrometers.

The fourth group of experiments (L044–L079, Table 18) comprised a series of replicates with CT01, OV01, and BR01 that were intended to quantify repeatability for a given burner and fuel combination, and thus inform the levels of emissions changes that are statistically discernible for experiments conducted with different fuels. In the interest of executing more replicates overall, these experiments were conducted by operating all three burners with the same fuel in a given day, with only one fuel tested per day. The set of experiments thus provides useful information about between-day repeatability and includes several experiments conducted in very low ambient humidity (combustion air) conditions. This intensive period additionally included evaluation of the cooktop (CT05) and oven (OV05) of another used range and a new power-vent water heater (WH04) which was purchased and setup for energy efficiency testing as part of a separate California Energy Commission contract. Experiments in this group were conducted December 2007 through February 2008. The flow problem in the aldehyde sampling train (described above in subsection 2.2.8) was identified toward the end of this period. The aldehyde sampling system was reconfigured to use peristaltic pumps and flows were measured during each sample for all subsequent experiments.

Table 18. Fourth intensive group of experiments: conducted at LBNL

Expt ID ¹	Date	Burner ID	Fuel ID	HHV (Btu/scf)	Wobbe (Btu/scf)	Notes
L044	12/18/07	OV01	PG&E	1017	1334	Manifold RH very high
L045	12/18/07	CT01	PG&E	1017	1334	Manifold RH very high; one burn only
L046	12/18/07	BR01	PG&E	1017	1334	Room temp bad for Burn 2; other data ok
L047	12/19/07	OV01	3A	1124	1418	Manifold RH high
L048	12/19/07	CT01	3A	1124	1418	Manifold RH high
L049	12/19/07	BR01	3A	1124	1418	All data ok
L050	12/20/07	OV01	3A	1125	1419	All data ok
L051	12/20/07	CT01	3A	1124	1418	All data ok
L052	12/20/07	BR01	3A	1125	1418	All data ok
L053	01/16/08	BR01	3A	1126	1419	All data ok
L054	01/16/08	CT01	3A	1126	1419	All data ok
L055	01/16/08	OV01	3A	1123	1417	All data ok
L056	01/18/08	CT01	3A	1122	1417	All data ok
L057	01/23/08	BR01	3A+N2	1103	1385	All data ok
L058	01/23/08	CT01	3A+N2	1100	1382	All data ok
L059	01/23/08	OV01	3A+N2	1099	1382	All data ok
L060	01/24/08	BR01	3A	1123	1418	All data ok
L061	01/24/08	CT01	3A	1124	1418	All data ok
L062	01/24/08	OV01	3A	1122	1417	All data ok
L063	02/07/08	OV01	PG&E	1011	1326	All data ok; SMPS ²
L064	02/08/08	CT01	PG&E	1014	1329	All data ok; SMPS ²
L065	02/08/08	CT01	3A+N2	1100	1382	C ₂ tank empty; Burn 2 composition uncertain: NG vol may be off for Burn 2; SMPS ²
L067	02/11/08	CT01	1C	1071	1390	All data ok
L068	02/12/08	OV01	1C	1071	1390	All data ok
L069	02/13/08	CT05	PG&E	1016	1333	All data ok; SMPS ²
L070	02/13/08	CT05	PG&E	1016	1333	All data ok; SMPS ²
L071	02/13/08	CT05	1C	1071	1390	All data ok; SMPS ²
L072	02/13/08	CT05	3C	1125	1419	All data ok; SMPS ²
L073	02/20/08	OV05	PG&E	1012	1320	All data ok; SMPS ²
L074	02/20/08	OV05	1C	1071	1390	Problem with PN data logging; SMPS ²
L075	02/20/08	OV05	3C	1125	1419	All data ok; SMPS ²
L076	02/20/08	OV05	1C	1071	1390	All data ok; SMPS ²
L077	02/25/08	WH04	PG&E	1007	1318	All data ok; SMPS ²
L078	02/25/08	WH04	1C	1071	1390	All data ok; SMPS ²
L079	02/25/08	WH04	3C	1125	1419	All data ok; SMPS ²

¹Missing experiment numbers: L066, no experiment conducted. ²Data collected but not analyzed in this report.

The fifth group of experiments (F028–F050) constituted the final campaign of residential sampling and occurred during March 2008. This series evaluated three tankless water heaters (TW02–TW04), two forced air furnaces (CF03–CF04), and a legacy storage water heater (WH05). These were the first experiments in which the combustion gas analyzer (Horiba PG-250) was set to measure NO_x instead of NO in the direct exhaust stream.

Table 19. Fifth group of experiments: residential field sites

Expt ID	Date	Burner ID	Fuel ID	HHV (Btu/scf)	Wobbe (Btu/scf)	Location & Notes
F028	03/04/08	TW02	PG&E	1011	1330	Res5; 4 burns; All data okay;
F029	03/04/08	TW02	1C	1071	1390	Res5; 4 burns; All data okay;
F030	03/04/08	TW02	3C	1125	1419	Res5; 4 burns; Burn 2: PG250 NO _x over range;
F031	03/07/08	TW03	PG&E	1011	1329	Res6; All data okay
F032	03/07/08	TW03	1C	1071	1390	Res6; All data okay
F033	03/07/08	TW03	3C	1125	1419	Res6; All data okay
F034	03/07/08	TW03	PG&E	1011	1329	Res6; All data okay
F035	03/11/08	TW04	PG&E	1014	1330	Res7; All data okay
F036	03/11/08	TW04	1C	1071	1390	Res7; All data okay
F037	03/11/08	TW04	3C	1125	1419	Res7; All data okay
F038	03/11/08	TW04	PG&E	1009	1324	Res7; All data okay
F039	03/12/08	CF03	PG&E	1012	1329	Res7; All data okay
F040	03/12/08	CF03	1C	1071	1390	Res7; All data okay
F041	03/12/08	CF03	3C	1125	1419	Res7; All data okay
F042	03/12/08	CF03	PG&E	1012	1329	Res7; Aerosol inlet disconnect: PN data bad
F043	03/19/08	CF04	PG&E	1010	1327	Res8; PN, TSI data bad
F044	03/19/08	CF04	1C	1071	1390	Res8; PN, TSI data bad
F045	03/19/08	CF04	3C	1125	1419	Res8; PN, TSI data bad
F046	03/19/08	CF04	PG&E	1007	1323	Res8; PN, TSI data bad
F047	03/20/08	WH05	PG&E	1011	1326	Res8; Line & Manifold P switched
F048	03/20/08	WH05	1C	1071	1390	Res8; All data okay
F049	03/20/08	WH05	3C	1125	1419	Res8; All data okay
F050	03/20/08	WH05	PG&E	1009	1320	Res8; All data okay

The sixth series of experiments (Table 20) occurred in the laboratory and included evaluation of TW01, two new tankless water heaters purchased for this study (TW05–TW06), the cooktop (CT06), oven (OV06) and broiler (BR01) burners of another used range, plus one additional oven bottom burner (OV07). Also included in this series were new sets of experiments for CT03, OV03, and WH01. Experiments L080 through L119 were conducted in April and May 2008.

Table 20. Sixth group of experiments: conducted at LBNL

Expt ID ¹	Date	Burner ID	Fuel ID	HHV (Btu/scf)	Wobbe (Btu/scf)	Notes
L080	03/27/08	WH01	PG&E	1011	1328	NG vol bad; PN response low before expt, looks OK during; water drips on range-finding run
L081	03/27/08	WH01	3C	1125	1419	NG vol bad
L082	04/02/08	TW01	PG&E	1008	1320	NG vol bad
L083	04/02/08	TW01	1C	1071	1390	NG vol bad
L084	04/02/08	TW01	3C	1125	1419	NG vol bad
L085	04/02/08	TW01	PG&E	1008	1320	NG vol bad
L086	04/25/08	CT03	PG&E	1012	1326	No manifold T/RH; SMPS ²
L087	04/25/08	CT03	3C	1125	1419	No manifold T/RH; SMPS ²
L088	04/25/08	CT03	1C	1071	1390	No manifold T/RH; SMPS ²
L089	04/28/08	OV03	PG&E	1012	1326	NG vol bad; no ma. T/RH; B1 at 300 F; SMPS ²
L090	04/28/08	OV03	3C	1125	1419	NG vol bad; no manifold T/RH; SMPS ²
L091	04/28/08	OV03	1C	1071	1390	NG vol bad; no manifold T/RH; SMPS ²
L092	04/28/08	OV03	PG&E	1012	1326	NG vol bad; no man. T/RH; B1 only; SMPS ²
L093	04/30/08	CT06	PG&E	1010	1324	No manifold T/RH; SMPS ²
L094	04/30/08	CT06	1C	1071	1390	No manifold T/RH; SMPS ²
L095	04/30/08	CT06	3C	1125	1419	No manifold T/RH; SMPS ²
L096	05/01/08	OV06	PG&E	1012	1328	No manifold T/RH; SMPS ²
L097	05/01/08	OV06	1C	1071	1390	PN data bad; no manifold T/RH; SMPS ²
L098	05/01/08	OV06	3C	1125	1419	PN data questionable; no manifold T/RH; SMPS ²
L100	05/07/08	BR06	3C	1125	1419	No man. T/RH; PN data bad; SMPS ²
L101	05/07/08	BR06	3C	1125	1419	No manifold T/RH; SMPS ²
L102	05/07/08	BR06	1C	1071	1390	No manifold T/RH; SMPS ²
L103	05/07/08	BR06	PG&E	1000	1302	No manifold T/RH; SMPS ²
L104	05/08/08	OV06	1C	1071	1390	All data ok
L105	05/08/08	OV06	PG&E	1008	1317	All data ok
L106	05/13/08	TW05	PG&E	1009	1322	All data ok
L107	05/13/08	TW05	1C	1071	1390	All data ok
L108	05/13/08	TW05	3C	1125	1419	All data ok
L109	05/13/08	TW05	PG&E	1009	1322	All data ok
L110	05/19/08	TW06	PG&E	1010	1332	NG vol bad; CO over-range on B1; SMPS ²
L111	05/19/08	TW06	1C	1071	1390	NG vol bad; SMPS ²
L112	05/19/08	TW06	3C	1125	1419	NG vol bad; CO over-range on B1; SMPS ²
L113	05/19/08	TW06	PG&E	1010	1332	NG vol maybe OK; SMPS ²
L114	05/19/08	TW06	PG&E	1011	1327	All data ok; SMPS ²
L115	05/19/08	TW06	3C	1125	1419	All data ok; SMPS ²
L116	05/23/08	OV07	PG&E	1015	1328	All data ok; SMPS ²
L117	05/23/08	OV07	3C	1125	1419	All data ok; SMPS ²
L118	05/23/08	OV07	1C	1071	1390	All data ok; SMPS ²
L119	05/23/08	OV07	PG&E	1015	1328	All data ok; SMPS ²

¹Missing experiment numbers: L099, no experiment conducted. ²Data collected but not analyzed in this report.

An additional group of experiments was conducted for the purposes of obtaining more robust estimates of both baseline emission rates and the effect of LNG on emissions from cooking burners. These additional experiments were requested by members of the project advisory

committee to support indoor exposure modeling that is being conducted as part of this research project. These experiments, summarized in Table 21, occurred in December 2008 through April 2009. In all of these experiments, size-resolved particle number concentrations were measured with the SMPS, and firing rates were determined by stopwatch and gas meter (the gas flow counter did not function).

Table 21. Experiments to expand data on cooking burners

Expt IDs ¹	Date	Burner ID	Fuels (in order)	PG&E HHV (Btu/scf)	PG&E Wobbe (Btu/scf)	Notes ¹ and missing data
L124-126	12/10/08	CT02	PG&E, 1C, 3C	1015	1332	
L127-130	12/15/08	OV02	1C, 3C, PG&E, PG&E	1018	1334	
L131-134	12/19/08	CT07	PG&E, 3C, 1C, PG&E	1018	1334	
L135-138	1/5/09	CT08	PG&E, 1C, 3C, PG&E	1018	1334	
L139-142	1/8/09	OV08	PG&E, 1C, 3C, 2C	1015	1331	
L143-146	1/12/09	CT09	PG&E, 2C, 3C, 1C	1016	1329	Serial number illegible.
L147-150	1/15/09	OV09	PG&E, 2C, 1C, 3C	1015	1329	Serial number illegible.
L151-154	1/20/09	CT10	PG&E, 3C, 1C, 2C	1017	1332	
L155-159	1/22/09	OV10	PG&E, 2C, 1C, 3C, 2C	1018	1333	
L160-163	1/26/09	CT11	2C, PG&E, 3C, 1C	1017	1333	Purchased at store.
L164-167	1/27/09	OV11	PG&E, 1C, 3C, 2C	1018	1334	Purchased at store.
L168-171	2/2/09	CT12	2C, PG&E, 3C, 1C	1015	1330	
L172-175	2/11/09	OV12	PG&E, 1C, 2C, 3C	1016	1329	
L176-179	2/13/09	BR12	3C, 2C, 1C, PG&E	1019	1334	
L180-183	2/18/09	CT13	1C, 3C, PG&E, 2C	1019	1333	
L184-187	2/19/09	OV13	PG&E, 1C, 3C, PG&E	1018	1332	No PN data for L185-L187.
L188-191	2/20/09	BR13	3C, 1C, PG&E, 2C	1017	1331	
L192-193	2/23/09	CT13	PG&E, PG&E	1016	1329	With/out pots to assess effect on HCHO emissions.

¹ As noted in text, all experiments in this series had SMPS and required hand-timing of gas flow to obtain firing rate.

3.2. Experimental Results

3.2.1. Overview of Results

The results presented in this section are organized as follows.

The presentation begins with a comparison of end-of-burn and full-burn baseline pollutant emission metrics for each burner based on experiments conducted with PG&E line gas. Results are presented as dry air-free concentrations of particle number (PN), carbon monoxide (CO), and nitrogen oxides (NO_x), and the nominal NO₂ fraction of total NO_x (calculated as the difference between measured NO_x and measured NO) over full-burn (including transient effects) and end-of-burn (generally more stable) periods of operation. Air-free concentrations are calculated from measured exhaust CO₂ for non-venting appliances (cooktops, ovens,

broilers) and from measured exhaust O₂ for venting appliances (furnaces, storage water heaters, tankless water heaters). While the approaches give similar results, the CO₂-based calculation is preferred for cooking burners as the dilute hood-based sampling approach used for these burners yields a relatively small difference between exhaust and background O₂ measurements (and thus a higher relative uncertainty). These results are discussed in the context of understanding baseline emissions variability among units within a burner group and among burner groups. Differences between full-burn and end-of-burn emission rates provide information about the importance of transient effects and burner operating conditions. For this comparison the presented results are limited to burners evaluated through May 2008.

Presented next are the calculated full-cycle emission rates of formaldehyde.

Following the formaldehyde information are a series of figures showing full-burn emissions factors of PN, CO, NO_x, and NO₂ for all burners operated with all fuel blends. This section provides a consolidated visual record of results for each of these metrics for all burners, organized by pollutant.

3.2.2. Baseline Emission Levels: Air-Free Concentrations With PG&E Line Gas

In tables 22 through 27, each cell represents the mean air-free concentration calculated for all burns with line gas distributed by PG&E. As an example, the values shown for CT02 represent an average of six burns conducted during the three experiments (two burns per experiment) with line gas. In the context of this interchangeability study, these values should be considered baseline emission levels. The terms “emissions” and (exhaust) “concentrations” are used somewhat interchangeably in recognition that air-free concentrations are directly related to mass emission levels. Text is interspersed with the tables to elucidate important trends. Results are presented for burners evaluated through May 2008; results for cooking burners evaluated in later experiments are qualitatively similar.

Results are rounded as follows: values below 200 are rounded to nearest integer; values from 201–400 are rounded to 2.5 significant figures; values from 401–1000 are rounded to 2 significant figures; values from 1001–4000 are rounded to 2.5 significant figures and values above 4000 are rounded to 2 significant figures. The intent of this scheme is to narrow the range of fractional precision that is implied / lost relative to the more traditional approach of rounding by factors of 10.

The value labeled as “NO₂ fraction” represents the fraction of total measured NO_x that is not NO; this can include some nitrous acid (HONO) and potentially other nitrogen oxides.

Presented first are the cooking appliance burners. Baseline emissions of PN varied by more than an order of magnitude among the first six cooktops tested, and by more than two orders of magnitude among the first six ovens and three broilers. The larger variability observed among ovens and broilers results from values at the lower end of the distribution. Baseline PN exhaust concentrations for these six cooktops were above $100 \times 10^5 \text{ cm}^{-3}$; this contrasts with other burner groups that included at least some burners with lower PN emissions. Baseline CO varied by more than an order of magnitude among cooktops and among ovens at each temperature setting. Baseline NO_x emissions were more consistent, mostly falling in the range of 70–100 ppm

air-free. The full-burn NO₂ fraction of total NO_x varied from 13% to 35% for these six cooktop burner sets, from < 10% to 45% for the broilers and from < 10% to > 50% for the six ovens. The cooktop and broiler burners with the lowest NO₂ fractions also had low end-of-burn CO levels.

Table 22. Mean air-free concentrations (calculated based on CO₂) for cooktop burner sets using PG&E line gas. Results are shown for full-burn and end-of-burn periods.

Burner	PN (10 ⁵ /cm ³)		CO (ppm)		NO _x (ppm)		NO ₂ Fraction	
	Full	End	Full	End	Full	End	Full	End
CT01	120	172	41	36	73	78	0.21	0.19
CT02	152	110	121	116	89	96	0.23	0.22
CT3A ¹	117	163	880	790	82	89	0.35	0.32
CT3B ¹	110	171	870	810	79	85	0.33	0.29
CT04 ²	-	-	162	86	110	120	0.21	0.18
CT05 ³	1900	3300	330	295	97	102	0.27	0.26
CT06	440	710	48	36	90	96	0.13	0.11

¹ CT3A and CT3B indicate series of experiments conducted in different periods; refer to CT03 burner report for details.

² The CPC was not functioning during this experiment.

³ PN concentrations exceeded the particle counter upper limit during roughly the last five minutes of one of four burns used to calculate mean PN results for this burner. Actual mean air-free PN concentrations for this burner were thus higher than the values shown; the under-reporting is likely larger for the end-of-burn result, suggesting an even more pronounced disparity between full burn and end-of-burn periods.

Table 23. Mean air-free concentrations (calculated based on CO₂) for broiler burners using PG&E line gas. Results are shown for full-burn and end-of-burn periods.

Burner ¹	PN (10 ⁵ /cm ³)		CO (ppm)		NO _x (ppm)		NO ₂ Fraction	
	Full	End	Full	End	Full	End	Full	End
BR01	22	16	169	48	71	92	0.09	0.03
BR02	1150	2250	560	265	71	85	0.37	0.37
BR03	195	305	470	178	73	86	0.41	0.34
BR06	46	65	450	126	39	45	0.45	0.33

¹ BR01, BR03, and BR06 are “waist-high” burners; BR02 is a bottom burner (same as OV02) set to broil mode.

Table 24. Mean air-free concentrations (calculated based on CO₂) for oven burners using PG&E line gas. Results are shown for full-burn and end-of-burn periods.

Burner ¹	Temperature	PN (10 ⁵ /cm ³)		CO (ppm)		NO _x (ppm)		NO ₂ Fraction	
		Full	End	Full	End	Full	End	Full	End
OV01	350°F	66	49	100	24	78	87	0.15	0.09
	425°F	17	20	46	7	86	84	0.11	0.09
	500°F	16	20	37	12	87	87	0.06	0.03
OV02	350°F	59	132	1060	340	60	72	0.38	0.20
	425°F	55	113	490	345	74	78	0.26	0.20
	500°F	1820	3150	390	290	81	86	0.26	0.21
OV3A	350°F	127	124	315	72	77	95	0.16	0.07
	425°F	13	18	198	82	78	84	0.14	0.10
	500°F	20	34	142	57	84	92	0.11	0.09
OV3B	350°F	53	57	340	70	82	100	0.18	0.10
	425°F	38	66	220	50	90	106	0.14	0.07
	500°F	42	66	187	47	93	106	0.12	0.07
OV05	350°F	11	20	810	570	65	74	0.56	0.49
	425°F	1	14	590	470	74	77	0.44	0.40
	500°F	131	365	480	390	81	87	0.36	0.33
OV06	300°F	52	66	480	177	79	88	0.24	0.13
	350°F	8	6	710	181	65	80	0.29	0.17
	425°F	1	2	380	200	73	77	0.27	0.19
	500°F	9	17	270	124	79	86	0.21	0.14
OV07	350°F	27	36	700	450	64	74	0.26	0.18
	425°F	134	245	570	450	73	76	0.19	0.17
	500°F	345	255	480	390	79	83	0.15	0.13

¹ OV3A and OV3B indicate two series of experiments conducted on burner OV03; refer to burner report for details.

Baseline air-free exhaust concentrations for venting burners are presented in tables 25 through 27. Baseline PN emissions were extremely low for all of the venting burners. The highest PN levels seen among these burners were similar to the lowest values seen among cooking burners. Baseline CO levels were close to zero for all of the storage water heaters and the wall furnace, and below 100 ppm for all four of the central forced air furnaces. As a group, tankless water heaters had baseline CO levels that were generally similar to cooking appliance burners. Tankless water heater TW06 had baseline CO emissions of thousands of ppm at 1 gallon per minute of water flow and over 1000 ppm at 2 gpm, and these high levels were seen across three

experiments with PG&E line gas conducted on two different days. Four of the other five tankless water heaters (TWs) also had baseline CO levels of hundreds of ppm air-free. There is thus a stark difference between baseline pollutant emission characteristics of tankless and storage water heaters. Baseline NO_x levels measured in these experiments varied somewhat among storage water heaters (56–76 ppm air-free) and furnaces (54–81 ppm air-free), and varied over a much larger range (15–80 ppm air-free) for TWs. Baseline NO₂ fractions were below 0.10 for all storage WHs and wall furnace WF01. Baseline NO₂ fractions were a bit higher for CFs as a group (0.07–0.23 over the full-burn period) and substantially higher again for TWs as a group (0.21–0.48 over the full-burn period). CO, NO_x, and the NO₂ fraction varied with water flow rate for many of the TWs, but there was no obvious trend with water flow for any of the analytes.

Baseline CO emissions for TW06 were much higher than other tankless WHs tested in this study and far in excess of what is expected for a properly functioning new unit. Based on knowledge of unpublished testing, project advisory committee members have affirmed that the CO emissions levels of TW06 are not indicative of the emissions measured from other units produced by the manufacturer. Responding to a request by the authors, the manufacturer inspected the unit and determined that the cause of the high emissions was a gas pressure regulator operating outside of manufacturer specifications. This caused an oversupply of fuel that affected the fuel-air mixing ratio and lead to higher CO emissions. The manufacturer communicated that the regulator malfunction is thought to be rare but did not provide estimates of frequency.

