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Hazardous air pollutant emissions from gas-fired combustion sources: emissions and the effects of design and fuel type

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Abstract

Air emissions from gas-fired combustion devices such as boilers, process heaters, gas turbines and stationary reciprocating engines contain hazardous air pollutants (HAPs) subjected to consideration under the federal clean air act (CAA). This work presents a recently completed major research project to develop an understanding of HAP emissions from gas-fired boilers and process heaters and new HAP emission factors based on field emission tests of gas-fired external combustion devices used in the petroleum industry. The effect of combustion system design and operating parameters on HAP emissions determined by both field and research tests are discussed. Data from field tests of gas-fired petroleum industry boilers and heaters generally show very low emission levels of organic HAPs. A comparison of the emission data for boilers and process heaters, including units with and without various forms of NO_x emission controls, showed no significant difference in organic HAP emission characteristics due to process or burner design. This conclusion is also supported by the results of research tests with different burner designs. Based on field tests of units fired with natural gas and various petroleum industry process gases and research tests in which gas composition was intentionally varied, organic HAP emissions were not determined to be significantly affected by the gas composition. Research data indicate that elevated organic HAP emission levels are found only under extreme operating conditions (starved air or high excess air combustion) associated with poor combustion. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The petroleum industry operates a large number of gas-fired boilers and process heaters for oil exploration, production, refining, and transportation. Section 112 of the CAA requires the US Environmental Protection Agency (EPA) to identify source categories that include major sources of hazardous air pollutants (HAPs) and to issue technology-based regulations for these source categories. EPA has listed seven source categories which include boilers and process heaters. In developing regulations, EPA must consider the application of "maximum achievable control technology" (MACT) to each source category. The clean air act (CAA) defines the MACT emission standard as the average emissions achieved by the best performing twelve percent of the sources in a source category. As such, emission

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standards are different for each source category, but the evaluation process is similar. EPA is evaluating MACT standards for industrial boilers and process heaters, which are scheduled to be proposed in 2000.

When the EPA first began the MACT rule development process for industrial boilers and heaters, there were few reliable data for HAP emissions from gas-fired devices and a thorough understanding of the physical and chemical processes controlling HAP formation, destruction, and escape in combustion systems did not exist. Two petroleum industry projects have since improved both the database of emission factors and the mechanistic understanding of processes controlling HAP emissions. This study presents and discusses the results of these studies:

- A three-year research program initiated by the petroleum environmental research forum (PERF) to determine the impacts of burner design, fuel properties, and furnace operating conditions on the formation and emissions of HAPs from gas fuel fired external combustion systems. This program included fundamental investigations consisting of lab-scale experiments and theoretical chemical mechanism development, and HAP emission measurements from full-scale refinery burners operated in a research furnace under well-defined conditions;
- A six-year field test and air toxics emission factor-development program for the California petroleum industry combustion sources. This program featured extensive HAP emission data screening and analysis to develop reliable emission factors.

2. PERF project 92-19: The origin and fate of toxic combustion by-products in refinery heaters

Gas-fired boilers' and process heaters' field test data in the 1980s included a small number of measurements showing the presence of certain HAPs at levels higher than expected based on hydrocarbon combustion principles. This prompted questions regarding the mechanisms by which these emissions could possibly occur and provided the genesis for a research program to answer these and other questions. In 1992, the PERF initiated a Cooperative Research and Development Agreement (CRADA) with the US Department of Energy to perform the "PERF Project 92-19: The origin and fate of toxic combustion by-products in refinery heaters: research to enable efficient compliance with the clean air Act". This project was an experimental and fundamental investigation of chemical and physical mechanisms governing organic HAP formation, destruction, and emissions (Seebold, 1997a,b). Although EPA maintained a strong interest in the project, they could not provide a direct funding of the program due to budget constraints. Nevertheless, EPA provided in-kind support throughout the program. EPA staff members actively participated in review meetings and workshops held periodically during the program and co-authored a report (Miller et al., 1996) comparing the research tests' results with field test data available at the time. Thus, the EPA was actively involved both in test planning and evaluation of the test results.

The PERF Project included two main activities:

- Fundamental investigations of HAP formation in gas fuel flames including lab-scale experiments and theoretical chemical mechanism development.
- Experimental full-scale burner tests in a research furnace to characterize HAP emissions from various burners over a range of operating conditions.

2.1. Fundamental investigations of HAP formation

Aromatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) may readily be formed in the most fuel-rich processes occurring in the flames of practical combustion devices. Fuel-rich pockets which escape the high-temperature fuel-lean portions of the flame due to inadequate mixing can result in aromatics and PAH emissions from combustion. Fundamental investigations of aromatics and PAH formation included flame studies at the Sandia National Lab (SNL) and the University of California at Los Angeles (UCLA) and development of chemical kinetic mechanisms at the Lawrence Livermore National Laboratory (LLNL). SNL studied the effects of fuel composition and excess air on burner fluid mechanics and flame structure. Aromatics and PAHs in premixed and diffusion hydrocarbon flames were characterized at UCLA. The premixed flame studies simulated regions of a process heater burner where fuel and air are mixed rapidly and fuel-rich pockets of gas are formed and heated by the surrounding flames producing aromatics and PAHs. Counterflow diffusion flames were used to simulate areas of a process heater where the limiting factor in combustion is the mixing of fuel and air. LLNL developed new chemical kinetic mechanisms for the formation and destruction of air toxic species in gas-fired process heaters and boilers. The chemical kinetic mechanism work showed aromatic rings first evolve from the combination of resonantly stabilized propargyl radicals and from the combination of propargyl and allyl radicals. Once aromatics are formed, it becomes possible to form PAHs. A new kinetic pathway to larger ring PAHs was discovered with the cyclopentadienyl radical as the building block. Low levels of oxygen can promote cyclopentadienyl radical, and thus PAH formation. Another pathway that was found was the reaction of phenyl and propargyl to form naphthalene and H atoms (Marinov et al., 1998). A reasonable agreement between mechanism results and the experimentally observed trends in the simple flames experiments at UCLA was achieved (Castaldi and Senkan, 1996; Marinov et al., 1996,1999; Senkan and Castaldi, 1996). These new mechanisms were used in conjunction with the flame structure data produced at SNL to develop models for predicting the formation and destruction of combustion by-products. Modeling results for fuel-lean conditions, identical to those evaluated in the experimental full-scale refinery burner tests, showed PAH concentrations well below experimentally detectable limits, suggesting that emissions observed in practice are caused by