Table 25. Mean air-free concentrations (calculated based on O₂) for storage water heater burners using PG&E line gas¹

Burner ²	PN (10 ⁵ /cm ³)		CO (ppm)		NO _x (ppm)		NO ₂ Fraction	
	Full	End	Full	End	Full	End	Full	End
WH1A	1	1	0	-1	32	34	0.02	0.02
WH1B	7	5	-3	-5	62	65	0.06	0.05
WH02	0	-0	-1	-3	76	79	0.07	0.07
WH03	3	0	-4	-5	56	59	0.02	0.01
WH04	3	5	7	4	65	67	0.08	0.06
WH05	18	0	2	0	70	76	0.06	0.05

¹ Results are shown for full-burn and end-of-burn periods.

² WH1A and WH1B indicate two series of experiments conducted on burner WH01; refer to burner report for details. NO_x results for the 1A series are much lower than expected for this type of burner; the cause for this dubious result has not been identified.

Table 26. Mean air-free concentrations (calculated based on O₂) for furnace burners using PG&E line gas¹

Burner	PN (10 ⁵ /cm ³)		CO (ppm)		NO _x (ppm)		NO ₂ Fraction	
	Full	End	Full	End	Full	End	Full	End
CF01	-0	-0	15	10	81	83	0.07	0.07
CF02	3	1	51	35	65	66	0.22	0.18
CF03	10	5	77	58	54	55	0.23	0.21
CF04	0	0	67	44	56	57	0.19	0.17
WF01	5	11	0	-6	78	86	0.02	0.01

¹ Results are shown for full-burn and end-of-burn periods.

Table 27. Mean air-free concentrations (calculated based on CO₂) for tankless water heater burners using PG&E line gas. Results are shown for full-burn and end-of-burn periods.

Burner	Water flow	PN (10 ⁵ /cm ³)		CO (ppm)		NO _x (ppm)		NO ₂ Fraction	
		Full	End	Full	End	Full	End	Full	End
TW01	1 gpm	1	0	106	91	57	58	0.36	0.36
	2 gpm	2	1	335	330	58	59	0.40	0.39
	4 gpm	1	0	142	130	56	56	0.35	0.35
TW02	1 gpm	-0	-0	152	148	44	46	0.38	0.37
	2 gpm	0	0	145	145	42	44	0.39	0.39
	4 gpm	0	0	128	127	29	30	0.46	0.45
TW03	1 gpm	-0	-0	315	280	44	45	0.35	0.34
	2 gpm	-0	-0	285	265	42	43	0.33	0.32
	3 gpm	5	8	420	410	39	39	0.37	0.37
TW04	1 gpm	1	0	75	71	25	25	0.44	0.44
	2 gpm	6	3	84	81	25	26	0.42	0.43
	4 gpm	6	2	70	66	15	15	0.48	0.49
TW05	1 gpm	5	6	225	225	49	49	0.45	0.45
	2 gpm	7	9	133	129	52	53	0.38	0.38
	4 gpm	6	6	178	175	49	50	0.37	0.37
TW06	1 gpm	2	2	3250	5100	80	87	0.21	0.19
	2 gpm	1	1	1100	1150	71	72	0.28	0.27
	4 gpm	3	3	275	300	64	70	0.29	0.28

3.2.3. Comparison of Full-Burn and End-of-Burn Emission Metrics

The relationship between end-of-burn (EB) and full-burn (FB) air-free concentrations varied by pollutant, by burner group, and among burners. End-of-burn and full-burn levels for CO were similar among the first six cooktops; whereas for the first group of broilers (n=3) and ovens (n=6) the FB levels were much higher than EB levels. For the broilers, full-burn CO levels were

roughly two to three times higher than end-of-burn levels. For ovens, the differences between FB and EB CO levels were < 20% in some cases (e.g., for the higher temperature burns of OV07) and more than a factor of three in other cases (e.g., the first burn of OV02).

In general, the values for the two periods were more similar at higher emission levels, reflecting the requirement that substantial full-burn levels occur only with sustained emissions. For cooking burners, end-of-burn PN levels were generally higher than full-burn PN levels, and the highest emissions were associated with burners for which PN increased over the course of the burn; examples include CT05, BR02, and the 500°F burn of OV02. Among the first six ovens tested, the highest PN levels were consistently observed during 500°F burns. This apparent temperature dependence for high PN emission rates may be related to volatilization of low-volatility organic compounds (grime) from oven surfaces, even though ranges were cleaned and operated through a multi-hour, high-temperature “bake-out” cycle before evaluation. Among cooking burners, air-free NO_x concentrations over the end-of-burn periods were higher in all cases than those averaged over the full-burns; this is presumed to result from an increase in flame zone temperature as nearby materials (e.g., oven top, pots) are heated and thus draw less heat from the flame. By contrast, the similarity of EB and FB NO_x concentrations for the venting appliances indicate that stable NO_x levels are reached much earlier in the burns. This is reinforced by the time-resolved NO_x plots shown in the individual burner reports. The NO₂ fraction of total NO_x was similar for FB and EB periods for cooktops and all three groups of venting burners; whereas for ovens and broilers the NO₂ fraction was similar or slightly greater during FB relative to EB periods.

Plots of the time-resolved exhaust concentrations measured during each experiment are provided in the burner reports; these provide much more rich and detailed information about the transient nature of emissions for each burner and burner group. The appendices also provide end-of-burn exhaust concentrations for cooking burners tested in late 2008 and 2009.

3.2.4. Aldehyde Emission Factors

Table 28 below provides summary results for aldehydes, expressed as the emission factors of formaldehyde and acetaldehyde resolved by burner and fuel group. Results are presented for all burners including those tested in the last stage of experiments in late 2008 and early 2009. The focus of the aldehyde measurements was on obtaining data for formaldehyde; the acetaldehyde results were obtained using the same sample and chemical analysis procedures, and these are presented to enhance the data record. The results indicate low acetaldehyde emission rates for all of the burners.

Formaldehyde emissions were consistently very low in all storage water heater experiments, but varied across a wide range among burners in all other groups. Across the burner groups, tankless water heaters had the highest baseline formaldehyde emission rates. The substantial difference in formaldehyde emission rates between storage and tankless water heaters is interesting in the context of sharply increasing sales of tankless water heater sales in recent years. With on-demand water heaters being promoted for energy efficiency and the market share projected to continue to increase in coming years, the potential effects on the overall formaldehyde emission inventory and ambient concentrations warrants further study.

Table 28. Calculated aldehyde emission rates (ng per J fuel energy) by burner and fuel¹

Burner ID	Formaldehyde (ng/J)				Acetaldehyde (ng/J)			
	PG&E WN= 1317-1333	Fuel 2C WN= 1359	Fuel 1C WN= 1390	Fuel 3C WN= 1419	PG&E WN= 1317-1333	Fuel 2C WN= 1359	Fuel 1C WN = 1390	Fuel 3C WN= 1419
CT01	0.31	-	(2) 0.43	no data	0.01	-	(2) 0.06	no data
CT02	0.55	-	0.58	0.72	0.03	-	0.04	0.07
CT03	1.00	-	1.76	2.15	0.10	-	0.14	0.19
CT05	(2) 0.67	-	0.75	0.68	(2) 0.13	-	0.10	0.11
CT06	0.12	-	0.10	0.11	0.03	-	0.02	0.02
CT07	(2) 0.44	-	0.62	0.73	(2) 0.04	-	0.05	0.08
CT08	(2) 0.09	-	0.09	0.09	(2) 0.02	-	0.01	0.02
CT09	4.67	4.41	4.43	4.65	0.33	0.33	0.32	0.40
CT10	1.15	1.11	0.60	0.71	0.04	0.07	0.04	0.07
CT11	0.31	0.31	0.21	0.26	0.04	0.07	0.03	0.04
CT12	0.81	0.95	0.90	0.97	0.10	0.14	0.09	0.13
CT13	0.10	0.11	0.19	0.11	0.02	0.02	0.06	0.03
OV01	0.48	-	0.46	no data	0.02	-	0.06	no data
OV02	(2) 0.38	-	0.43	0.45	0.03	-	0.04	0.07
OV03	0.46	-	0.39	0.42	0.10	-	0.05	0.09
OV05	0.43	-	(2) 0.51	0.65	0.10	-	(2) 0.10	0.12
OV06	(2) 1.01	-	(2) 0.91	1.03	(2) 0.16	-	(2) 0.20	0.15
OV07	(2) 0.57	-	0.64	0.63	(2) 0.23	-	0.25	0.27
OV08	2.98	1.95	2.23	1.63	0.08	0.08	0.10	0.11
OV09	0.60	1.11	0.73	0.63	0.08	0.10	0.07	0.09
OV10	0.32	0.29	0.30	0.30	0.07	0.05	0.05	0.06
OV11	5.51	5.83	5.81	5.14	0.43	0.48	0.48	0.54
OV12	0.25	0.23	0.24	0.23	0.03	0.02	0.03	0.03
BR06	0.93	-	1.00	(2) 1.10	0.11	-	0.13	(2) 0.16
BR12	0.13	0.13	0.14	0.17	0.02	0.02	0.02	0.03
BR13	0.79	0.81	1.11	1.01	0.04	0.04	0.07	0.08
CF03	0.38	-	0.24	0.18	0.03	-	0.03	0.04
CF04	(2) 0.13	-	0.09	0.08	(2) 0.02	-	0.03	0.03
WH01	0.04	-	-	0.03	0.02	-	-	0.02
WH04	0.05	-	0.04	0.04	0.13	-	0.12	0.11
WH05	(2) 0.05	-	0.04	0.04	(2) 0.05	-	0.04	0.05
TW01	(2) 1.68	-	1.21	0.94	(2) 0.07	-	0.10	0.10
TW02	0.77	-	0.70	0.55	0.03	-	0.04	0.05
TW03	(2) 2.39	-	2.19	2.27	(2) 0.10	-	0.17	0.22
TW04	(2) 0.26	-	0.23	0.22	(2) 0.03	-	0.04	0.05
TW05	(2) 2.16	-	2.39	1.95	(2) 0.12	-	0.13	0.18
TW06	(3) 0.25	-	0.21	(2) 0.23	(3) 0.03	-	0.04	(2) 0.05

¹Based on results from a single experiment or number of experiments indicated in parentheses. Results unavailable for CT04, BR01, BR03, and selected burner and fuel combinations as indicated owing to uncertainty in air sample collection rate.

The data presented in this table suggest fuel sensitivity that can drive formaldehyde emissions in different directions for different burners. Cooktop CT03 had the largest increase of 115% from line gas to 3C and the emission rate of CT03 with 3C was the highest for any cooking

burner. Cooking burners CT02, OV02, OV05, and BR06 had substantial baseline levels and formaldehyde emissions increased monotonically with increasing fuel Wobbe number; the overall increase was approximately 30%, 20%, 50%, and 20% for these burners when moving from line gas to fuel 3C. Formaldehyde decreased with increasing fuel WN for several of the venting burners; compared to line gas, emissions with fuel 3C were lower by about 50% for CF03, 40% for CF04, 45% for TW01, and 30% for TW02.

3.2.5. Full-Burn Emission Rates for All Experiments

Presented below are a series of charts that display the calculated full-burn emission factors for CO, NO_x, NO₂, PN, and HCHO for all valid experimental burns. These plots present emission factors calculated from measured CO₂ for both cooking and vented burners. Results are presented for burners grouped into six panels for each figure. In each figure, results for all broilers, furnaces, storage water heaters, and tankless water heaters are each displayed in a single panel. The larger number of cooktops and ovens are distributed across two panels each. Results for each burner are presented categorically by fuel, as noted in the legend for each figure. Fuel categories are arranged from left to right (with slight offset for each fuel group) above each burner label in order of increasing Wobbe number. Results labeled as “1360” are from fuel mix 2C. Results labeled as “1390” are mostly from fuel mix 1C, but include also fuel mix 1B and N₂-dilutions of mix 3A from early experiments; the Wobbe number for these fuels fell in the range 1380–1390 Btu/scf. Results labeled as “1420” mostly represent mix 3C, but include also early experiments with fuel mix 3A; Wobbe numbers for these fuels were in the range 1415–1425 Btu/scf.

This presentation is intended to allow readers to quickly view the variability of emissions across burners within a group (e.g., cooktops) and across burner groups. The plots show the range of results obtained for replicate burns for cooktops, broilers, furnaces, and storage water heaters; and for the varied operation of ovens (at 350°F, 425°F, and 500°F) and tankless water heaters (1, 2, and 3 or 4 gallons per minute). Relatively large differences in some pollutant emission rates between fuels are apparent for some burners.

The text that follows elucidates some of the more prominent and important results. Statistical analysis of gas quality (fuel Wobbe number) effects on pollutant emissions for each burner is provided in a subsequent section.

Error! Reference source not found. shows that CO emissions were extremely low for the storage water heaters, low for the furnaces, and higher for the cooking burners and tankless water heaters. The strikingly low CO emission rates of the five WHs evaluated in this part of the study are consistent with results from two additional WHs tested during the range-finding experiments (results not shown) and three storage water heaters tested by Southern California Gas (Gutierrez et al. 2004; Gutierrez et al. 2005; Miller et al. 2005). The most prominent results for CO were the very high emissions of TW06, with a sharp increase in CO with higher WN fuels. As noted previously, the high CO emissions for this burner are thought to have been caused by a faulty gas regulator. Three other burners had full-burn CO emissions above 400 ng/J. Of these, only CT03 had emissions increase to a large extent with fuel WN (roughly 30%–60% from line gas with WN=1326–1329 to fuels 3A and 3C with WN=1417–1419). Full-burn CO

increased roughly 10% from lowest to highest Wobbe fuels for CT09 and decreased with fuel WN for OV11. CO emissions near or above 100 ng/J were observed for another four cooktops, three broilers, and most of the ovens. CO emissions varied by more than an order of magnitude among oven burners and by several times across burns at different conditions for each oven. Within-burner variability for ovens derived from the higher emissions associated with the first burn at 350°F (starting with cold burner and spreader) relative to the burns resulting from resetting the temperature of the already warm oven to 425°F then 500°F. Clear trends of increasing CO with increasing fuel WN are apparent for burners spanning a range from very low (WH05) to high (CT03, TW06). CO clearly declined with fuel WN for CF03 and CF04.

Error! Reference source not found. shows broadly similar trends for NO₂ as observed for CO. NO₂ emissions were very low for storage water heaters, and lower for furnaces relative to cooking burners and tankless water heaters. NO₂ varied less than CO among appliances within each burner group and for each oven across varied burner conditions. With the exception of TW06, the burners with the highest CO in each group generally also had the highest NO₂ (e.g., BR13, CF02, CT03, CT09, OV05, and OV11). As with CO, an increase in NO₂ with increasing fuel WN is apparent across a range of NO₂ levels, from very low (WH05) to relatively high (CT03). As with CO, NO₂ emission rates decreased with fuel WN for CF03 and CF04.

NO_x emission factors showed less variability among burners within each group. Among the atmospheric burners (all but tankless water heaters), NO_x generally varied by a factor of 1.5–2 with each burner group. In two sets of experiments—BR06, and a first set with WH01—measured NO_x exhaust concentrations and calculated emission factors were roughly half the expected values. The cause for these results was not determined. A replicate set of experiments with WH01 yielded NO_x results in the expected range. NO_x emissions are expected to vary with the effect of heat sinks near the flame zone. Consistent with this, the highest NO_x emissions from oven burners occurred during the burns with the highest oven temperature setting (less heat loss from the flame to nearby surfaces, allowing for higher temperatures). The TWs evaluated in this study utilize premix ribbon burners with confined combustion chambers and fan-controlled combustion air. The basic design can be manipulated to achieve lower NO_x emission levels (e.g., TW02–TW04), but results indicate that these systems were sensitive to changes in fuel WN. The largest increases in NO_x emissions with fuel WN (> 10%) occurred with tankless water heaters TW02, TW04, and TW06. Several other burners had increases on the order of 10% (CF01, CF03, CF04, and TW05) from lowest to highest WN fuels.

The most prominent feature of the PN data (**Error! Reference source not found.**) is the split between the relatively low levels emitted by vented burners (furnaces, water heaters, tankless) and the much higher and more variable emission levels for cooking burners. Within each group of vented burners there were some with near-zero emission rates and some with rates approaching 100 x10²/J. Particle number emission factors from cooking burners varied over several orders of magnitude across burners and sometimes by an order of magnitude for a single burner. Large variability was seen even for nominally replicate burns. Some of this variability is associated with the observed pattern of high PN for the first few burns and the first experiment each day (refer to individual burner reports in appendices C through J).

Formaldehyde emission factors are displayed in **Error! Reference source not found.** Water heaters had the lowest HCHO emissions of any burner group. Formaldehyde emissions varied among burners within other burner groups, typically ranging from values as low as 0.1 ng/J to values as high as 2–5 (CT), 5–6 (OV), 2–2.5 (TW), and 1.2 (BR). Most of the highest CO-emitting burners were also the highest HCHO emitters; the notable exception is TW06, which had very high CO but low HCHO.

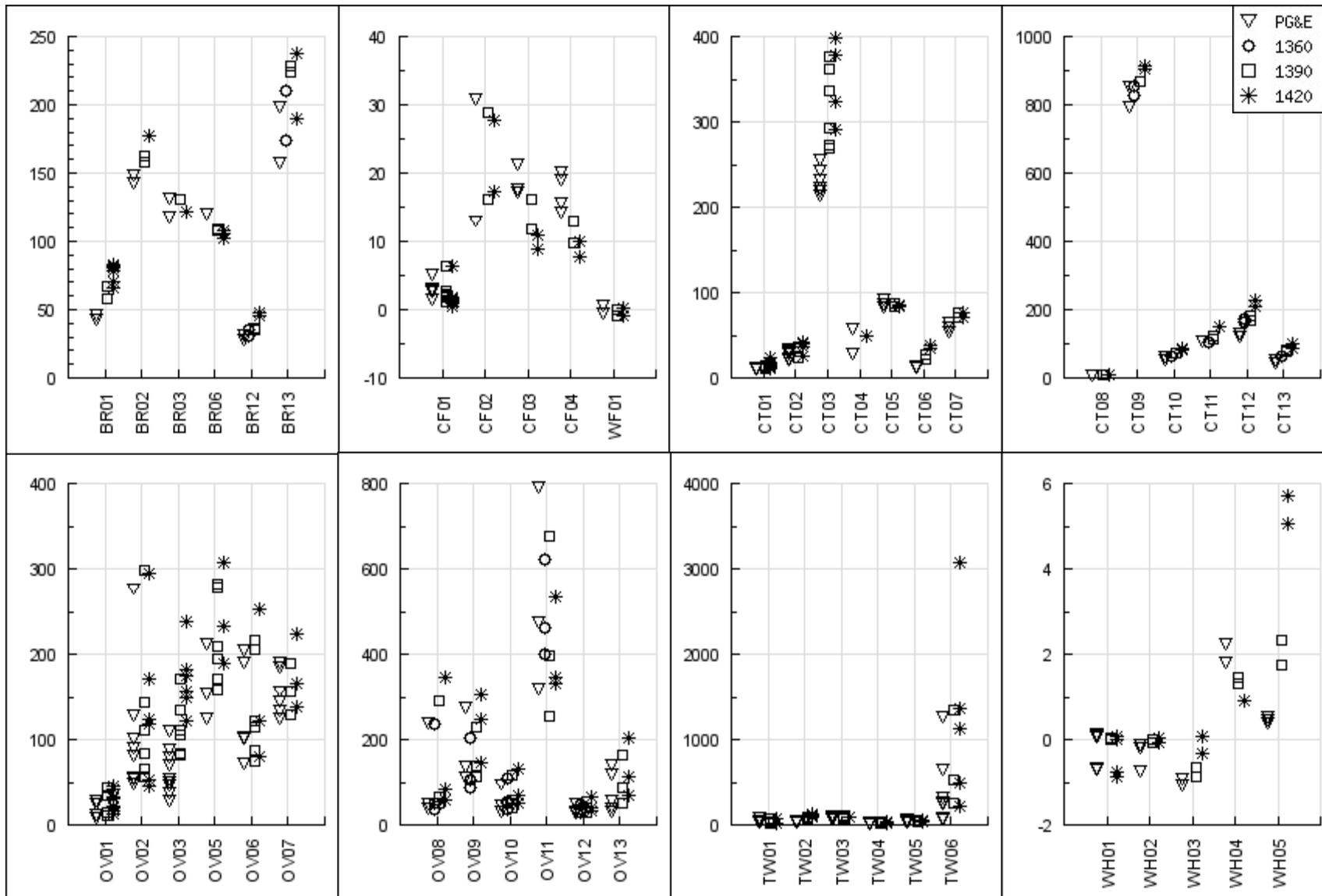


Figure 8. Full-burn CO emission factors (ng/J), by burn, for all burners studied

Results grouped by fuel Wobbe number (WN). PG&E mostly 1320–1340 Btu/scf. 1390 fuels in range of 1380–1390. 1420 fuels in range of 1415–1425 Btu/scf.

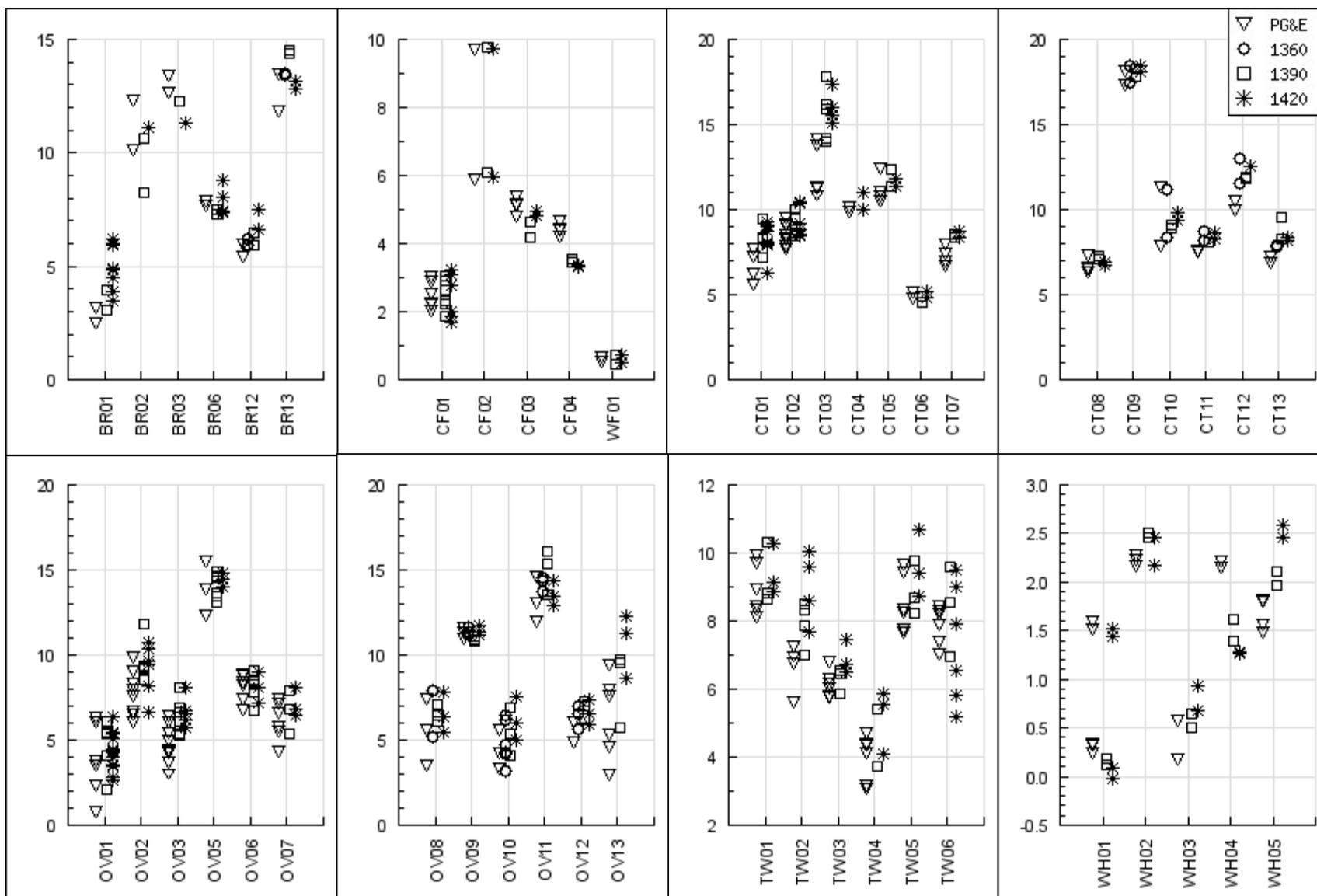


Figure 9. Full-burn NO₂ emission factors (ng/J), by burn, for all burns studied

Results grouped by fuel Wobbe number (WN). PG&E mostly 1320–1340 Btu/scf. 1390 fuels in range of 1380–1390. 1420 fuels in range of 1415–1425 Btu/scf.

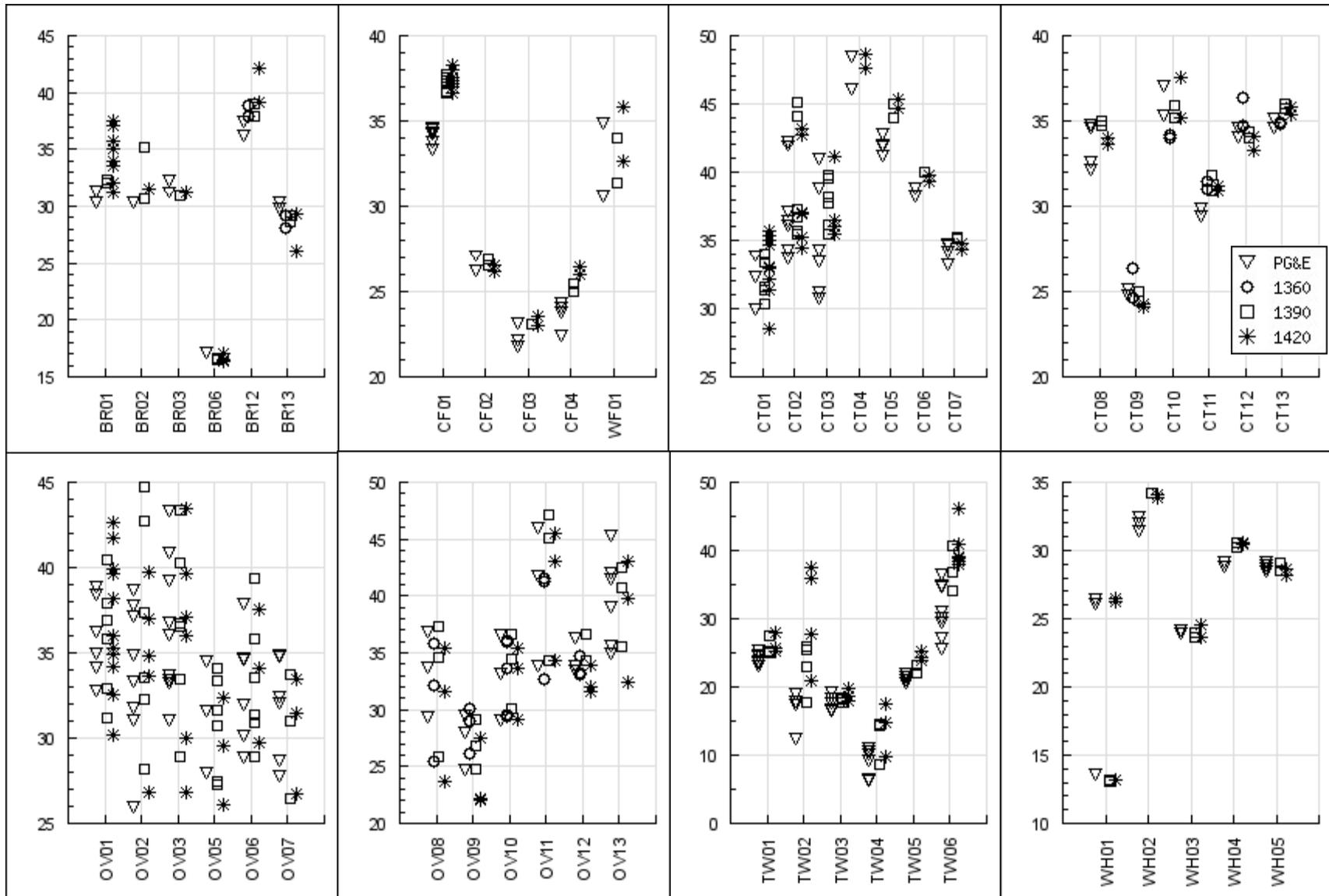


Figure 10. Full-burn NO_x emission factors (ng/J), by burn, for all burners studied

Results grouped by fuel Wobbe number (WN). PG&E mostly 1320–1340 Btu/scf. 1390 fuels in range of 1380–1390. 1420 fuels in range of 1415–1425 Btu/scf.

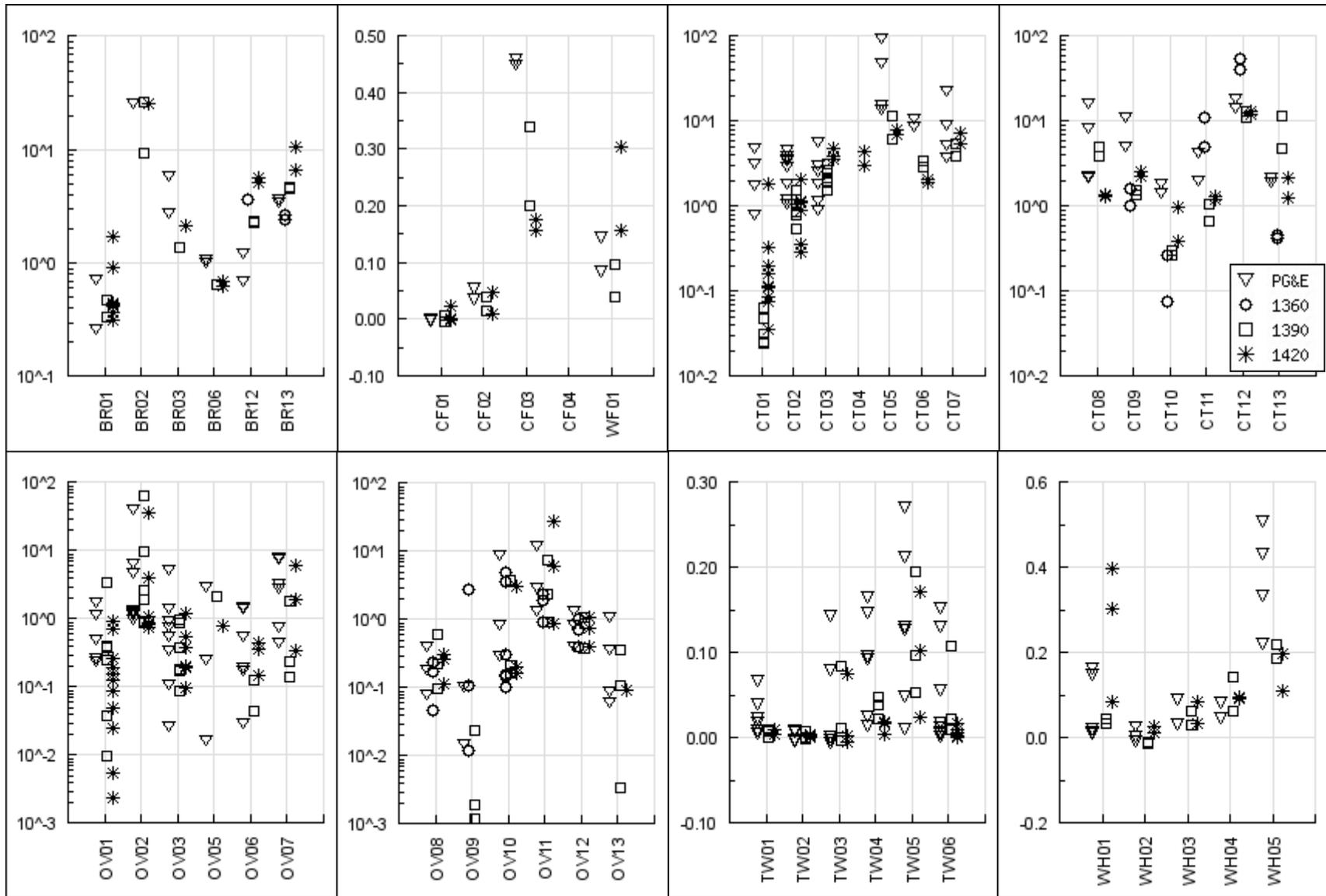


Figure 11. Full-burn PN emission factors ($10^2/J$), by burn, for all burns studied

Results grouped by fuel Wobbe number (WN). PG&E mostly 1320–1340 Btu/scf. 1390 fuels in range of 1380–1390. 1420 fuels in range of 1415–1425 Btu/scf.

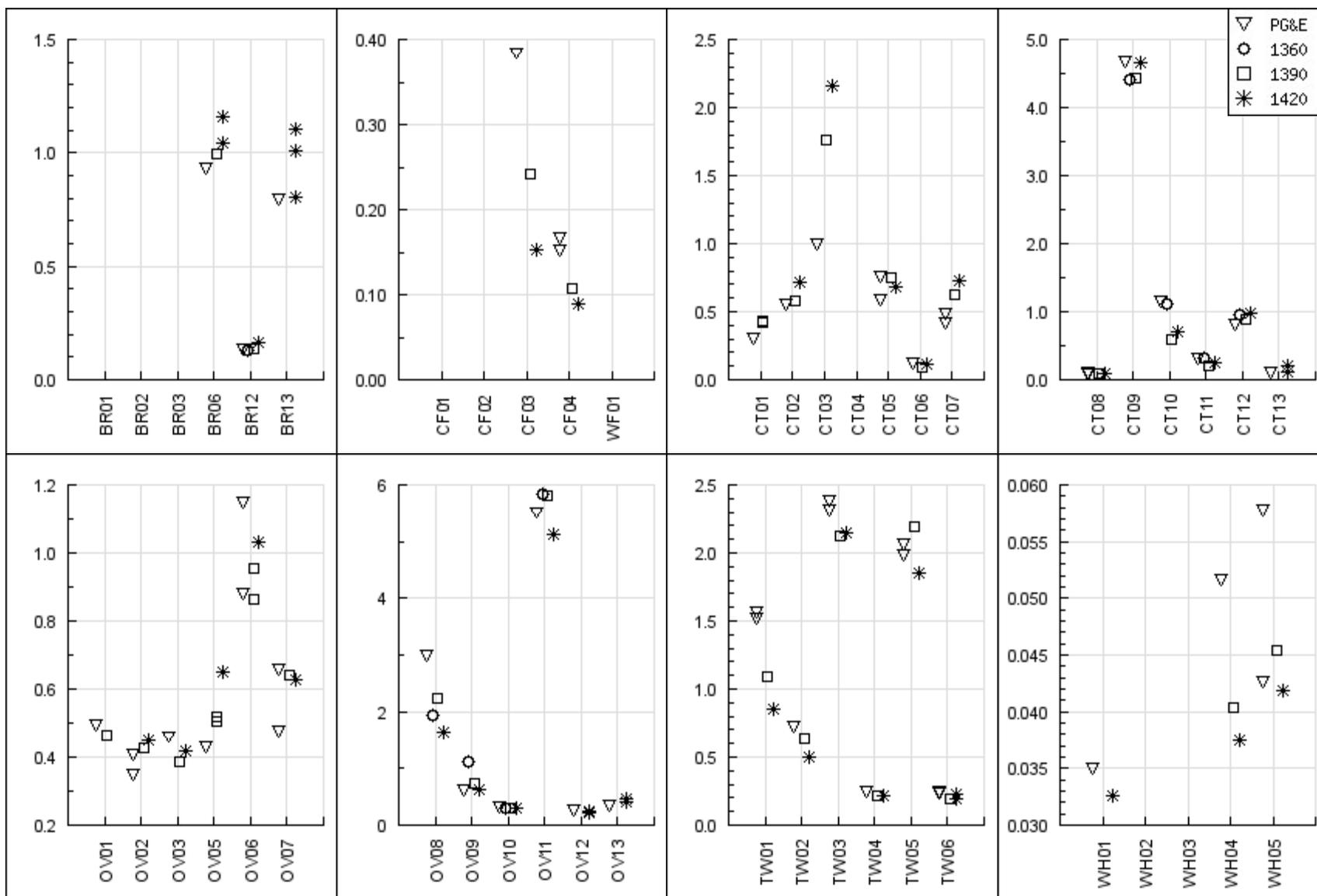


Figure 12. Full-burn HCHO emission factors (ng/J), by burn, for all burners studied

Results grouped by fuel Wobbe number (WN). PG&E mostly 1320–1340 Btu/scf. 1390 fuels in range of 1380–1390. 1420 fuels in range of 1415–1425 Btu/scf.

3.2.6. Particle Size Distributions

Selected results from measurements of size-resolved particle number concentrations are presented and discussed in Appendix B. Preliminary analysis of these data lead to the following findings. First, the size-resolved measurements confirmed that the vast majority of particles emitted from the residential appliance burners examined in this study were in the ultrafine mode (having aerodynamic diameters less than 100 nanometers). Second, larger particle number emission rates were associated with the smallest measured particles. This was true for both higher-emitting burners and for the transient periods of burner operation associated with the highest total particle number emissions for a given burner. Third, the particle number emission rates presented in this report likely understate actual emissions for the highest emitting burners and conditions. This observation derives from the observed difference between total particles as measured by the CPC that was used to collect data on total PN and the CPC used in conjunction with the SMPS size-resolved measurements. The latter had a lower minimum cut-point and thus could count smaller particles. The fourth point relates to particle formation mechanisms. Temporal data from the SMPS reinforces measurements of total PN that indicate ongoing particle formation following oven and some cooktop burns. The collection and analysis of size-resolved particle data were beyond the scope of this task. The initial analysis of these data did not provide insight into the potential effect of gas quality in general, or fuel WN in particular, on particle emissions from residential gas appliances.

3.3. Statistical Analysis Results

3.3.1. Experimental Repeatability

Results from the analysis of experimental repeatability are presented below. The repeatability measures are the means of the relative deviations (for $n=2$ replicates) and standard deviations ($n\geq 3$ replicates) for each group of burns conducted with the same burner and fuel combination (refer to Section 2, Methods for additional explanation of the calculation). The repeatability measures are calculated for replicates conducted on the same day and any day for experiments completed through May 2008. The analysis was limited to burners with non-negligible emission levels; at levels below those indicated, uncertainty increases as the absolute measured concentration levels approached the resolution levels for the analytical instruments. These values provide a measure of the overall uncertainty of a given result and suggest minimum emissions changes that can be resolved with the experimental procedures employed in this study. The analysis was conducted for both end-of-burn and full-burn emission factors of CO, NO_x, NO, NO₂, and PN. The first table in each case provides the mean relative deviation; the second table provides the number of sets of replicates, then the total number of replicate burns.

Tables 29 through 32 indicate repeatability generally on the order of 10% for CO; 5% for NO_x, NO, and NO₂; and much more variability for PN. For the gaseous pollutants, repeatability was similar for end-of-burn and full-burn emission rates. Large values for PN repeatability measures indicate large variations in the calculated emission rates in experiments with similar conditions; since these variations are so much greater than the rated instrument precision, these

results suggest that emissions are being affected to the first order by a factor other than burner and fuel.

Table 29. Repeatability measure* for end-of-burn emission factors

Burner Group	Period	CO [†]	NO _x	NO	NO ₂ [†]	PN [†]
Cooktop	Any Day	0.10	0.04	0.04	0.06	0.48
Cooktop	Same Day	0.08	0.02	0.03	0.05	0.42
Oven	Any Day	0.10	0.06	0.07	0.15	0.76
Oven	Same Day	0.09	0.03	0.04	0.14	0.37
Broiler	Any Day	0.03	0.03	0.03	0.05	0.34
Broiler	Same Day	0.04	0.02	0.02	0.05	0.34
Storage WH	Any Day		0.01	0.01		0.16
Storage WH	Same Day		0.01	0.01		0.16
Forced air furnace	Any Day		0.01	0.02	0.04	0.26
Forced air furnace	Same Day		0.01	0.02	0.04	0.26
Wall furnace	Any Day		0.12	0.13		1.10
Wall furnace	Same Day		0.12	0.13		1.10
Tankless WH	Any Day	0.13	0.05	0.06	0.05	1.02
Tankless WH	Same Day	0.13	0.05	0.07	0.04	1.02

Calculation described in Methods section.

[†] Excluding low values for CO, NO₂, and PN; includes only CO replicates with mean > 20 ng/J, NO₂ replicates with mean NO₂ > 4 ng/J, and PN replicates with mean PN > 10⁵/J.

Table 30. Replicate counts for end-of-burn emission factors*

Burner Group	Period	CO [†]		NO _x		NO		NO ₂ [†]		PN [†]	
Cooktop	Any Day	16	44	22	66	22	66	22	66	19	59
Cooktop	Same Day	21	44	31	64	31	64	31	64	25	52
Oven	Any Day	13	26	24	54	24	54	14	30	20	44
Oven	Same Day	6	12	9	18	9	18	7	14	7	14
Broiler	Any Day	4	10	7	22	7	22	4	10	7	22
Broiler	Same Day	3	8	9	20	9	20	4	10	9	20
Storage WH	Any Day			17	38	17	38			6	12
Storage WH	Same Day			17	38	17	38			6	12
Forced air furnace	Any Day			15	35	15	35	3	8	3	8
Forced air furnace	Same Day			15	35	15	35	3	8	3	8
Wall furnace	Any Day			3	6	3	6			3	6
Wall furnace	Same Day			3	6	3	6			3	6
Tankless WH	Any Day	19	41	21	45	21	45	20	43	4	8
Tankless WH	Same Day	16	32	18	36	18	36	17	34	4	8

Columns for each pollutant show number of replicate groups and total number of burns in all replicate groups.

[†] Excluding low values for CO, NO₂, and PN; includes only CO replicates with mean >20 ng/J, NO₂ replicates with mean NO₂ > 4 ng/J, and PN replicates with mean PN >10⁵/J.

Table 31. Repeatability measure* for full-burn emission factors

Burner Group	Period	CO [†]	NO _x	NO	NO ₂ [†]	PN [†]
Cooktop	Any Day	0.12	0.05	0.06	0.08	0.36
Cooktop	Same Day	0.11	0.02	0.04	0.06	0.38
Oven	Any Day	0.15	0.07	0.10	0.20	0.46
Oven	Same Day	0.22	0.05	0.08	0.20	0.15
Broiler	Any Day	0.06	0.02	0.03	0.08	0.40
Broiler	Same Day	0.08	0.01	0.02	0.07	0.33
Storage WH	Any Day		0.01	0.01		
Storage WH	Same Day		0.01	0.01		
Forced air furnace	Any Day		0.01	0.02	0.05	
Forced air furnace	Same Day		0.01	0.02	0.05	
Wall furnace	Any Day		0.10	0.11		
Wall furnace	Same Day		0.10	0.11		
Tankless WH	Any Day	0.13	0.05	0.06	0.05	
Tankless WH	Same Day	0.08	0.05	0.07	0.04	

* Calculation described in methods section.

† Excluding low values for CO, NO₂, and PN; includes only CO replicates with mean >20 ng/J, NO₂ replicates with mean NO₂ > 4 ng/J, and PN replicates with mean PN >10⁵/J.

Table 32. Replicate counts for full-burn emission factors*

Burner Group	Period	CO [†]		NO _x		NO		NO ₂ [†]		PN [†]	
Cooktop	Any Day	17	46	22	66	22	66	22	66	17	46
Cooktop	Same Day	23	48	31	64	31	64	31	64	22	46
Oven	Any Day	21	46	24	54	24	54	22	48	6	12
Oven	Same Day	9	18	9	18	9	18	9	18	4	8
Broiler	Any Day	7	22	7	22	7	22	5	18	2	4
Broiler	Same Day	9	20	9	20	9	20	6	14	2	4
Storage WH	Any Day			17	38	17	38				
Storage WH	Same Day			17	38	17	38				
Forced air furnace	Any Day			15	35	15	35	4	12		
Forced air furnace	Same Day			15	35	15	35	4	12		
Wall furnace	Any Day			3	6	3	6				
Wall furnace	Same Day			3	6	3	6				
Tankless WH	Any Day	19	41	21	45	21	45	20	43		
Tankless WH	Same Day	16	32	18	36	18	36	17	34		

* Columns for each pollutant show number of replicate groups and total number of burns in all replicate groups.

† Excluding low values for CO, NO₂, and PN; includes only CO replicates with mean > 20 ng/J, NO₂ replicates with mean NO₂ > 4 ng/J, and PN replicates with mean PN > 10⁵/J.

Repeatability for aldehyde sampling is indicated by the results of duplicates presented in Table 33. Relative deviations of calculated emission factors are larger than the values shown for those samples in which exhaust concentrations were closer to background (e.g., L184 for acetaldehyde).

Table 33. Duplicate aldehyde samples of exhaust stream concentrations

Expt.	Burner	Fuel	Formaldehyde ($\mu\text{g m}^{-3}$)			Acetaldehyde ($\mu\text{g m}^{-3}$)		
			A	B	Rel. dev.	A	B	Rel. dev.
L127	OV02	1C	20.3	20.9	3%	5.2	5.2	0%
L131	CT07	Line	50.6	52.1	3%	6.2	6.1	0%
L135	CT08	Line	12.1	12.3	2%	3.2	3.6	12%
L139	OV08	Line	158	168	6%	5.6	5.8	3%
L143	CT09	Line	556	542	3%	41.1	40.0	3%
L147	OV09	Line	42.3	42.1	1%	6.4	6.3	2%
L151	CT10	Line	130	127	2%	6.7	5.7	16%
L155	OV10	Line	41.7	35.7	16%	9.5	8.8	7%
L160	CT11	2C	39.1	38.9	1%	9.3	9.6	3%
L168	CT12	2C	106	105	1%	18.3	18.2	0%
L172	OV12	Line	18.5	18.0	2%	2.7	3.1	14%
L176	BR12	3C	14.4	14.1	2%	3.0	3.3	10%
L180	CT13	1C	30.4	29.0	5%	10.2	9.8	5%
L184	OV13	Line	15.1	23.8	44%	2.0	3.7	59%
L188	BR13	3C	71.3	72.3	1%	6.6	7.1	8%
Mean relative deviation			6%			10%		

3.3.2. Fuel Wobbe Number Effects on Cooking Burner Emissions

The tables that follow present results of the statistical analyses aimed at quantifying the effect of fuel Wobbe number on pollutant emissions from cooking burners. Results are presented for both bivariate and multivariate analyses. Bivariate analysis was conducted to compare emission factors with varying fuels for burners operating under the same nominal conditions. Bivariate analysis was conducted for CO, NO₂, NO_x, and PN emission factors for all burns from cooktops and broilers, and for the first burn of each oven temperature setting (initial heating to 350°F followed by resetting to 425°F then 500°F). Oven bivariate results are presented here for the first burn only. Bivariate analysis was additionally conducted for HCHO emission factors measured over the course of each full experiment (incorporating the entire operating pattern).

Multivariate analysis combined all oven burns to assess the effect of fuel WN on emissions of CO, NO₂, NO_x, and PN adjusted for oven operating temperature. Since pollutant emissions clearly varied with oven temperature set point, multivariate analysis facilitated the combining of all data for each burner to develop a more robust estimate of fuel WN effect on emissions across a range of oven operation.

The effect of fuel WN on PN emissions was additionally examined through multivariate analysis that considered the order in which experiments were conducted. The impetus for this analysis arose from the observation that for all cooktops and broilers evaluated in the last series of experiments, PN emissions were routinely highest during the first experiment and decreased

with succeeding experiments. The complicating factor is that the first experiment was most often conducted with PG&E line gas. This covariance could lead to the apparent indication of a fuel effect when the actual effect is related to experiment order. Multivariate analysis was used to assess the dependence of full-burn PN emission factors on experiment order (class variable) and a fuel WN (continuous variable). For ovens, the analysis also considered the dependence of PN on oven temperature setting. There likely were insufficient data to distinguish the fuel effect from the other (apparently larger effects) for most of the burners studied. Sufficiently large samples with variation in the order of experiment were available for some burners.

The key result of these analyses is the slope of the change of pollutant emission change relative to a change in fuel Wobbe number (WN). The approach assumes that the change in pollutant emissions is linear with respect to fuel WN. The slope is expressed as the change in emissions per WN increase of 25 Btu/scf. As an example, the results could be used to assess directly the impact of increasing fuel Wobbe number from 1335 (a common value for many PG&E and SoCal Gas service areas) to 1360. An increase from current conditions to a 1385 Btu/scf WN fuel would lead to an emission change that is double the value indicated by a change of 25 Btu/scf WN. A fuel change of 10 Btu/scf WN would be expected to produce a change in emissions of 40% of the amount of a 25 Btu/scf WN increase.

In Tables 34 to 57, results indicating a very statistically significant ($p \leq 0.05$) relationship between an emission rate and fuel Wobbe numbers are displayed in bold and results indicating a likely relationship ($0.05 < p \leq 0.15$ for most pollutants and $0.05 < p \leq 0.20$ for formaldehyde) are displayed in italics.

Since cooking burners emit pollutants directly into the indoor environment, the first concern is indoor exposures. Results are therefore presented first for the primary pollutants CO, NO₂, HCHO, and PN. NO_x is of potential concern as an indoor pollutant (contributing to indoor chemistry) and for the contribution of residential appliances to overall NO_x emissions in an air basin (with the potential to affect ambient ozone formation).

The first results shown are for CO emissions from cooktops. Table 34 indicates a statistically significant ($p < 0.05$) effect of Wobbe number on both full-burn and end-of-burn CO emission factors for 10 of the 13 cooktops, with a likely effect ($p = 0.10, 0.12$) for one additional cooktop (CT02). The magnitude of the effect is small (3% for a 25 Btu/scf change in fuel WN) for the burner with the highest CO emissions (CT09) and largest for a burner (CT06) with very low emissions. The effect was sizeable (13%–15%) for CT03 with the second-highest CO emissions. CO increases of roughly 10% and 20% were observed for two other cooktops (CT11, CT12) with full-burn emissions above 100 ng/J. Results across burners were consistent for full-burn and end-of-burn periods.

Table 34. Bivariate regression results for CO emissions (ng/J) from cooktop burners

Burner	N ¹	Mean ² (PG&E)	Δ CO / Δ 25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value	r ²
Full-Burn								
CT01	19	11	1	0	3	13%	0.01	0.310
CT02	20	29	2	0	3	5%	0.10	0.143
CT03	16	231	34	21	48	15%	<0.001	0.673
CT04	4	42	2	-15	19	4%	0.70	0.088
CT05	8	87	-1	-2	1	-1%	0.34	0.151
CT06	6	13	6	3	8	47%	0.003	0.913
CT07	8	59	5	2	7	8%	0.005	0.763
CT08	8	7	1	0	1	7%	0.02	0.637
CT09	8	823	24	11	37	3%	0.004	0.783
CT10	8	57	8	6	9	13%	<0.001	0.962
CT11	8	107	12	6	19	11%	0.004	0.772
CT12	8	123	25	16	33	20%	0.003	0.901
CT13	8	48	13	10	16	27%	<0.001	0.955
End-of-Burn								
CT01	19	10	1	0	2	10%	0.07	0.183
CT02	20	28	1	0	3	5%	0.12	0.131
CT03	16	209	28	16	40	13%	<0.001	0.627
CT04	4	23	3	-6	12	12%	0.34	0.438
CT05	8	78	-1	-2	1	-1%	0.26	0.208
CT06	6	10	5	2	7	50%	0.006	0.880
CT07	8	63	5	3	8	9%	0.004	0.775
CT08	8	6	1	0	1	10%	0.002	0.817
CT09	8	726	22	9	35	3%	0.007	0.731
CT10	8	64	9	8	10	14%	<0.001	0.991
CT11	8	119	10	4	17	9%	0.009	0.711
CT12	8	95	20	15	24	21%	<0.001	0.946
CT13	8	29	9	7	10	30%	<0.001	0.975

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Table 35 shows that full-burn emission factors of CO had statistically discernible dependence of fuel WN for four of six broiler burners, with three increasing and one decreasing. End-of-burn emissions were affected by fuel WN for three of these burners, with two increasing at roughly 10% (for an increase in 25 Btu/scf of fuel WN) and one decreasing by a similar amount. Of the four broilers with full-burn CO emission factors above 100 ng/J, BR02 would increase by 9%, BR06 would decreased by 3%, BR13 likely would increase, and BR03 would be unaffected.

Table 35. Bivariate regression results for CO emissions (ng/J) from broiler burners

Burner	N ¹	Mean ² (PG&E)	Δ CO / Δ 25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value	r ²
Full-Burn								
BR01	12	44	10	7	13	23%	<0.001	0.856
BR02	5	145	13	10	15	9%	0.001	0.986
BR03	4	124	0	-11	11	0%	1.0	0.000
BR06	8	120	-3	-4	-2	-3%	<0.001	0.947
BR12	8	29	5	3	7	16%	0.001	0.868
BR13	8	178	12	-4	28	7%	0.11	0.365
End-of-Burn								
BR01	12	13	1	0	2	10%	0.014	0.469
BR02	5	69	-1	-16	15	-1%	0.89	0.008
BR03	4	47	-4	-5	-3	-9%	0.003	0.994
BR06	8	34	0	-1	0	-1%	0.39	0.127
BR12	8	9	1	0	2	11%	0.005	0.763
BR13	8	67	1	-5	6	1%	0.74	0.019

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Table 36 displays bivariate results for the first burn of each oven experiment. This table indicates statistically discernible ($p \leq 0.05$) increases in CO (with increase of 25 WN) for six ovens and a likely increase ($p = 0.09$) for another. The WN-dependent increase in CO was 9%–16% (for change of 25 WN) for six of the seven with $p \leq 0.09$; the largest increase was for an oven with moderate baseline emissions of 86 ng/J CO. Results for the highest CO-emitting (OV11) oven indicate a likely decrease in CO related to increasing fuel WN.

Table 36. Bivariate regression results for CO emissions (ng/J) from oven burners at 350°F

Burner	N ¹	Mean ² (PG&E)	Δ CO / Δ 25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value	r ²
Full-Burn								
OV01	8	26	4	1	7	16%	0.019	0.627
OV02	7	149	28	-52	107	19%	0.41	0.138
OV03	8	86	32	17	47	37%	0.002	0.821
OV05	4	212	24	23	26	11%	<0.001	1.000
OV06	5	198	11	-3	25	6%	0.091	0.668
OV07	4	187	8	-9	25	4%	0.19	0.657
OV08	4	237	32	-1	66	14%	0.053	0.897
OV09	4	275	10	-74	93	3%	0.67	0.108
OV10	5	94	10	8	12	11%	0.001	0.987
OV11	4	790	-60	-179	58	-8%	0.16	0.705
OV12	4	49	4	-2	11	9%	0.091	0.826
OV13	4	130	20	0	40	15%	0.052	0.899

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Oven multivariate results are presented in Table 37 below. The incorporation of results from all burns provided a larger dataset to reveal statistically significant ($p < 0.05$) or likely ($p = 0.10$) effects of fuel Wobbe number on CO emissions for all oven burners. The largest increase (46%) was observed for OV03, which had one of the lowest emission levels for ovens and moderate CO emissions in relation to other cooking burners. The single burner (OV11) for which CO dropped with increasing fuel Wobbe number was the burner with the highest baseline emissions across the three temperature settings. The next five highest emitters—with baseline CO in the range of 108-174 ng/J averaged across burn conditions—are predicted to have CO increase by 3%–15% for each 25 Btu/scf increase in fuel WN.

Table 37. Multivariate regression results for ovens: effect of fuel Wobbe number on CO emissions (ng/J) adjusted for oven temperature setting

Burner	N ¹	Mean ² (PG&E)	Δ CO / Δ 25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	WN p-value
Full-burn emission factor (ng/J)							
OV01	24	16	3	2	4	19%	<.0001
OV02	21	99	17	-3	37	17%	0.11
OV03	24	61	28	23	33	46%	<.0001
OV05	12	163	20	17	22	12%	<.0001
OV06	15	124	6	3	9	5%	<.0001
OV07	12	156	5	2	7	3%	0.0007
OV08	12	108	16	9	24	15%	<.0001
OV09	12	174	17	3	31	10%	0.018
OV10	15	58	7	6	9	13%	<.0001
OV11	12	528	-37	-62	-12	-7%	0.004
OV12	12	36	3	2	4	7%	<.0001
OV13	12	70	16	13	20	23%	<.0001

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

The next few tables present results for NO₂. Table 38 indicates a statistically significant effect of fuel WN on NO₂ full-burn or end-of-burn emission factors for six cooktops, with a likely effect indicated for a seventh cooktop, CT11 (p-values of 0.12 and 0.06). The magnitude of the emissions change (for a change in WN of 25 Btu/scf) was in the range of 2%–10% for both full-burn and end-of-burn periods. Fuel WN impacted NO₂ emissions for cooktops that spanned much of the range of baseline emission levels, and the magnitude of change for those with statistically discernible impacts was not correlated with the baseline emission level.

Table 38. Bivariate regression results for NO₂ emissions (ng/J) from cooktop burners

Burner	N ¹	Mean ² (PG&E)	Δ NO ₂ / Δ 25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value	r ²
Full-Burn								
CT01	19	6.7	0.5	0.2	0.8	7%	0.007	0.360
CT02	20	8.5	0.2	0.0	0.5	3%	0.038	0.217
CT03	16	12.1	1.2	0.7	1.7	10%	<0.001	0.620
CT04	4	10.0	0.1	-0.5	0.8	1%	0.46	0.296
CT05	8	11.2	0.2	-0.3	0.6	1%	0.39	0.124
CT06	6	5.0	0.0	-0.2	0.2	0%	0.95	0.001
CT07	8	7.3	0.4	0.2	0.7	6%	0.007	0.734
CT08	8	6.7	0.1	-0.1	0.3	1%	0.42	0.112
CT09	8	17.7	0.1	-0.1	0.4	1%	0.24	0.223
CT10	8	9.6	-0.1	-0.9	0.8	-1%	0.86	0.006
CT11	8	7.6	0.2	-0.1	0.4	2%	0.12	0.355
CT12	8	10.2	0.6	0.1	1.0	5%	0.032	0.563
CT13	8	7.1	0.4	0.0	0.8	6%	0.050	0.500
End-of-Burn								
CT01	19	6.6	0.5	0.2	0.9	8%	0.007	0.360
CT02	20	9.0	0.2	0.0	0.4	2%	0.058	0.186
CT03	16	11.8	1.2	0.6	1.7	10%	<0.001	0.613
CT04	4	9.5	0.1	-0.4	0.5	1%	0.63	0.134
CT05	8	11.4	0.1	-0.3	0.5	1%	0.46	0.094
CT06	6	4.6	0.0	-0.1	0.1	0%	0.88	0.007
CT07	8	8.4	0.5	0.3	0.7	6%	0.001	0.864
CT08	8	6.8	0.1	-0.2	0.4	1%	0.39	0.123
CT09	8	17.9	0.2	-0.1	0.4	1%	0.16	0.304
CT10	8	10.8	0.0	-0.9	0.8	0%	0.90	0.003
CT11	8	8.0	0.2	0.0	0.5	3%	0.064	0.461
CT12	8	10.1	0.5	-0.1	1.0	5%	0.083	0.419
CT13	8	6.7	0.5	0.0	1.0	7%	0.049	0.502

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Table 39 below indicates that increasing fuel Wobbe number by 25 Btu/scf would be expected to increase full-burn NO₂ emissions by 7% for BR12 and 24% for BR01; a slight decrease in NO₂ from BR03 is also likely (p=0.09). It is noteworthy that BR01 had the lowest, and BR12 the second lowest baseline NO₂ emissions of the six broilers evaluated. Of the three highest NO₂-emitting broilers, only one showed a likely effect of fuel WN on NO₂.

Table 39. Bivariate regression results for NO₂ emissions (ng/J) from broiler burners

Burner	N ¹	Mean ² (PG&E)	Δ NO ₂ / Δ 25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value	r ²
Full-Burn NO ₂								
BR01	12	2.8	0.7	0.2	1.1	24%	0.009	0.508
BR02	5	11.2	-0.1	-2.6	2.4	-1%	0.91	0.005
BR03	4	13.0	-0.5	-1.1	0.2	-4%	0.086	0.836
BR06	8	7.8	0.0	-0.2	0.3	0%	0.82	0.010
BR12	8	5.7	0.4	0.1	0.6	7%	0.015	0.655
BR13	8	12.6	0.2	-0.4	0.8	1%	0.50	0.081

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Table 40 shows that NO₂ emissions from the first oven burn increased with increasing fuel WN by 3% for OV07, 7% for OV03, and 10% for OV10; a small increase (5%) is also likely (p=0.10) for OV12. No discernible change in NO₂ was observed for the three highest NO₂-emitting ovens.

Table 40. Bivariate regression results for NO₂ emissions (ng/J) from oven burners at 350°F

Burner	N ¹	Mean ² (PG&E)	Δ NO ₂ / Δ 25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value	r ²
Full-Burn								
OV01	8	4.9	-0.1	-0.8	0.6	-2%	0.73	0.022
OV02	7	8.5	0.6	-0.4	1.6	7%	0.18	0.331
OV03	8	6.0	0.4	0.0	0.9	7%	0.047	0.579
OV05	4	15.5	-0.2	-0.5	0.1	-1%	0.10	0.805
OV06	5	8.6	-0.1	-0.4	0.1	-1%	0.22	0.449
OV07	4	7.3	0.2	0.1	0.4	3%	0.028	0.945
OV08	4	7.4	0.0	-0.7	0.8	0%	0.90	0.011
OV09	4	11.3	0.1	-0.6	0.7	1%	0.73	0.076
OV10	5	5.6	0.5	0.4	0.7	10%	0.001	0.980
OV11	4	12.0	0.2	-1.3	1.7	2%	0.62	0.148
OV12	4	6.0	0.3	-0.2	0.8	5%	0.10	0.806
OV13	4	8.7	0.7	-0.6	2.0	8%	0.16	0.710

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Multivariate results for oven NO₂ emissions are presented in Table 41. As with CO, the incorporation of all burns revealed statistically significant relationships between fuel WN and NO₂ for more burners than was apparent for the 350°F burn alone. NO₂ emissions are predicted to increase by 4%–19% per 25 Btu/scf increase in fuel WN for seven of the 13 ovens. NO₂ emissions were not found to increase with fuel WN for the four highest-emitting ovens.

Table 41. Multivariate regression results for ovens: effect of fuel Wobbe number on NO₂ emissions (ng/J) adjusted for oven temperature setting

Burner	N ¹	Mean ² (PG&E)	Δ NO ₂ / Δ25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value
Full-burn emission factor (ng/J)							
OV01	24	3.8	0.1	-0.2	0.5	4%	0.42
OV02	21	7.5	0.7	0.3	1.1	9%	<0.001
OV03	23	5.1	0.4	0.2	0.6	8%	<0.001
OV05	12	13.9	0.1	-0.1	0.3	1%	0.20
OV06	15	8.1	0.0	-0.1	0.1	0%	0.93
OV07	12	6.1	0.3	0.1	0.4	4%	0.001
OV08	12	5.5	0.3	0.1	0.5	5%	0.015
OV09	12	11.3	0.0	-0.1	0.1	0%	0.93
OV10	15	4.4	0.5	0.4	0.6	12%	<0.001
OV11	12	13.2	0.2	-0.2	0.5	1%	0.38
OV12	12	5.6	0.3	0.1	0.4	5%	<0.001
OV13	12	6.3	1.2	0.8	1.6	19%	<0.001

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Table 42 presents bivariate analysis results for formaldehyde. The analysis used average values of duplicates samples; the sample size was the number of experiments. Statistically significant ($p < 0.05$) changes in formaldehyde with fuel WN were obtained for only four (shown in bold) of the 26 cooking burners with data for three or more fuels. These burners had substantial baseline values of HCHO (0.31–1.00 ng/J) that were found to increase 10%–31% for each 25 WN change in fuel. A likely effect of fuel WN on HCHO emissions (based on $p \leq 0.20$ and $r^2 > 0.6$) was indicated for seven additional burners. Of these, two had HCHO decrease by 14% and 10% (from baselines of 1.15 and 2.98 ng/J); the other five had HCHO increase 4%–11% from baseline values of 0.13–0.93 ng/J. There were no discernible changes in formaldehyde emissions with fuel WN for the two highest-emitting cooking burners (CT09 and OV11).

Table 42. Bivariate regression results for HCHO emissions (ng/J) from cooking burners

Burner	N ¹	Mean ² (PG&E)	Δ HCHO / $\Delta 25$ WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value	R ²
BR06	4	0.93	0.04	-0.04	0.11	4%	0.19	0.65
BR12	4	0.13	0.01	-0.01	0.03	7%	0.13	0.76
BR13	4	0.79	0.08	-0.11	0.27	10%	0.20	0.64
CT01	3	0.31	0.05	0.03	0.08	17%	0.03	1.00
CT02	3	0.55	0.04	-0.29	0.38	8%	0.34	0.73
CT03	3	1.00	0.31	0.22	0.40	31%	0.01	1.00
CT04	0	-	-	-	-	-	-	-
CT05	4	0.67	0.01	-0.13	0.15	2%	0.78	0.05
CT06	3	0.12	0.00	-0.06	0.06	-2%	0.67	0.25
CT07	4	0.44	0.08	0.03	0.13	19%	0.02	0.96
CT08	4	0.09	0.00	-0.02	0.02	-1%	0.92	0.01
CT09	4	4.67	0.00	-0.28	0.27	0%	0.97	0.00
CT10	4	1.15	-0.16	-0.45	0.13	-14%	0.14	0.74
CT11	4	0.31	-0.02	-0.09	0.05	-7%	0.32	0.46
CT12	4	0.81	0.04	-0.06	0.13	5%	0.23	0.59
CT13	4	0.10	0.01	-0.07	0.10	12%	0.61	0.15
OV01	2	0.49	-0.01	-	-	-2%	-	1.00
OV02	4	0.38	0.02	-0.02	0.07	6%	0.18	0.68
OV03	3	0.46	-0.01	-0.19	0.16	-3%	0.49	0.52
OV05	4	0.43	0.05	-0.02	0.12	11%	0.10	0.81
OV06	5	1.01	-0.01	-0.13	0.12	-1%	0.88	0.01
OV07	4	0.57	0.02	-0.10	0.14	3%	0.57	0.19
OV08	4	2.98	-0.31	-0.94	0.32	-10%	0.17	0.69
OV09	4	0.60	-0.03	-0.48	0.43	-4%	0.83	0.03
OV10	4	0.32	0.00	-0.03	0.02	-1%	0.52	0.23
OV11	4	5.51	-0.10	-0.69	0.48	-2%	0.53	0.23
OV12	4	0.25	0.00	-0.02	0.01	-1%	0.61	0.15
OV13	4	0.33	0.03	0.03	0.04	10%	0.002	1.00

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Particle number emissions clearly varied with the daily order of experiments for all cooktops and broilers evaluated during the last phase of experiments in late 2008 through early 2009. The effect is large and appears independent of the order in which fuels were evaluated, as shown in Figure 13 below.

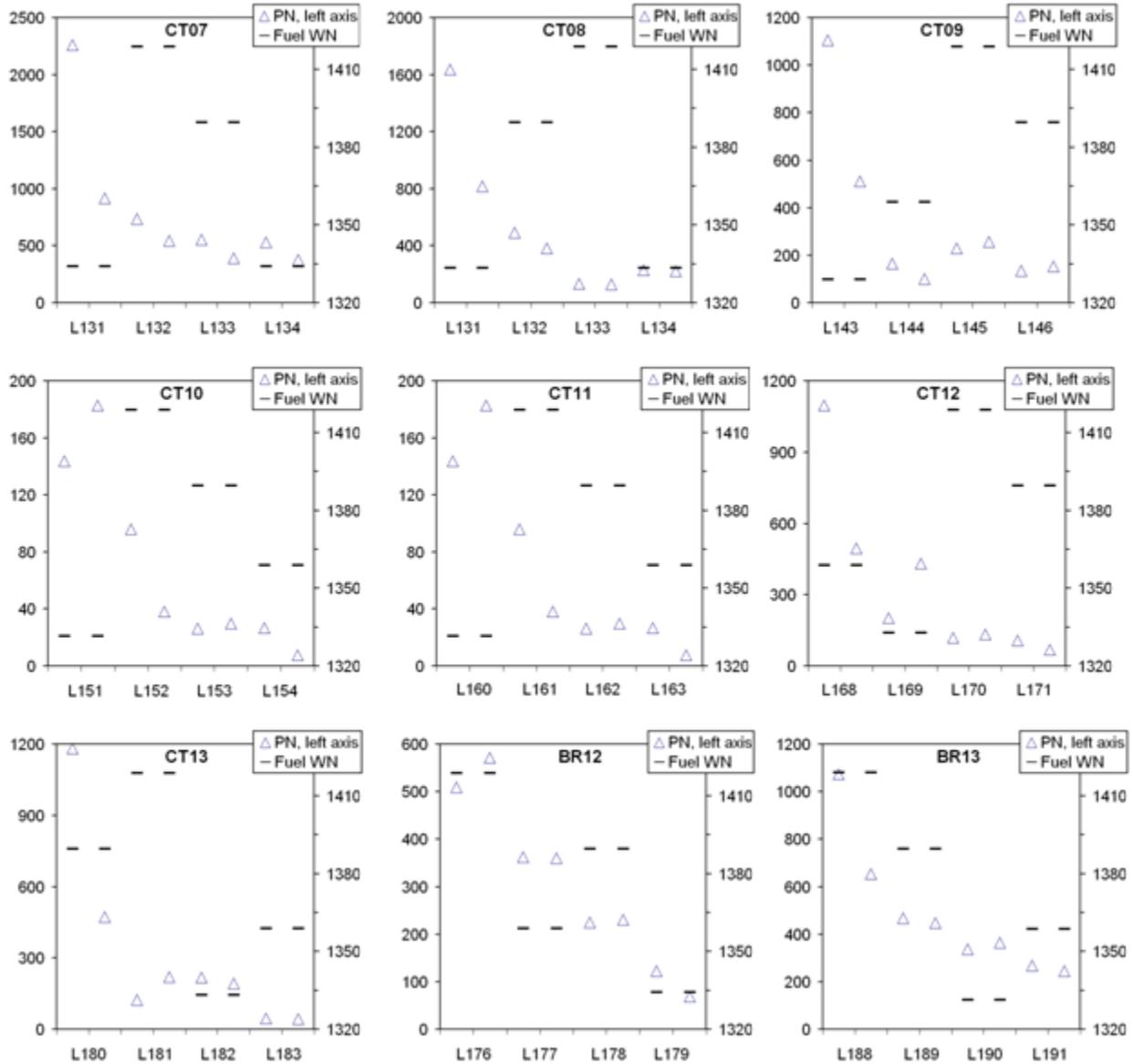


Figure 13. PN emission factors (#/J) for cooktops and broilers evaluated in the last series of experiments, by daily order of experiment; results shown for each burn

Multivariate analysis treating experiment (not burn) order as an independent class variable and fuel Wobbe number as an independent continuous variable indicated that the former was robustly predictive ($p < 0.05$) and the latter was not significantly predictive for all cooktops and broilers tested during the last phase (CT07-CT13 and BR12-BR13). The order of experiment effect was observed for some burners during the earlier phases, but the structure of the data was not as conducive to asserting this conclusion for various reasons. Prior phases included only three experiments with the same burner on many days and PG&E fuel was tested first in

almost all cases (including some cases in which the day started with duplicate PG&E experiments). For example, both CT05 and CT06 showed a trend of PN decreasing sharply with successive burns. However, since these burners were tested first with PG&E, then simulated LNGs in order of increasing fuel Wobbe number, the test order cannot be separated from the progression of WNs. The last set of experiments also started in many cases with PG&E fuel but several of these included a later replicate experiment with PG&E fuel.

There is not a similarly obvious order of experiment effect for ovens evaluated during either period. Oven PN emissions varied much more strongly with temperature setting than with fuel or order of day, as shown in Figure 14.

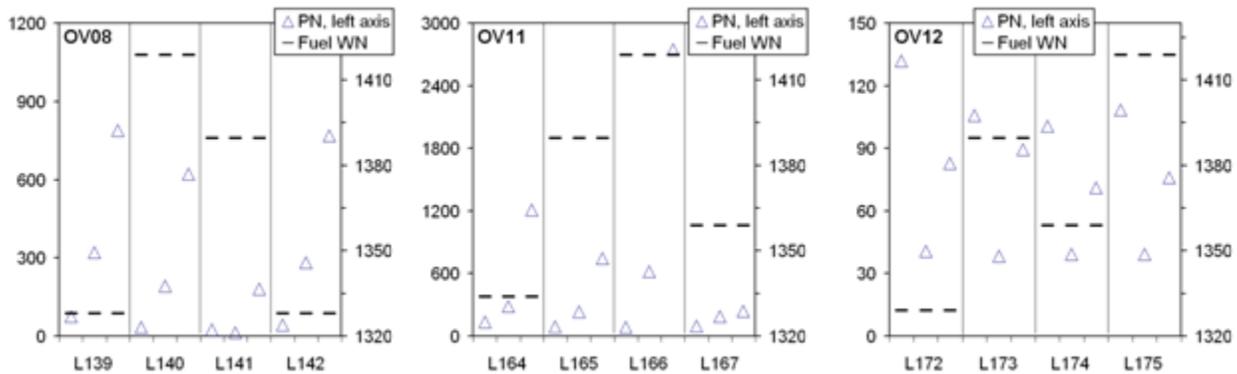


Figure 14. PN emission factors (#/J) for ovens evaluated in last series of experiments, by daily order; results for burns at 350°F, 425°F, and 500°F

The potential effects of gas quality on PN emissions can be assessed independently of these other, apparently more prominent effects with larger and more randomly executed series of experiments. Such data are available for CT01–CT03, BR01, and OV01–OV03. As noted earlier, burners CT01, BR01, and OV01 were each evaluated over multiple days with a single fuel being used for all three burners each day. These data are somewhat limited in that BR01 was always the first or third burner tested, and CT01 was always the first or second burner tested in a day. Burners CT02, CT03, OV02, and OV03 were each evaluated with two or more fuels on multiple days; on at least one test day (for each burner), PG&E fuel was not the first fuel evaluated. It is therefore possible to separate the order of day effect from an effect the fuel may have had on PN emissions from these burners. The results of multivariate analysis (as described in the preceding paragraph) for the cooktops and broilers indicate a statistically significant effect of fuel WN on PN full-burn emissions for all three of the cooktops and a likely effect ($p=0.06$) for BR01; these results are provided in Table 43.

Table 43. Effect of fuel Wobbe number on PN emissions (#/J) from cooktops and broilers, adjusted for order of experiment

Burner	N ¹	Mean ² (PG&E)	Δ PN / Δ 25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	WN p- value ³	Exp. order p-value
CT01	19	266	-67	-99	-35	-25%	<0.001	0.09
CT02	20	280	-51	-84	-18	-18%	0.003	0.13
CT03	16	253	48	1	96	19%	0.044	0.09
<i>BR01</i>	<i>12</i>	<i>48.2</i>	<i>12.7</i>	<i>-0.8</i>	<i>2.6</i>	<i>26%</i>	<i>0.065</i>	<i>0.003</i>

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas.

³ Model estimate of change in pollutant emission factor (#/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Table 44 presents results from a multivariate analysis of dependence of PN full-burn emission factors on fuel WN (continuous variable) and order of experiment (class variable) for each oven temperature setting. Results are presented for the three ovens for which a large number of experiments were conducted with fuels tested in some varying order. Statistically significant dependences of PN on fuel WN were obtained for all three settings on OV01 and for the middle burns for OV02 and OV03. The first burn of OV02 showed a likely dependence on fuel WN. In all of these cases, PN decreased with increasing WN. Experiment order had a significant effect on PN emission for OV01 and OV02 but not OV03. It is relevant to note that the effect of fuel WN (5%–50%) is small relative to the variations in baseline emission rates with oven operating temperature (in Table 44 below) and relative to the variation with order of experiment as show in Figure 14 above.

Table 44. Effect of fuel Wobbe number on PN emissions (#/J) by oven burn, adjusted for order of experiment

Burner, burn ¹	N ²	Mean ³ (PG&E)	Δ PN / Δ 25 WN ⁴	Lower 95% CI ⁵	Upper 95% CI ⁵	% change ⁶	WN p- value ³	Exp. order p-value
OV01, B1	8	147	-16	-29	-2	-11%	0.024	0.06
OV01, B2	8	38	-6.9	-10.1	-3.7	-18%	<0.001	0.002
OV01, B3	8	36	-5.4	-8.7	-2.1	-15%	0.001	0.003
<i>OV02, B1</i>	<i>7</i>	<i>44</i>	<i>-7.3</i>	<i>-16.6</i>	<i>-2.0</i>	<i>-17%</i>	<i>0.13</i>	<i><0.0001</i>
OV02, B2	7	115	-6.3	-12.4	-0.0	-5%	0.047	<0.0001
<i>OV02, B3</i>	<i>7</i>	<i>1700</i>	<i>-330</i>	<i>-1000</i>	<i>1700</i>	<i>-19%</i>	<i>0.63</i>	<i>0.50</i>
<i>OV03, B1</i>	<i>8</i>	<i>199</i>	<i>-13.9</i>	<i>-143</i>	<i>116</i>	<i>-7%</i>	<i>0.83</i>	<i>0.32</i>
OV03, B2	8	56	-29	-49	-8	-52%	0.006	0.054
<i>OV03, B3</i>	<i>8</i>	<i>68</i>	<i>-15</i>	<i>-52</i>	<i>22</i>	<i>-22%</i>	<i>0.43</i>	<i>0.50</i>

¹ Each burn represents an oven temperature setting: B1=350°F; B2=425°F; B3=500°F.

² Number of data points (burns).

³ Mean value of emission metric for all burns with PG&E line gas.

⁴ Model estimate of change in pollutant emission factor (#/J) per 25 Btu/scf change in fuel Wobbe number.

⁵ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁶ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Tables 45 through 47 present results for fuel WN effects on NO_x emissions from cooking burners. Table 45 indicates that fuel Wobbe number had a statistically discernible influence (p<0.05) on full-burn or end-of-burn NO_x emission factors for three cooktops and a likely effect (p<0.1) for three others. The magnitude of this effect was very small, roughly 1%–2%.

Table 45. Bivariate regression results for NO_x emissions (ng/J) from cooktop burners

Burner	N ¹	Mean ² (PG&E)	Δ NO _x / Δ25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value	r ²
Full-Burn								
CT01	19	31.5	0.5	-0.2	1.2	2%	0.15	0.118
CT02	20	37.3	0.4	-0.8	1.6	1%	0.45	0.032
CT03	16	34.9	0.7	-0.4	1.9	2%	0.18	0.124
CT04	4	47.3	0.2	-1.3	1.8	1%	0.58	0.180
CT05	8	41.9	0.9	0.6	1.3	2%	0.001	0.872
CT06	6	38.5	0.3	0.0	0.7	1%	0.057	0.636
CT07	8	34.2	0.2	-0.2	0.5	1%	0.29	0.184
CT08	8	33.5	0.2	-0.4	0.9	1%	0.47	0.091
CT09	8	25.0	-0.3	-0.7	0.1	-1%	0.16	0.300
CT10	8	36.2	0.2	-0.7	1.1	0%	0.63	0.041
CT11	8	29.6	0.4	-0.1	0.8	1%	0.089	0.406
CT12	8	34.3	-0.3	-0.8	0.3	-1%	0.27	0.197
CT13	8	34.9	0.3	0.0	0.5	1%	0.038	0.540
End-of-Burn								
CT01	19	33.6	0.7	-0.1	1.5	2%	0.080	0.170
CT02	20	40.1	0.5	-0.8	1.7	1%	0.44	0.034
CT03	16	37.7	1.0	-0.1	2.2	3%	0.065	0.223
CT04	4	51.8	0.3	-1.4	2.0	1%	0.53	0.224
CT05	8	43.8	1.0	0.7	1.4	2%	<0.001	0.899
CT06	6	41.2	0.4	0.1	0.7	1%	0.021	0.772
CT07	8	36.7	0.3	0.0	0.6	1%	0.054	0.489
CT08	8	36.1	0.2	-0.6	0.9	0%	0.61	0.046
CT09	8	27.0	-0.3	-0.7	0.2	-1%	0.22	0.237
CT10	8	39.4	0.1	-0.7	1.0	0%	0.74	0.021
CT11	8	31.6	0.5	-0.1	1.0	2%	0.084	0.417
CT12	8	36.7	-0.3	-0.9	0.4	-1%	0.35	0.147
CT13	8	38.0	0.4	0.2	0.6	1%	0.003	0.797

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Table 46 indicates discernible effects of fuel WN on broiler NO_x emissions on the order of a few percent. Of the four burners with p<0.1, two are expected to have NO_x increase by 3%–4% and two to have NO_x decrease by 1%–2%.

Table 46. Bivariate regression results for NO_x emissions (ng/J) from broiler burners

Burner	N ¹	Mean ² (PG&E)	Δ NO _x / Δ 25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value	r ²
Full-Burn NO _x (ng/J)								
BR01	12	30.8	1.2	0.2	2.1	4%	0.023	0.419
BR02	5	30.3	0.7	-2.6	4.0	2%	0.57	0.122
BR03	4	31.7	-0.2	-1.0	0.6	-1%	0.40	0.361
BR06	8	17.1	-0.1	-0.2	0.0	-1%	0.025	0.598
BR12	8	36.8	1.0	0.2	1.8	3%	0.021	0.619
BR13	8	30.1	-0.6	-1.3	0.1	-2%	0.093	0.399

¹ Number of data points (burns).² Mean value of emission metric for all burns with PG&E line gas.³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Table 47 shows that there were no effects of fuel WN on NO_x for the first oven burn at 350°F. But as with CO and NO₂, the incorporation of all burns (multivariate analysis) revealed some burners with statistically significant relationships between fuel WN and NO_x emissions. NO_x emissions are predicted to decrease by 1%–2% for four ovens and by 4% for a fifth oven (per increase of 25 WN). These results reflect the relatively small changes observed in NO_x emission rates as fuel was varied in experiments between PG&E (WN mostly in range of 1330–1340) through fuels with WN of roughly 1390 and 1420 Btu/scf. Overall the results indicate a very small effect of fuel WN on NO_x emissions from ovens.

Table 47. Multivariate regression results for ovens: effect of fuel Wobbe number on NO_x emissions (ng/J) adjusted for oven temperature setting

Burner	N ¹	Mean ² (PG&E)	Δ NO _x / Δ 25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	WN p- value ³
Full-burn emission factor (ng/J)							
OV01	24	35.9	0.3	-0.2	0.9	1%	0.21
OV02	21	34.4	0.0	-1.0	1.0	0%	0.99
OV03	23	36.3	-0.1	-1.1	0.9	0%	0.83
OV05	12	31.4	-0.4	-0.6	-0.3	-1%	<0.001
OV06	15	33.0	0.2	-0.3	0.7	1%	0.44
OV07	12	31.8	-0.4	-0.5	-0.3	-1%	<0.001
OV08	12	33.3	-0.6	-1.1	-0.2	-2%	0.010
OV09	12	27.4	-1.0	-1.5	-0.5	-4%	<0.001
OV10	15	32.9	0.0	-0.2	0.2	0%	0.82
OV11	12	40.5	0.5	-0.2	1.1	1%	0.14
OV12	12	34.5	-0.4	-0.7	0.0	-1%	0.042
OV13	12	39.7	-0.3	-0.7	0.1	-1%	0.14

¹ Number of data points (burns).² Mean value of emission metric for all burns with PG&E line gas.³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

3.3.3. Fuel Wobbe Number Effects on Vented Burner Emissions

The tables that follow present statistical analysis results for outdoor venting burners, including furnaces, storage water heaters, and on-demand/tankless water heaters. Results are presented in similar formats and in the same order as above for cooking burners. One contrast is that only multivariate results are presented for tankless water heaters. Whereas for ovens the first burn is recognized to have more importance than the other operating conditions (since it represented the only burn with a cold burner), the individual burns in the TW cycle are independent and thus equally relevant to the analysis. Bivariate results are presented for end-of-burn emissions under high, low, or mixed firing rates for central furnaces CF01 and CF02; the other furnaces fired at only one rate. Mixed firing rate full-burn results indicate a transition from low to high firing during CF01 burns.

The first series of tables presents results for CO emissions. The Table 48 indicates that all four of the central furnaces showed statistically significant or likely impacts of fuel WN on CO during at least some operating mode(s). CO decreased on the order of 10%–20% in most cases in which there was a discernible effect. For CF02, the analysis indicates that increasing fuel WN will marginally reduce CO at low firing conditions and increase CO under high firing conditions.

Table 48. Bivariate regression results for CO emissions (ng/J) from furnace burners

Burner	Firing rate	N ¹	Mean ² (PG&E)	Δ CO / Δ 25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value	r ²
Full-Burn									
CF01	Mixed	7	3.8	-0.2	-2.1	1.7	-5%	0.82	0.012
CF02	High	3	13.0	1.3	-0.9	3.6	10%	0.083	0.983
CF02	Low	3	30.8	-1.0	-1.2	-0.7	-3%	0.015	1.000
CF03	-	8	19.4	-2.5	-3.7	-1.4	-13%	0.002	0.825
CF04	-	8	17.2	-2.2	-3.4	-1.0	-13%	0.004	0.776
WF01	-	6	0.0	-0.1	-0.7	0.4	NR	0.52	0.112
End-of-Burn									
CF01	High	6	2.9	-0.4	-0.9	0.1	-14%	0.085	0.564
CF01	Low	6	2.2	-0.5	-1.0	0.0	-23%	0.053	0.649
CF01	Mixed	7	2.5	-0.4	-0.7	-0.1	-17%	0.015	0.727
CF02	High	3	8.9	1.9	-1.8	5.6	22%	0.095	0.978
CF02	Low	3	24.2	-0.9	-4.9	3.0	-4%	0.21	0.897
CF03	-	8	14.6	-2.1	-2.5	-1.7	-15%	<0.001	0.961
CF04	-	8	11.2	-1.8	-2.3	-1.3	-16%	<0.001	0.940
WF01	-	6	-1.6	0.0	-0.1	0.1	NR	0.30	0.266

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Despite their very low CO emissions, two of the storage water heaters had discernible though small (in absolute terms) increases in CO with increasing fuel WN (Table 49). Two others (WH02 and WH04) had small decreases in CO. The first water heater showed a possible small decrease in a first set of experiments and a likely small increase in the next set. Negative values for mean emission factors (PG&E) theoretically indicate net destruction of CO with the burner operating.

Table 49. Bivariate regression results for CO emissions (ng/J) from storage water heaters

Burner	N ¹	Mean ² (PG&E)	Δ CO / Δ 25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value	r ²
WH1A	7	0.09	-0.02	-0.06	0.02	-22%	0.23	0.27
WH1B	4	-0.70	-0.03	-0.09	0.02	5%	0.13	0.76
WH02	7	-0.35	0.09	-0.03	0.22	-27%	0.12	0.42
WH03	6	-1.00	0.23	0.03	0.43	23%	0.032	0.72
WH04	6	2.02	-0.27	-0.39	-0.15	-13%	0.003	0.91
WH05	8	0.43	1.12	0.65	1.59	263%	0.001	0.85

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas. Negative values may result from net destruction of CO or from uncertainty of low-value measurements.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Five of the six tankless water heaters (TWs) showed significant dependence of CO on fuel WN (Table 50). In two cases—including the high-emitting (with malfunctioning regulator) TW06—the CO increase was on order of 50%–70% per 25 WN increase. TW04 showed an increase of 10%, whereas TW01 and TW05 indicate small decreases in CO with increasing fuel WN.

Table 50. Multivariate regression results for tankless water heaters: effect of fuel Wobbe number on CO emissions (ng/J) adjusted for water flow

Burner	N ¹	Mean ² (PG&E)	Δ CO / Δ 25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value ³
Full-Burn							
TW01	12	50	-3.2	-3.8	-2.7	-6%	<0.001
TW02	12	37	20	14	25	54%	<0.001
TW03	12	87	1.1	-1.0	3.2	1%	0.30
TW04	12	19	2.1	1.4	2.7	11%	<0.001
TW05	12	47	-0.3	-0.5	-0.1	-1%	0.001
TW06	16	434	242	129	354	56%	<0.001
End-of-Burn							
TW01	12	47	-3.2	-3.8	-2.5	-7%	<0.001
TW02	12	36	19	13	25	52%	<0.001
TW03	12	81	1.5	-0.7	3.8	2%	0.19
TW04	12	18	1.9	1.2	2.5	10%	<0.001
TW05	12	46	-0.3	-0.4	-0.1	-1%	0.004
TW06	18	590	388	213	563	66%	<0.001

¹ Number of data points (burns).

² Mean value of emission metric with PG&E line gas; mean of results for 1, 2, and 3 or 4 gpm water flow.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

The next series of tables presents results for NO₂ from vented burners. Table 51 indicates a statistically significant WN effect on NO₂ for only one furnace, a decrease of 7%.

Table 51. Bivariate regression results for full-burn NO₂ emissions (ng/J) from furnace burners

Burner	Firing rate	N ¹	Mean ² (PG&E)	Δ NO ₂ / Δ25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value	r ²
CF01	Mixed	7	2.4	0.1	-0.2	0.4	4%	0.51	0.09
CF02	High	3	5.9	0.0	-0.6	0.7	1%	0.62	0.31
CF02	Low	3	9.7	0.0	-0.1	0.1	0%	0.61	0.33
CF03	-	8	5.1	-0.1	-0.3	0.1	-2%	0.19	0.27
CF04	-	8	4.4	-0.3	-0.4	-0.2	-7%	<0.001	0.94
WF01	-	6	0.6	0.0	-0.1	0.1	1%	0.89	0.01

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Table 52 indicates that despite their low absolute emission rates of NO₂, three of five storage water heaters had statistically significant WN effects and a fourth had a likely effect. It is interesting (though unimportant owing to the low levels overall) that the effects cancel each other out: increases of 0.1 and 0.2 ng/J (12% and 33%) are offset by decreases of 0.1 and 0.2 ng/J (10% and 34%).

Table 52. Bivariate regression results for NO₂ emissions (ng/J) from storage water heaters

Burner	N ¹	Mean ² (PG&E)	Δ NO ₂ / Δ25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value	r ²
WH1A	7	0.30	-0.10	-0.15	-0.05	-34%	0.003	0.86
WH1B	4	1.55	-0.02	-0.09	0.05	-1%	0.33	0.45
WH02	7	2.22	0.04	-0.04	0.12	2%	0.25	0.25
WH03	6	0.37	0.12	-0.02	0.27	33%	0.08	0.57
WH04	6	2.18	-0.23	-0.28	-0.17	-10%	<0.001	0.97
WH05	8	1.67	0.20	0.12	0.29	12%	0.001	0.85

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Table 53 shows a strong dependence of full-burn NO₂ emissions on fuel WN for tankless water heaters as a group, with five of six having very robust trends (p<0.01). An increase in fuel WN of 25 Btu/scf is associated with an increase of full-burn NO₂ emissions of 1%–3% in three burners and 8%–10% in two others. The second half of the table shows that the increase in NO₂ mass emission rates results, despite a decrease in the fraction of NO_x that is emitted as NO₂.

Table 53. Multivariate regression results for tankless water heaters: effect of fuel Wobbe number on NO₂ emissions (ng/J) adjusted for water flow

Burner	N ¹	Mean ² (PG&E)	Δ NO ₂ / Δ25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	WN p- value
Full-Burn NO ₂							
TW01	12	8.9	0.12	0.08	0.17	1%	<0.001
TW02	12	6.6	0.64	0.49	0.78	10%	<0.001
TW03	12	6.1	0.16	0.04	0.28	3%	0.007
TW04	12	4.0	0.33	0.28	0.39	8%	<0.001
TW05	12	8.5	0.25	0.19	0.31	3%	<0.001
TW06	18	7.9	-0.12	-0.33	0.09	-2%	0.270
Full-Burn NO ₂ /NO _x							
TW01	12	0.37	-0.003	-0.005	-0.001	-1%	<0.001
TW02	12	0.41	-0.027	-0.032	-0.023	-7%	<0.001
TW03	12	0.35	0.004	0.000	0.008	1%	0.19
TW04	12	0.45	-0.020	-0.023	-0.017	-5%	<0.001
TW05	12	0.40	-0.003	-0.004	-0.001	-1%	0.004
TW06	18	0.26	-0.021	-0.026	-0.017	-8%	<0.001

¹ Number of data points (burns).

² Mean value of emission metric with PG&E line gas; mean of results for 1, 2, and 3 or 4 gpm water flow.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Analysis of particle number results for vented burners started with assessment of whether factors other than fuel may affect PN emission factors for each type of burner. As with cooking burners, these factors included burner operational mode and potentially experiment order.

Storage water heaters and some furnaces operated in only one mode. Two of the furnaces (CF01 and CF02) operated at low and high firing rates but only CF02 had full burn data for each condition; CF01 started each burn on low firing rate. In each of three experiments with CF02, the high firing rate condition had higher full-burn emission factors than the low firing operation. Each tankless water heater was operated at three water flow rates. Figure 15 shows that for each TW, variations in PN emission rates between burns within a given experiment (i.e., with same fuel) were as large or larger as variations between experiments (i.e., between fuels).

The potential effect of experiment order (as observed clearly for CT and BR burners, though not as clearly for ovens) could be assessed for only a subset of the vented burners: those burners with valid data for three or more experiments that were not ordered by fuel WN. This condition was satisfied for five of six TW burners (not TW02), WH01, and WH05. CF03 and CF04 each had four experiments, but neither had valid PN data for all four. Results for TW01, TW03, TW05, and TW06 all suggest an order of experiment effect; for each, a later replicate with PG&E line

gas had lower PN emission factors (by water flow rate) than the first experiment with the same fuel. TW04 results showed the opposite trend, with higher PN emissions for each flow rate in the later experiment. As with the cooking burners, the order of experiment effect appears most prominently for the first experiment.

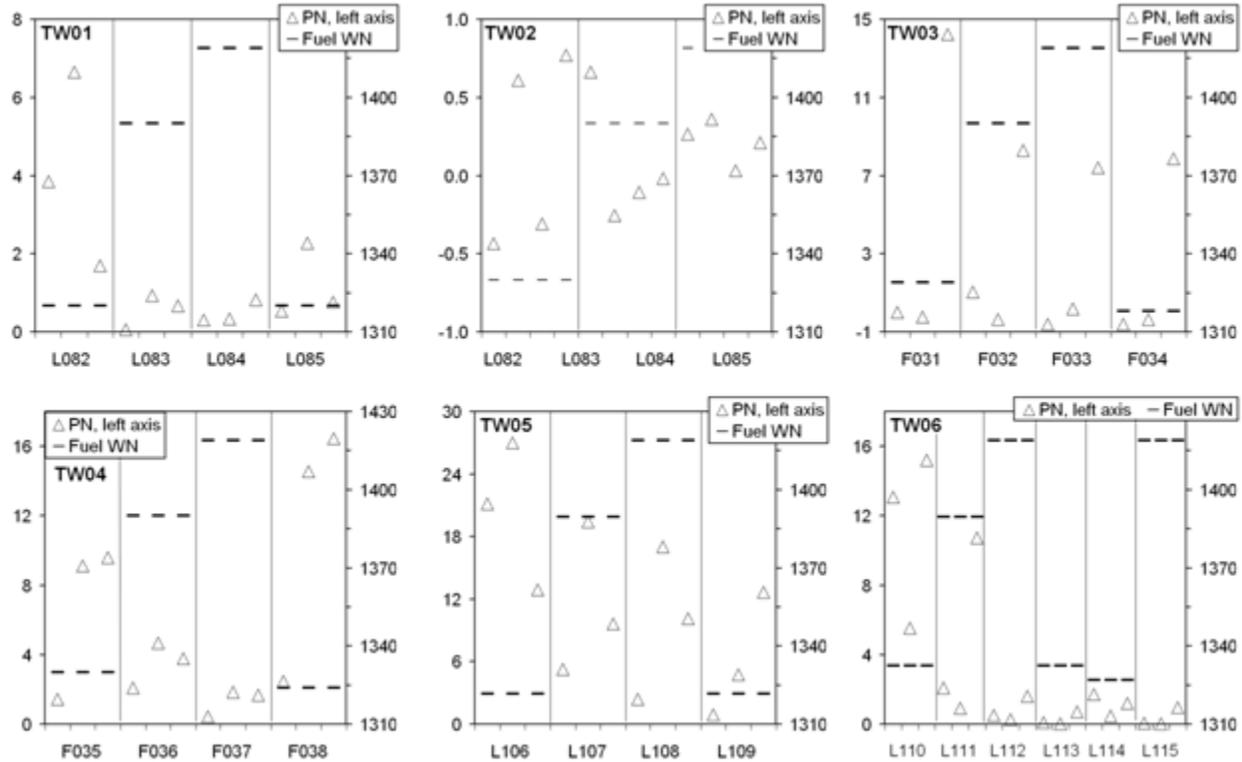


Figure 15. PN emission factors (#/J) for tankless water heaters, by daily order of experiment; results shown for each burn

An independent effect of fuel WN on PN emissions was indicated by results for several of the vented appliances with sufficient data to make this distinction. As can be seen in Figure 15 above, for both TW01 and TW04, the final experiment with PG&E fuel had higher emissions than the preceding experiments (comparing burns with the same water flow rate). While this result suggests a fuel effect independent of experiment order, the multivariate analysis determined that this effect is not statistically significant ($p=0.32$) with a mean estimate of the effect as being roughly an order of magnitude less than the effect of experiment order or water flow rate. For TW04, the effect of fuel WN was highly certain ($p<0.0001$) and of similar magnitude as the effects of order of experiment and water flow rate. The multivariate analysis including experiment order indicated no statistically significant fuel effects on full-burn PN emissions for the other TW burners.

As a complement to the TW results shown above, Figure 16 presents results for the two storage water heaters with data relevant to experiment order. In the first set of WH01 experiments, L041 was effectively the second experiment on October 30, 2007, following some earlier test runs on that day. The primary results show higher emissions for L042 (the first experiment of day), compared with L041 and L043, each of which was the second experiment of the day on which it

was conducted. During the second set of WH01 experiments, the first experiment had lower PN emissions relative to the second. In both sets, it was the experiment with higher WN fuel that had higher emissions. Results from the multivariate analysis of the first set (see Table 54) indicate a statistically significant and large percentage increase in WH01 PN emissions adjusted for experiment order. The increase is estimated at roughly 140% for a 25 Btu/scf increase in fuel WN. For WH05, full burn PN emissions decreased by 16%.

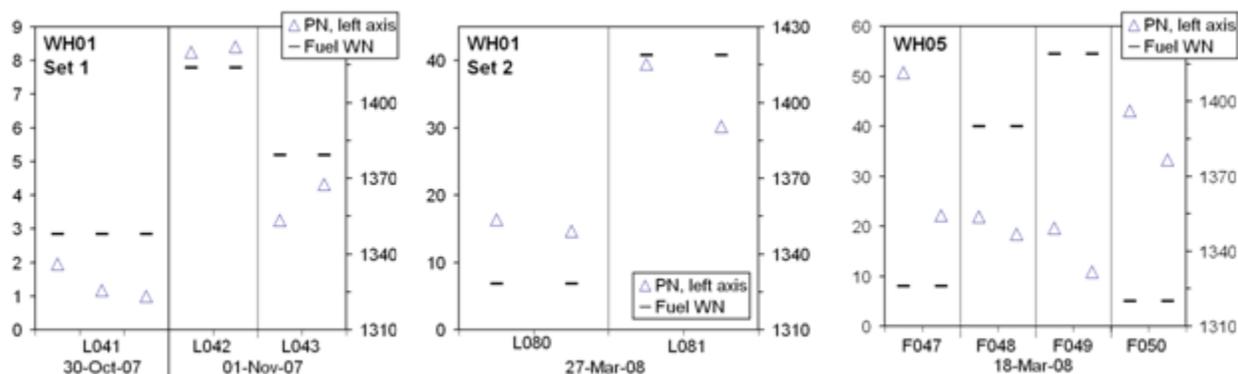


Figure 16. PN emission factors (#/J) for storage water heaters, by daily order of experiment; results shown for each burn

Table 54. Effect of fuel Wobbe number on full-burn PN emissions (#/J) for storage water heaters, adjusted for water flow rate

Burner	N ¹	Mean ² (PG&E)	Δ PN / Δ 25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value	Exp. order p-value
WH1A	7	1.4	1.9	1.4	2.5	140%	<0.001	0.008
WH05	8	37.3	-5.8	-9.7	-1.9	-16%	0.003	0.97

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Table 55 presents bivariate results for vented burners with valid formaldehyde measurements; these include two of five furnaces, all six tankless water heaters and three of five water heaters (though one of these had valid data for only two fuels). Of the four calculated trends with $p \leq 0.05$, there were decreases of 4%, 11%, 12%, and 17% on baseline emission factors (measured with PG&E line gas) of 0.25, 1.54, 0.16, and 0.38 ng/J, respectively. Another four burners (in italics, selected with slightly looser p-value and r^2 criteria than were used for cooking burners) showed HCHO likely to decrease by 2%–8% with increasing fuel WN. Overall these results suggest that HCHO from vented appliances will decrease or remain unchanged with an increase in fuel WN.

Table 55. Bivariate regression results for HCHO emissions (ng/J) from vented burners

Burner	N ¹	Mean ² (PG&E)	Δ HCHO / Δ 25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value	R ²
CF03	3	0.38	-0.06	-0.13	0.00	-17%	0.05	0.99
CF04	4	0.16	-0.02	-0.03	-0.01	-12%	0.01	0.98
TW01	4	1.54	-0.17	-0.21	-0.13	-11%	0.003	0.99
TW02	3	0.72	-0.06	-0.31	0.19	-8%	0.21	0.90
TW03	4	2.35	-0.06	-0.15	0.03	-2%	0.11	0.80
TW04	4	0.25	-0.01	-0.02	0.00	-4%	0.03	0.95
TW05	4	2.02	-0.02	-0.24	0.20	-1%	0.78	0.05
TW06	6	0.24	-0.01	-0.02	0.00	-3%	0.15	0.44
WH01	2	0.03	0.00	-	-	-2%	-	1
WH04	3	0.05	0.00	-0.01	0.00	-7%	0.06	0.99
WH05	4	0.05	0.00	-0.01	0.01	-4%	0.49	0.26

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

The next series of tables presents results for full-burn NO_x from vented burners. Table 56 indicates a statistically significant WN effect on NO_x for three of the four central furnaces. For these three burners, NO_x increases of 1%–4% are expected for fuel WN changes of 25 Btu/scf.

Table 56. Bivariate regression results for NO_x emissions (ng/J) on furnace burners

Burner	Firing rate	N ¹	Mean ² (PG&E)	Δ NO _x / Δ 25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value	r ²
CF01	High	6	34.4	1.2	0.5	2.0	4%	0.012	0.830
CF01	Low	6	34.4	1.2	0.5	1.9	4%	0.008	0.856
CF01	Mixed	7	33.6	1.2	0.7	1.7	4%	0.002	0.873
CF02	High	3	27.1	-0.2	-0.7	0.4	-1%	0.17	0.928
CF02	Low	3	26.2	0.0	-1.4	1.4	0%	0.89	0.028
CF03	-	8	22.3	0.3	0.0	0.5	1%	0.037	0.544
CF04	-	8	23.6	0.7	0.3	1.0	3%	0.004	0.780
WF01	-	6	32.7	0.4	-1.3	2.1	1%	0.57	0.088

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Table 57 shows negligible effects of fuel WN on full-burn NO_x emissions from storage water heaters. For the three WHs with statistically significant results, two increased by 1% and 2%, and the third decreased by 1%.

Table 57. Bivariate regression results for NO_x emissions (ng/J) from storage water heaters

Burner	N ¹	Mean ² (PG&E)	Δ NO _x / Δ25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value	r ²
WH1A	7	13.6	-0.2	-0.3	0.0	-1%	0.018	0.706
WH1B	4	26.3	0.0	-0.3	0.3	0%	0.72	0.078
WH02	7	31.9	0.6	0.3	0.9	2%	0.005	0.824
WH03	6	24.0	0.0	-0.3	0.3	0%	0.94	0.002
WH04	6	29.0	0.4	0.2	0.6	1%	0.002	0.925
WH05	8	28.8	-0.1	-0.2	0.1	0%	0.27	0.195

¹ Number of data points (burns).

² Mean value of emission metric for all burns with PG&E line gas.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

Table 58 shows that NO_x emissions from all six of the tankless water heaters evaluated in this study were significantly dependent on fuel WN. Full-burn NO_x increased by marginal amounts (1%–2%) for two units, by small to moderate amounts of 4% and 8% for two units, and by substantial amounts of 15% and 23% for the other two units. The largest percentage increases were for the units with lowest baseline emissions.

Table 58. Multivariate regression results for tankless water heaters: effect of fuel Wobbe number on full-burn NO_x emissions (ng/J) adjusted for water flow

Burner	N ¹	Mean ² (PG&E)	Δ CO / Δ25 WN ³	Lower 95% CI ⁴	Upper 95% CI ⁴	% change ⁵	p-value
TW01	12	24	0.6	0.4	0.7	2%	<0.001
TW02	12	16	3.7	2.6	4.8	23%	<0.001
TW03	12	18	0.3	0.1	0.4	1%	0.004
TW04	12	9	1.4	1.1	1.7	15%	<0.001
TW05	12	21	0.8	0.6	0.9	4%	<0.001
TW06	16	31	2.6	1.8	3.4	8%	<0.001

¹ Number of data points (burns).

² Mean value of emission metric with PG&E line gas; mean of results for 1, 2, and 3 or 4 gpm water flow.

³ Model estimate of change in pollutant emission factor (ng/J) per 25 Btu/scf change in fuel Wobbe number.

⁴ 95% confidence interval (uncertainty) around estimate of change in metric per 25 Btu/scf change in Wobbe.

⁵ Change in baseline emission rate (PG&E) resulting from increase in fuel Wobbe number of 25 Btu/scf.

4.0 Conclusions

4.1. Overview and Context

The overall aim of this research was to assess the impacts of natural gas variability on performance and pollutant emissions of residential appliances. Based on results and deficiencies of previous studies, the focus was on emissions of carbon monoxide (CO), nitrogen oxides (NO_x), nitrogen dioxide (NO₂), formaldehyde (HCHO), and the number of ultrafine particles (PN). Specific attention was focused on NO₂, HCHO, and PN as these were not examined in prior studies. This project also focused on emission rates during full-cycle operation, i.e., including transient modes, and on evaluation of in-use and used appliances.

The experimental program achieved these research objectives. Emission rates were measured for 13 sets of cooktop burners (CT), 12 oven burners (OV), five dedicated broiler burners (BR) plus one oven burner operated in broil mode, six tankless water heaters (TW), four central furnaces (CF), one wall furnace (WF) and five storage water heaters (WH). Each was operated with line gas provided by PG&E and (in all but one case) with two or more simulated liquefied natural gas blends having higher fractions of C₂–C₄ hydrocarbons and higher Wobbe numbers than the PG&E line gas. Emission rates were calculated by burn for both full-burn (including transient operation) and end-of-burn (more stable) conditions.

Consistent with past studies, there were no observable operational issues with any of the simulated LNG blends on any of these residential appliances.

Pollutant emissions were affected by operational mode and transient effects starting with ignition; modes included variations in temperature setting for ovens and water flow rate for TWs. PN emissions were additionally affected by the daily order of experiment for at least some burners.

Pollutant emissions varied by pollutant and burner, with some broad trends by burner group. Across all burners, the largest variability was observed for PN and CO—each of which varied from roughly 0 to emissions of thousands of ng/J (CO) or 10⁴/J (PN) for one or more burners at one or more conditions. CO emissions were generally higher for cooking burners and tankless water heaters, relative to other groups; the highest-emitting burner for CO was a new tankless water heater that was subsequently diagnosed by the manufacturer to have a faulty regulator. Cooking burners also had higher PN emissions compared with other groups. Formaldehyde data were obtained for most but not all burners evaluated; results are available for all of the ovens and tankless water heaters, twelve cooktops, three broilers, two central furnaces, and three storage water heaters. Formaldehyde emissions were lowest for storage water heaters (all <0.1 ng/J) and highest and most variable for cooktops, ovens, and tankless water heaters, collectively varying over the range of 0.1 to 5.5 ng/J. Nitrogen dioxide varied from 0.4 ng/J (WH03) to 18 ng/J (CT09). While storage water heaters had the lowest NO₂ emissions, the ranges of NO₂ for other burner groups overlapped substantially. NO_x emissions were the least variable within and between burner groups; the largest variability occurred among tankless water heaters.

The context for considering the effects of gas quality on pollutant emissions is the potential hazard or concern posed by each pollutant.

Carbon monoxide, NO₂, HCHO, and the number of ultrafine particles (as measured by PN) are primary pollutants which can adversely impact human health. The impact of a given quantity of emitted pollutant is inversely related to the amount of dilution that occurs before the pollutant is inhaled by humans. Indoor emissions of these pollutants can result in much higher concentrations and therefore are of greater concern than outdoor emissions. Gas quality effects on emissions of these primary pollutants are thus considered separately for cooking burners and vented appliances. Another key distinction is that, for indoor emissions, the focus is on potential emission changes for individual burners or appliances. Each individual appliance is a pollutant source for the residence in which it is located. For any individual cooking burner, gas quality-related changes to emissions are of interest if the following criteria are satisfied: (1) baseline emissions (with currently-distributed natural gas) of a given pollutant are at a level that presents a potential hazard, and (2) changes in the emission rate related to gas quality are non-negligible. The relatively small sample size of this study limits the certainty with which conclusions can be made for the entire population of residential cooking burners. It is possible that some effect could apply to a non-negligible fraction of the in-use cooking burner population with the effect not being present in the limited sample examined in this study. It is much less likely that an effect observed in one of the appliances that were evaluated in this study is unique or rare.

Relevant impacts on emissions of primary pollutants to outdoor air are assessed by considering mean baseline emission rates and changes across the population. High-emitting appliances are of interest to the extent that they represent a portion of the population and thus affect overall emissions.

The chief concern related to NO_x is its role in the photochemical processes that produce ozone (outdoors). As with outdoor emissions of primary pollutants, the chief consideration for NO_x is the effect of gas quality across the entire population of natural gas burners.

The relevance to overall ambient air quality of potential LNG-induced changes to the residential natural gas emission inventory depends not only on the magnitude of LNG-induced emissions change, but also on the baseline inventories (i.e., on the relative importance of residential gas appliances as contributors to the overall emission inventory). This is true for the primary pollutants and for NO_x (or CO) contributions to ozone formation. This latter assessment is beyond the scope of this task and is being addressed in a separate task. For this report, discussion will focus on the extent to which changes to gas quality will impact pollutant emissions from natural gas appliances. Since the majority of natural gas used for residential appliances is used for space heating (furnaces) and water heating, the impact on overall ambient pollutant emissions will derive primarily from these burners. At present, the vast majority of residential water heating is being done with conventional storage water heaters. Tankless water heaters comprise a rapidly growing fraction of sales and are considered for their potential future impact.

4.2. Effect of Gas Quality on Pollutant Emissions

The effect of gas quality on pollutant emissions was examined by bivariate and multivariate analysis of experimental results by burner. Pollutant emission factors (calculated for individual burns) were treated as dependent variables and fuel Wobbe number was treated as a continuous independent variable. Additional independent variables were oven temperature setting, TW water flow rate, and order of experiment.

Descriptions of gas quality effects in the following paragraphs are relevant to an increase of 25 Btu/scf in fuel Wobbe number. This roughly corresponds to the difference between the natural gas that is currently distributed to many of the large population centers in northern and southern California (with Wobbe number of roughly 1330–1340) to a substitute fuel with Wobbe number in the range of 1355–1365. The emissions change for a substitute fuel with Wobbe number of 1385 Btu/scf would be roughly twice the percentages quoted below. In the discussion below, a p-value of 0.15 is used to distinguish if calculated effects are statistically discernible. Readers are encouraged to refer to tables in the Results section to view confidence intervals around the mean effects cited below.

4.2.1. Primary Pollutants from Cooking Burners

Baseline CO emissions at or above 100 ng/J were measured in four cooktops, seven ovens (averaged across burns at 350°F, 425°F, and 500°F) and three dedicated broiler burners (excluding BR02, which was the oven burner operated on “broil” setting). The highest-emitting oven (OV11 at 528 ng/J) showed a 7% decrease in CO, whereas the highest emitting cooktop (CT09 at 823 ng/J) indicated a 3% increase with increasing fuel WN. Of the other cooking burners with baseline CO above 100 ng/J, the three cooktops showed increases of 11%, 15%, and 20%; the six ovens had increases of 3%, 5%, 10%, 12%, 15%, and 17%, and two broilers had increases of 7% and 9%. One of the broilers had no significant change and one had a decrease of 3% in CO emissions. Of the four cooktops with baseline CO in the range of 48–87 ng/J, one had no significant change and three had increases of 8%, 13%, and 27% with increasing fuel WN. Of three ovens with baseline CO in the range of 58–70 ng/J, emissions increased by 13%, 23%, and 46% with an increase of 25 Btu/scf in fuel WN. Collectively these results indicate that substantial increases in CO emissions are common for cooking burners, including those with moderate to high emissions. It is noteworthy, though not conclusive, that for the two highest emitting burners one had only a small increase and the other a small decrease in CO with increasing fuel WN.

Baseline NO₂ emissions above 10 ng/J were measured in five cooktops, three ovens, two dedicated broiler burners, and the OV02 burner used in broil mode (though not for the same burner used in oven mode). Of these, an increase in fuel WN produced statistically relevant ($p < 0.15$) NO₂ emissions changes in only three burners; increases of 5% and 10% occurred in two cooktops and a decrease of 4% occurred in one broiler. Of the eight cooktops with NO₂ emissions in the range of 5.0–9.6 ng/J, three had no statistically discernible change and the other had NO₂ increase in the range of 2%–7%. Seven ovens had baseline NO₂ in the range of 5.1–8.1 ng/J; of these, one had no change and the others had NO₂ increase by 4–9%, 12%, and 19% with increasing fuel WN. Of the two broilers with baseline NO₂ of 5.7 and 7.8 ng/J, the effect of

increasing fuel WN was +7% and no change. These results suggest that some of the highest NO₂-emitting cooking burners may have small (on the order of 10% or less) increases in NO₂; whereas many of the moderate NO₂-emitting burners will have NO₂ increase with increasing fuel WN.

Baseline formaldehyde emissions above 1.0 ng/J were measured in three of 12 cooktops, three of 12 ovens, and none of the three broilers for which valid results were obtained. The ovens had no change, a decrease of 10%, and no change with increasing fuel WN on baseline emissions of 1.0, 3.0, and 5.5 ng/J. For the cooktops the results were +10%, -14%, and no change to baseline HCHO of 1.0, 1.1 and 4.7 ng/J. At the next tier, two ovens and three cooktops with baseline emissions of 0.57–0.60 ng/J and 0.55–0.81 ng/J, respectively, showed no change in HCHO emissions with increasing fuel WN. Two broilers with baseline emission rates of 0.93 ng/J and 0.79 ng/J had HCHO increase by 4% and 10%. Of the seven ovens with baseline HCHO in the range of 0.25–0.49 ng/J four had no statistically relevant change, and the other three had increases of 6%–11%. Of the three cooktops with baseline HCHO in the range of 0.31–0.44, one had no change, and the others had HCHO increase by 17% and 19%, with increasing fuel WN. Collectively, these results suggest that only a small fraction of cooking burners with moderate or higher baseline emissions will see any substantial increase in HCHO with increasing fuel WN.

Particle number emissions varied widely across burns and appeared to be very strongly affected by oven temperature and the daily order of experiments. An effect of fuel WN on PN emissions was examined for three cooktops, three ovens, and one broiler for which a large and diverse (vis-à-vis experiment order) set of data was available. Statistically relevant effects of fuel WN, adjusted for experiment order, were seen for all three of the cooktops and the broiler, with two burners having PN increase (by 19% and 26%) and two burners having PN decrease (by 18% and 25%) with increasing fuel WN. For the three ovens, statistically relevant effects (of fuel WN on PN, adjusted for experiment order) were observed for three, two, and one of the burns. In all cases, PN decreased with fuel WN, by 5–18% and 52%. The key result is that PN emission rates were affected much more by recent operational history (as expressed in the order of experiments) than they were affected by gas quality. This effect occurred despite protocols that included prior pre-conditioning and a return of the appliance to room temperature before proceeding with subsequent experiments.

4.2.2. Primary Pollutants from Vented Burners

The most prominent finding related to CO from vented residential appliances is that emissions from the first five tankless water heaters (excluding TW06) were much higher than emissions from conventional storage water heaters. Baseline emission rates (mean across three water flow rates) for TW01–TW05 centered around 50 ng/J; whereas baseline CO emissions of the storage water heaters tested centered around 0 and in all but one case were < 1 ng/J. While residential natural gas water heaters currently contribute a very small fraction to overall CO in the major air basins of California—the vast majority of CO is from motor vehicles—the potential impact on ambient CO of a substantial shift to tankless water heaters should be examined. The most critical impact of concern may be the contribution of CO to ozone photochemistry, not direct

CO exposures. The occurrence of problematic units such as TW06 also deserves some attention. If such malfunctions were to occur at a rate of 1%, the effect on the baseline emission inventory for burners of this type would be 10% since baseline emissions of that unit were roughly an order of magnitude higher than other tankless water heaters. It is noteworthy that from the perspective of the user, this unit would not be regarded as problematic or malfunctioning. The unit would activate and start to heat water as expected with the start of water flow. Elevated pollutant emissions could occur without noticeably affecting performance. One important point is that tankless water heaters—which depend on relatively sophisticated control of both air and fuel flows—may be much more sensitive to faulty regulators; conventional storage water heater burners may be less sensitive to small variations in gas delivery rate.

Baseline CO emission rates were low for all furnaces tested, and as noted above, were negligible for all water heaters evaluated. And CO decreased with increasing fuel WN for the three highest emitting furnaces. TW06 had baseline CO emissions (mean across three water flow conditions) of 434 ng/J, and its emissions were estimated to increase by 56% for a 25 Btu/scf increase in fuel WN. The next highest CO-emitting TW had baseline emissions of 87 ng/J that were not sensitive to an increase in fuel WN. The next tier of three TWs had baseline emissions of 50, 47, and 37 ng/J, which changed with increasing fuel WN by -6%, -1%, and +54%, respectively. In summary, the burners tested in this study suggest that an increase in fuel WN may produce a net decrease in CO from the current population of furnaces and water heaters owing to a small decrease in CO from furnaces. Results of this study also suggest that as the prevalence of current technology tankless water heaters increases, baseline CO associated with water heating will increase and these emissions will tend to increase with increasing fuel WN.

Storage water heaters had the lowest NO₂ baseline emission rates of any burner group, below 3 ng/J for all five units tested. NO₂ changes with fuel WN were also small in absolute terms. Furnaces had somewhat higher baseline emission rates of NO₂, but none of the three highest (at 5.1, 5.7, and 9.7 ng/J) had NO₂ emissions change with fuel WN. Five TWs had baseline emissions above 5 ng/J; baseline emission of 8.9, 7.9 (TW06), 8.5, 6.6, and 6.1 ng/J corresponded to changes with fuel WN of +1, -2, +3, +10, and +3%, respectively. While the NO₂ emission rates for TWs were higher than for storage WHs, the difference of roughly a factor of four would require that a substantial percentage of the population of water heaters be replaced for this difference to affect overall NO₂ emissions associated with domestic water heating. Even if this change were to occur, results from this study suggest that an increase in fuel WN would not likely have a large effect on emissions from domestic furnaces and water heaters.

Formaldehyde results were obtained for two of five furnaces, three of five storage water heaters, and all of the tankless water heaters. The storage WHs had negligible HCHO emissions (≤ 0.05 ng/J). The two central furnaces had baseline HCHO of 0.16 and 0.38 ng/J with emissions decreasing by 12% and 17%, respectively, for an increase in fuel WN. Four TWs had HCHO above 0.5 ng/J. Baseline emission rates of 2.4, 2.0, 1.5, and 0.72 corresponded to a 2% decrease, no change, an 11% decrease, and an 8% decrease in HCHO with increasing fuel WN. These limited results suggest that increasing fuel WN could lead to a decrease in HCHO from current technology furnaces and water heaters. While substitution of tankless for storage water heaters could cause a relatively large increase in baseline HCHO, the inventory of HCHO from these

burners would tend to decrease with increasing fuel WN (though not nearly as much as the increase in going from storage to tankless).

Particle number emissions varied by burner within each group and by operating condition for each burner. Unlike CO, NO₂, and HCHO, storage water heaters as a group did not have substantially lower PN emission rates compared with furnaces and TWs. An effect of fuel WN on PN emissions was distinguished for two WHs, but the effect was small in absolute terms. As with cooking burners, PN emissions from vented burners appear to be affected much more by operating conditions than by fuel WN.

4.2.3. NO_x Emissions from All Burners

As noted above, the primary concern about NO_x emissions from natural gas appliances is related to ambient ozone formation. Since the majority (on the order of 80%–90%) of residential natural gas use is associated with space and water heating, and since NO_x emissions do not vary dramatically by burner group, the NO_x emission inventory from residential appliances will depend mostly on these two device groups. Of the five furnaces evaluated in this study, three of the four central furnaces had NO_x increase by 1%, 3%, and 4% with increasing fuel WN; there was no discernible change to NO_x emissions from the wall furnace. Two of the storage water heaters had NO_x increase by 1% and 2%. The first set of experiments with WH01 indicated a small decrease in NO_x, but the overall NO_x levels measured in this experiment were so low as to raise a question about their validity. These results are generally consistent with findings of previous studies (Singer 2007).

When considering these prior results, readers should take note that a fuel-induced change in emissions cited in units of ppm air-free (or 3% O₂) is not precisely equivalent to a change in fuel-based emission factor. Equation 6 of this report shows that the two units are related by the fuel-dependent factors of (mol C / MJ fuel energy) and (1/theoretical exhaust CO₂). (As a reminder, the latter quantity is the expected concentration of CO₂ from complete combustion with no excess air.) Using values of these quantities for a 1331 Wobbe number PG&E fuel (Exp. L139) and simulated LNG mixtures 2C (WN=1359), 1C (WN=1390), and 3C (WN=1419) produces the result that for the same air-free concentration, fuel-dependent emission factors for the simulated LNG mixtures would be 0.8%, 2.3%, and 1.9% higher than for the PG&E fuel. As described in the Methods section, these factors depend on the fuel composition, not just the Wobbe number. Readers are cautioned further that the adjustment is not additive, but multiplicative. Thus, a 2.5% increase in air-free NO_x concentration measured for fuel 1C would be equivalent to an increase of 4.9% ($1.025 * 1.023 = 1.049$).

The effect of an increase in fuel WN to overall NO_x emissions from the current population of residential appliances could be affected to a small extent by tankless water heaters (which comprise a small fraction of the installed water heaters), cooking burners, and other appliances such as clothes dryers and pool heaters. The magnitude of these effects will be estimated in a subsequent project task; the focus here is on changes to the emissions of each appliance technology. Compared to storage water heaters, TWs had lower baseline NO_x emissions but more sensitivity to fuel WN. NO_x increases of 8%, 2%, 4%, 1%, 23%, and 15% were found for TWs with baseline emissions of 31, 24, 21, 18, 16, and 9 ng/J, respectively. These results suggest

that an increase in fuel WN could reduce the NO_x benefits of a large scale switch from conventional storage to current technology tankless water heaters. The fuel sensitivity of ultra-low NO_x storage water heater burners was not assessed in this study. For the cooking burners, small NO_x increases of 1%–2% were found for 5 of 13 CTs and one oven, and increases of 3% and 4% were determined for two broilers. Decreases of 1%–2% were determined for one CT, six ovens, and two broilers.

Overall, the results of this study suggest that NO_x emissions from the current population of residential natural gas appliances would be only marginally affected (change of a few percent or less) by an increase in fuel WN of 25 Btu/scf.

4.3. Relevance to Overall Project Goals

Results presented in this report will be used in subsequent project tasks to assess potential impacts of gas quality changes on indoor pollutant exposures and outdoor air quality, including ozone formation. Outcomes of these tasks will be presented through interim project reports.

In separate project tasks, the Gas Technology Institute (GTI) is conducting experimental evaluations of gas quality impacts on the performance and emissions from industrial and commercial burners. Results from these evaluations will be presented via a detailed report for each burner tested. In a manner analogous to this report for residential appliance burners, GTI plans to compile their individual burner reports into an interim project report covering all of their experimental work. The results from the GTI study of commercial and industrial burners are informative of gas quality impacts across a wide range of burner technologies and scales. The results will be used to guide estimates of potential LNG impacts on sector-wide pollutant emissions in connection to the outdoor air quality impact assessment being conducted by LBNL.

The results of all research tasks being conducted by LBNL and GTI will be synthesized into a final project report that addresses the overall objective of this study, namely to evaluate the potential air quality and end-use device performance impacts of LNG use in California.

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6.0 Glossary

AGA	American Gas Association
ANSI	American National Standards Institute
APT	Automated Performance Testing System
B&K	Bruel & Kjaer
BR	Broiler burners
CEC	California Energy Commission
CF	Central furnaces
CO	Carbon monoxide
CP	Chemically pure
CPC	Condensation particle counter
CT	Cooktop burners
DMA	Differential mobility analyzer
DNPH	Dinitrophenylhydrazine
DR	Dilution ratio
EB	End of burn
ECD	Electron capture detectors
EI	Electronic ignition
FAF	Forced air furnace
FB	Full burn
FID	Flame ionization detectors
FVIR	Flammable vapor ignition resistant
GEE	Generalized estimating equations
GTI	Gas Technology Institute
HCHO	Formaldehyde
HEPA	High efficiency particulate air
HONO	Nitrous acid
HPLC	High performance liquid chromatography

LBNL	Lawrence Berkley National Laboratory
LNG	Liquefied natural gas
ME	Mixed effects
MJ	Megajoules
NDIR	Non-dispersive infrared
NO ₂	Nitrogen dioxide
NO _x	Nitrogen oxide
OV	Oven burners
PG&E	Pacific Gas and Electric Company
PN	Particle number
RH	Relative humidity
SA	Surface area of particles
SAS	Statistical analyses
SMPS	Scanning mobility particle spectrometer
SRI	SRI Instruments
T	Air temperature
TCD	Thermal conductivity detection
TSI	TSI Instruments
TW	Tankless water heaters
UFP	Ultrafine particles
UHP	Ultra high purity
UV	Ultraviolet
WF	Wall furnace
WH	Wall heaters
WN	Wobbe number

Appendix A. Project Advisory Committee

The following individuals contributed to this work through their service on the Project Advisory Committee. Affiliations are provided for identification purposes only and should not be construed as endorsement by the organizations of anything contained in this report.

Chuck	Baukal	John Zink Company, LLC
Leon	Brathwaite	California Energy Commission
Meredith	Colket	United Technologies Research Center
David	Collier	Eclipse Inc.
Donald	Dabdub	University of California, Irvine
Jorge	Gutierrez	Southern California Gas Co.
Ben	Ho	BP American Inc.
Peggy	Jenkins	California Air Resources Board
Marty	Kay	South Coast Air Quality Management District
Kimberly	Kemp	Pacific Gas & Electric Company
Edgar	Kuipers	Shell Trading Co.
Steve	Moore	San Diego County Air Pollution Control District
Glenn	Morrison	Missouri University of Science & Technology
Adriano	Pangelinan	Shell Trading Co.
Kevin	Shea	Sempra Utilities
Doug	Straub	US Department of Energy
Carl	Suchovsky	Gas Consultants Inc.
Jed	Waldman	California Department of Public Health
Bob	Wilson	Keyspan
Gary	Yee	California Air Resources Board
Steve	Ziman	Ziman Consulting
Ben	Zinn	Georgia Tech University

Appendix B. Selected Results for Particle Size Distributions

This appendix presents selected results for measured size-resolved particle number (PN) concentrations. These data were collected with a scanning mobility particle sizing (SMPS) system, as described in the Methods section of the report. The tables summarizing experiments conducted (found in the main report) and individual burner reports in Appendices C through J provide information about the experiments for which SMPS data were collected. The collection and analysis of these data were beyond the scope of this study; selected results are presented here to elucidate some aspects of particle emissions from residential natural gas appliances.

The SMPS system utilized a differential mobility analyzer (DMA) to separate particles by size coupled to a condensation particle counter (CPC) to count each group of size-segregated particles coming off the DMA. The system was configured to measure particles sized from 5 nanometers (nm) to 184 nm at one-minute intervals. The resulting data provide detailed information regarding the dynamics of particle formation and growth in the ultrafine size range (< 100 nm) that has been of particular concern to the exposure and health community.

Figure B-1 shows a time line of the SMPS data combined with measured concentrations of CO₂, O₂, and total PN concentration for cooktop CT05 for PG&E line gas and the two simulated LNG blends. The total PN data shown in Figure B-1 were measured independently by a separate CPC (see the Methods section of the main report). The colored matrix plot of SMPS data (bottom panel) is a useful way to show the dynamics of particle size distribution; the y-axis of this plot indicates particle diameter and the shading indicates the count-based particle distribution, $dN/d\log D_p$. The blue shading corresponds to higher numbers of particles at the corresponding particle diameter.

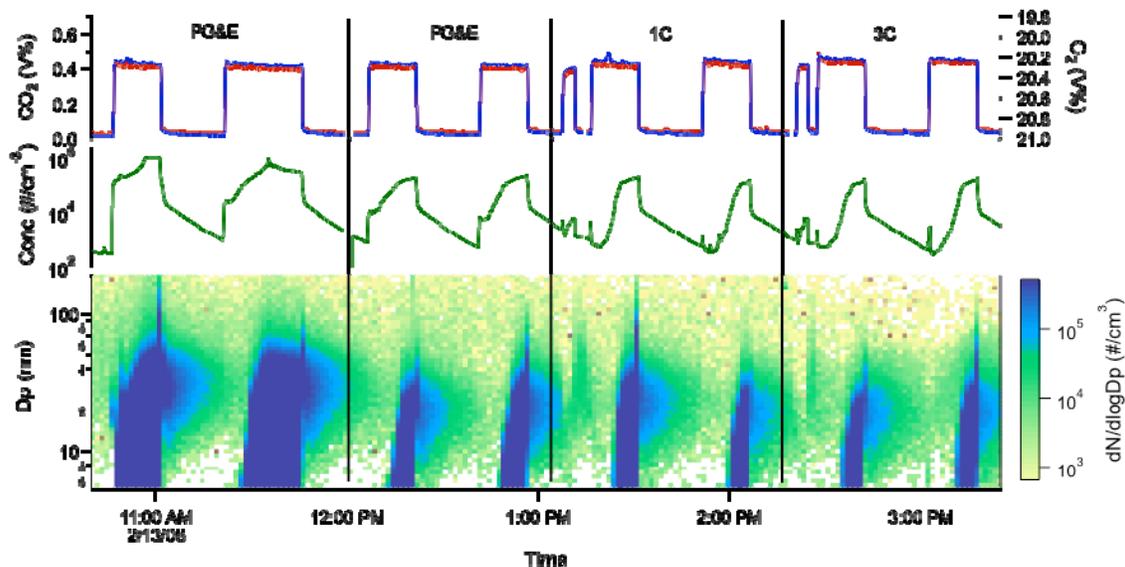


Figure B-1. SMPS size distribution measurements for cooktop CT05. The top panel shows concentrations of CO₂ (red line) and O₂ (blue line) as indicators of combustion, and the middle panel shows measured total particle concentration. Experiments with all gas mixtures are shown; horizontal lines indicate different individual experiments for the gas mixture indicated at the top of the figure.

The progression of total PN data in Figure B-1 reflects an order of day effect observed for PN from many cooking burners—namely that total PN was elevated on the first burn of the day and often for the second burn as well.

Figure B-2 provides an example exploration of the information contained in the size-resolved data. The left panel of this figure presents (again) the data shown for the third overall burn (the first burn on the second PG&E experiment) shown in Figure B-1. The right panel of the figure shows individual size distributions extracted from the time-resolved data. Each size distribution in the right panel corresponds to a specific time, as indicated by vertical lines in the left panel. The curves are color coded. The black curve shows the particle size distribution at the start of combustion. The total PN concentration at this time is elevated relative to the background before combustion, yet it is not obvious from the size-resolved data which particle sizes have increased in number. The increase in total PN at ignition could be related to particles above or below the range of the SMPS. Based on the observations noted below and no indication that the smallest particles (e.g., below the SMPS size detection limit) are nucleating (being formed) at this time, it may be presumed that the observed increase in total PN results from particles larger than the largest size bin of the instrument, i.e., larger than about 180 nm. At approximately 12:14 p.m., there is a sharp increase in number concentration of the smallest detectable particles (as shown by blue at bottom of left panel). As combustion proceeds, the number concentration remains high for the smallest particles (indicating ongoing formation) and the number concentration increases for larger particles. The distribution shown in blue in the right panel (peaking at 3×10^7) corresponds to the blue vertical line at 12:16 p.m. The progressive increase in concentration of large particles results from ongoing generation of smaller particles combined with increasing particle growth (presumed to be primarily through coagulation). This process continues, as shown by the red distribution (peaking above 10^7 for ~15 nm particles) and

corresponding to the vertical line at 12:20 p.m. When the burn ends at roughly 12:22 p.m., formation of the smallest particles ceases and the already formed smallest particles continue to grow to about 20–40 nm. The total PN concentration declines very gradually following combustion; this decline is much slower than the decline observed for CO₂ and other combustion products, indicating ongoing formation of particles. The size distribution remains relatively consistent through this period, with an example shown in green in the right panel below (corresponding to 12:25 p.m. with a peak of roughly 2×10^5).

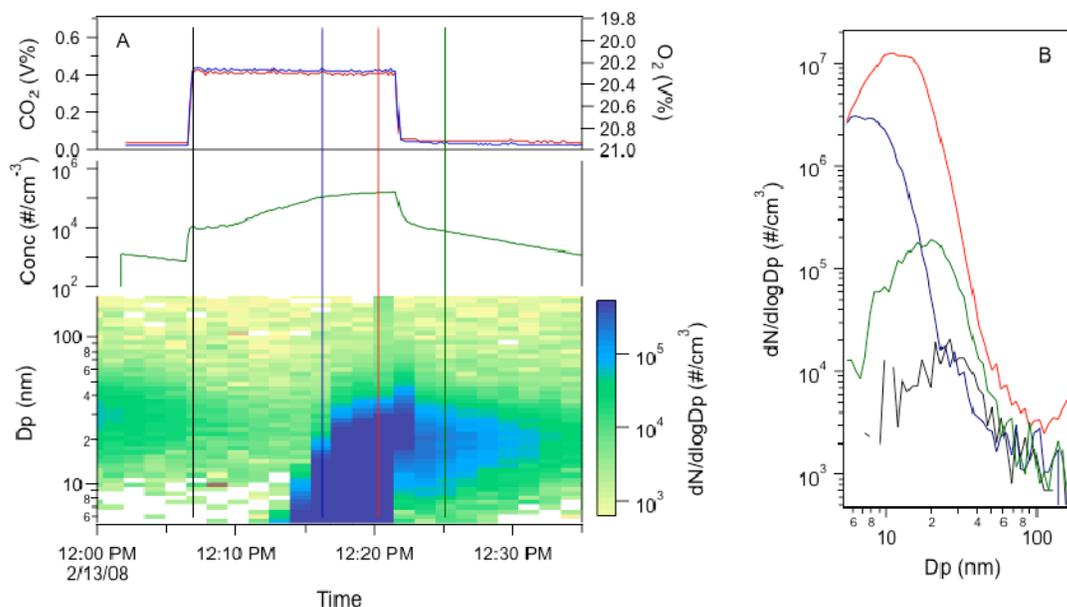


Figure B-2. Example of the correlation between time-resolved SMPS measurements and individual size distributions. The data shown are for cooktop CT05 and represent a subset of the measurements shown in Figure B-1.

The observed progression of particle size distribution shown in Figure B-2 can be considered in the terms of the physics of particle growth processes.

The smallest particles measured with this equipment, at around 5 nm, are termed *nucleation mode particles* because they are formed by nucleation from gas phase precursors. The initial size of nucleated particle depends on chemical composition and is thought to be around 1 to 1.5 nm for particles formed from condensable organic precursors (including particles formed from natural gas flames). These nucleated particles then grow by collision with other particles and condensation of additional mass. The appearance of 5 nm-sized particles indicates that the aforementioned processes have occurred at some previous time. The continuing presence of particles at these smallest sizes, as seen in CT05 data in Figures B-1 and B-2, indicates ongoing formation (nucleation) followed by growth to the sizes detectable by the particle counter used with the SMPS in these experiments.

Several observations regarding particle formation can be drawn from the data shown in Figure B-1. The size-resolved data indicate that the peak periods of particle number emissions (peaks

of particle numbers concentrations) are associated with nucleation and growth of the smallest particles. The terminal sizes of these particles following dilution are still well below the 100 nm cutoff that is commonly used to define ultrafine particles. The hazard of these small particles to health is backed by mechanistic, toxicological, and growing epidemiological evidence. Overall, the vast majority of particles emitted by CT05 and other cooktops appear to be in the ultrafine mode. Corollary to this point is the recognition that for every event in which 5–10 nm particles are observed, there are likely even larger numbers of smaller particles that are being nucleated on an ongoing basis. This nucleation process appears to be the largest contribution to particle emissions from the natural gas burners for which SMPS data were available. The physical chemistry of this process may be affected by fuel composition—including trace elements—and other factors indirectly impacted by gas quality. One example of such an indirect effect is possible changes in flame heat transfer and chemical kinetics that ultimately affect the products of incomplete combustion and thus particle formation. Examination of impacts at this level of detail was far beyond the scope of this project.

Size-resolved experimental measurements for cooktops CT03 and CT06 are shown in figures B-3 and B-4. The general features of particle emissions from these devices are similar to those seen in CT05. Particles are nucleated during combustion, and the size distribution grows in size and magnitude as combustion proceeds. All three cooktops show that particle nucleation is associated with the rapid increase in total PN concentrations and all have a long period of decay following the end of burner operation. The latter suggests ongoing emissions of condensable gases long after combustion ceases; this possibly could result from ongoing volatilization of condensable organics from hot surfaces such as the cooktop grill or the oven interior.

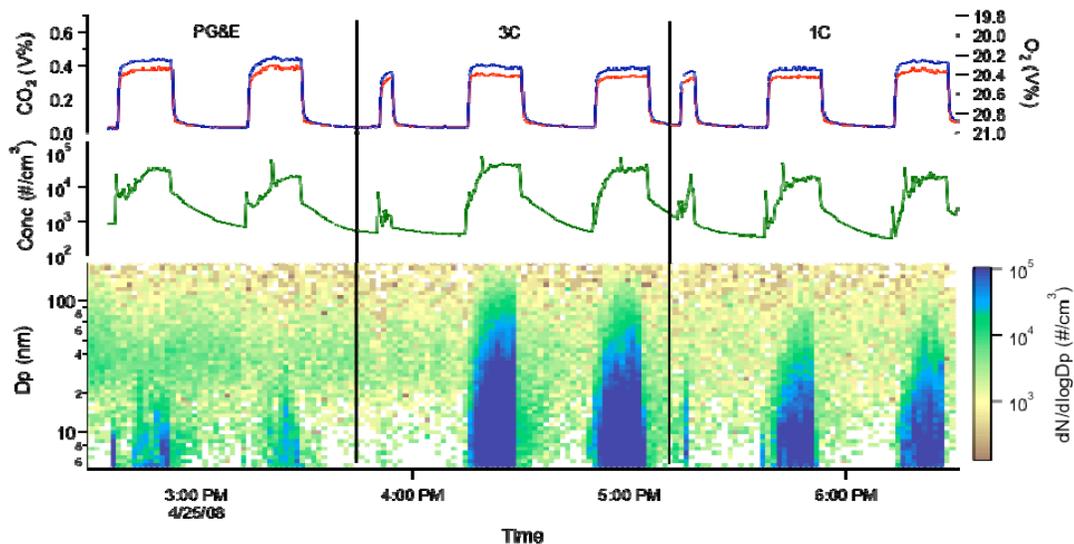


Figure B-3. SMPS size distribution measurements for cooktop CT03. The top panel shows concentrations of CO₂ (red line) and O₂ (blue line) as indicators of combustion, and the middle panel shows measured total particle concentration. Experiments with all gas mixtures are shown—horizontal lines indicate different individual experiments for the gas mixture indicated at the top of the figure.

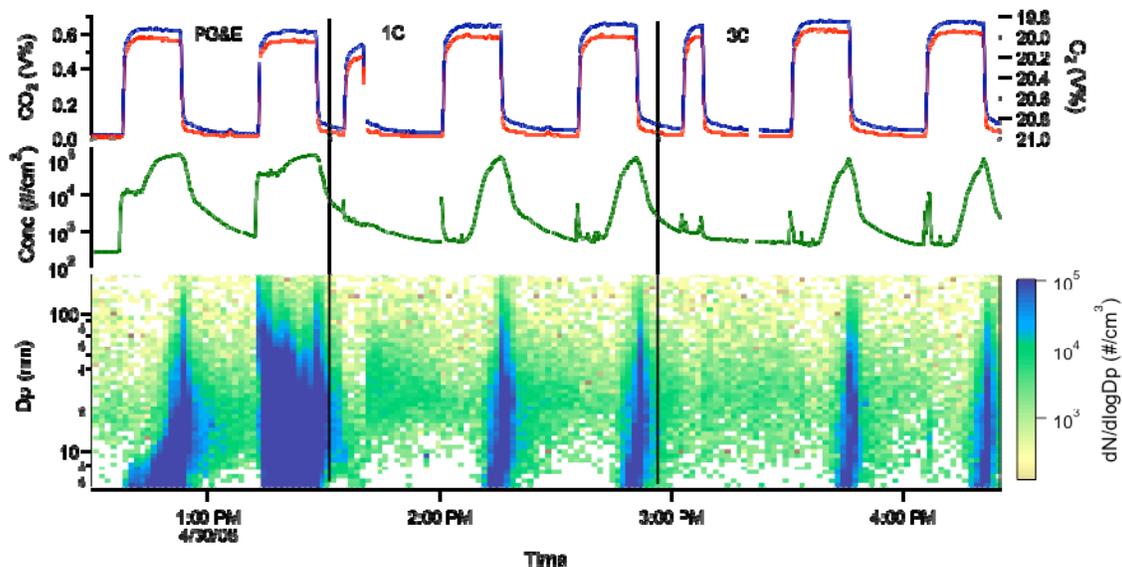


Figure B-4. SMPS size distribution measurements for cooktop CT06. The top panel shows concentrations of CO₂ (red line) and O₂ (blue line) as indicators of combustion, and the middle panel shows measured total particle concentration. Experiments with all gas mixtures are shown—horizontal lines indicate different individual experiments for the gas mixture indicated at the top of the figure.

Size-resolved SMPS data measured from two different ovens, OV03 and OV07, are shown in Figures B-5 and B-6, respectively. These two examples are reflective of the two different particle behaviors observed for the five different oven experiments for which size distribution data were obtained. Both experiments show that nuclei mode particles are produced during the long burn at the beginning of each oven temperature setting. Oven OV07 produces approximately an order of magnitude more particles than OV03, and exhibits nuclei mode particles present during the temperature maintenance burns. For OV07, the highest temperature burn (at 500 F, starting with the third broad CO₂ and O₂ peak of each experiment) is associated with the highest number of particle emissions. Oven OV03 exhibits small bursts of nuclei mode particles that correspond to the largest total PN emission events for that burner. But in contrast to OV07, the largest PN peaks for OV03 are associated with the first burn of each experiment (350 F temperature setting). In the OV03 experiment there also was a relatively consistent presence of 30-50 nm particles. That the concentration of these 30-50 nm particles is not obviously related to the total PN shown in the panel at the top of Fig B-6 is an issue requiring further investigation.

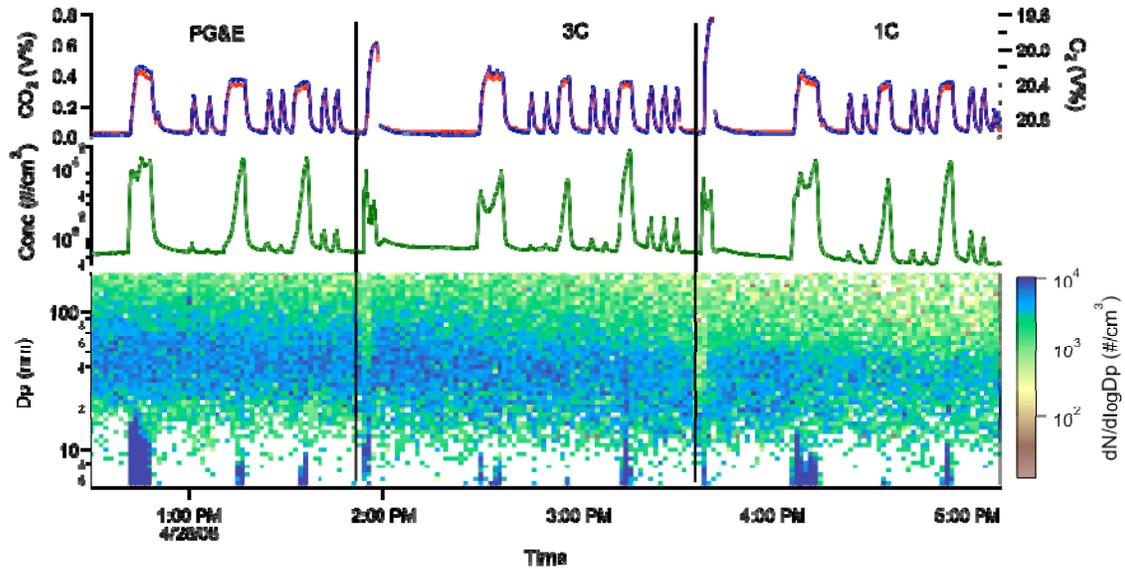


Figure B-5. SMPS size distribution measurements for oven OV03. The top panel shows concentrations of CO₂ (red line) and O₂ (blue line) as indicators of combustion, and the middle panel shows measured total particle concentration. Experiments with all gas mixtures are shown – horizontal lines indicate different individual experiments for the gas mixture indicated at the top of the figure.

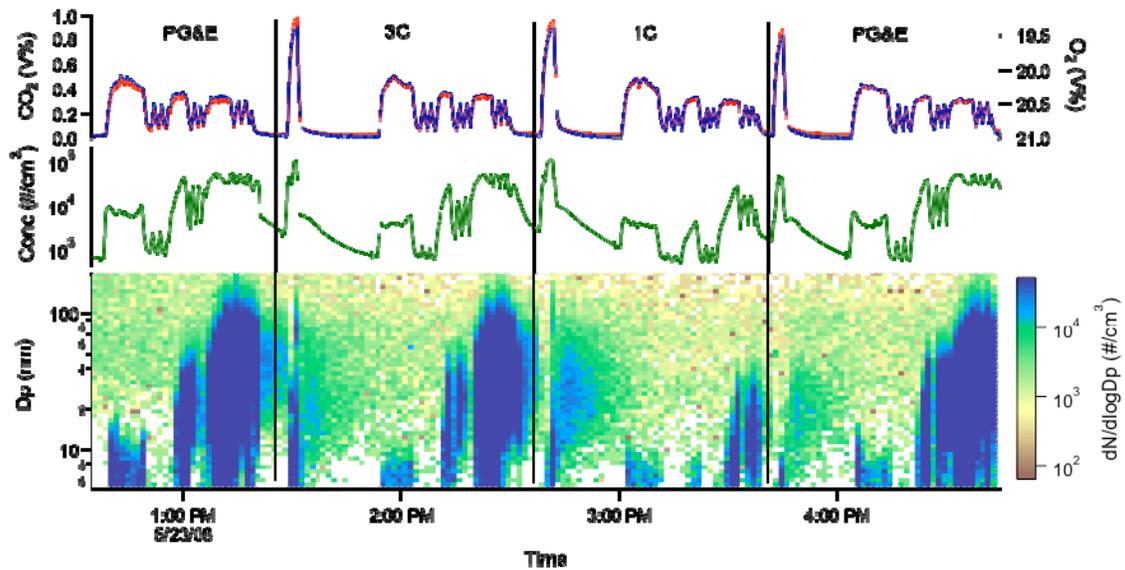


Figure B-6. SMPS size distribution measurements for oven OV07. The top panel shows concentrations of CO₂ (red line) and O₂ (blue line) as indicators of combustion, and the middle panel shows measured total particle concentration. Experiments with all gas mixtures are shown – horizontal lines indicate different individual experiments for the gas mixture indicated textually at the top of the figure.

The size-resolved data for broiler BR06 is shown in Figure B-7. For this burner, a short burst of nuclei mode particles occurs at each ignition event. This is followed by a sharp but brief drop in

PN emissions, then another burst of nucleation with sustained formation and growth to larger particle sizes (as seen in the CT and OV burners above). After combustion, the total particle number concentration and size distribution decay in a manner that is roughly similar to that noted above for the cooktop. It is interesting to note that the first experiment (with fuel mixture 3C) featured a much larger number concentration of particles (total PN plot) during the period between burns than were observed in the same period in later experiments. The explanation for this is unclear. The hypothesis that this is caused by prior deposits of condensed material is inconsistent with the heating cycle used to precondition each oven prior to first use. It is, however, conceivable that prior use of the oven burner led to migration of organic material from less to more accessible locations within the oven exhaust system.

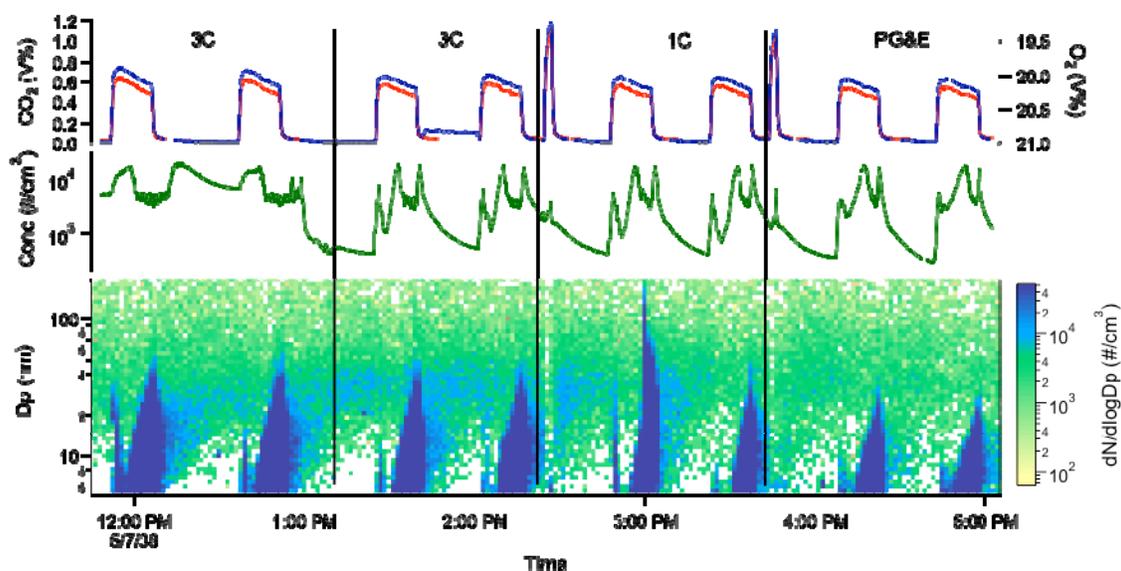


Figure B-7. SMPS size distribution measurements for broiler BR06. The top panel shows concentrations of CO₂ (red line) and O₂ (blue line) as indicators of combustion, and the middle panel shows measured total particle concentration. Experiments with all gas mixtures are shown—horizontal lines indicate different individual experiments for the gas mixture indicated at the top of the figure.

Figure B-8 shows the size-resolved particle data collected from tankless water heater TW06. Again, nuclei model particles are formed during combustion, with more of these particles formed during the final burn. The flow rate of four gallons per minute (gpm) during this burn likely lead to operation of more of the available burners than occurred during the earlier burns of one and two gpm. During this final burn, nuclei mode particles grow in during the combustion cycle in the manner seen in the cooktop and oven experiments, along with a post combustion decay of particles. With this device there again appears to be a pronounced effect of burn order on particle formation. After the first experiment, particle formation occurs mainly in the final burn (highest water flow rate) and the overall particle formation rate decreases with experiment order. As in the case of the broiler shown in Figure B-7, it appears that some particle forming material is liberated from heated surfaces when the cool unit is used for the first time.

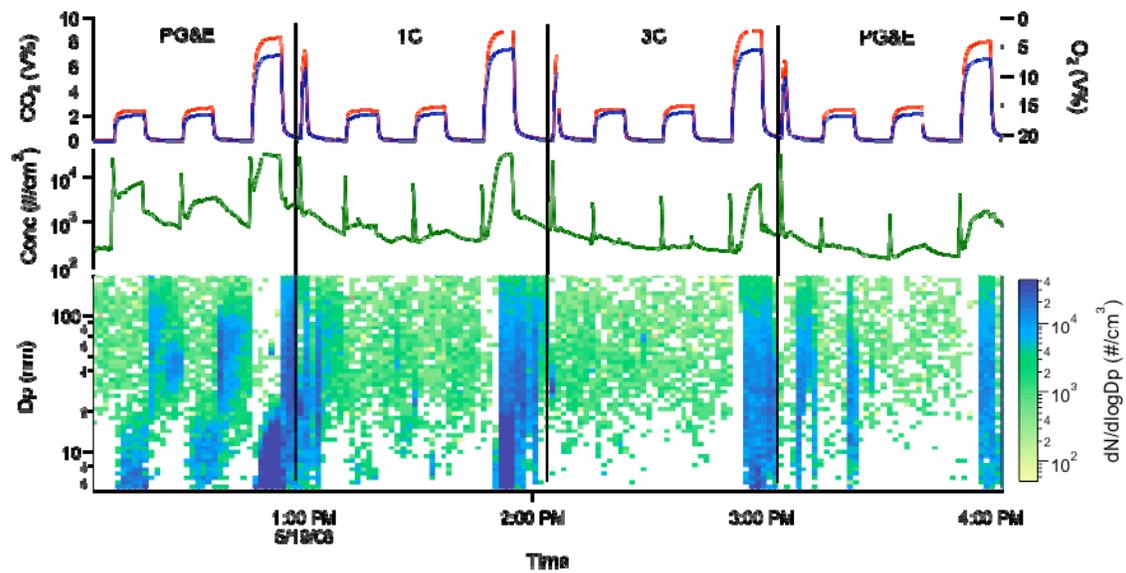


Figure B-8. SMPS size distribution measurements for tankless water heater TW06. The top panel shows concentrations of CO₂ (red line) and O₂ (blue line) as indicators of combustion, and the middle panel shows measured total particle concentration. Experiments with all gas mixtures are shown—horizontal lines indicate different individual experiments for the gas mixture indicated textually at the top of the figure.

Additional Appendices

Appendix C. Summary Reports for Cooktops CT01-CT07

This appendix is available in a separate volume, CEC-500-2009-APC.

Appendix D. Summary Reports for Cooktops CT08-CT13

This appendix is available in a separate volume, CEC-500-2009-APD.

Appendix E. Summary Reports for Ovens OV01-OV07

This appendix is available in a separate volume, CEC-500-2009-APE.

Appendix F. Summary Reports for Ovens OV08-CT13

This appendix is available in a separate volume, CEC-500-2009-APF.

Appendix G. Summary Reports for Broiler Burners

This appendix is available in a separate volume, CEC-500-2009-APG.

Appendix H. Summary Reports for Furnaces

This appendix is available in a separate volume, CEC-500-2009-APH.

Appendix I. Summary Reports for Storage Water Heaters

This appendix is available in a separate volume, CEC-500-2009-API.

Appendix J. Summary Reports for Tankless Water Heaters

This appendix is available in a separate volume, CEC-500-2009-APJ.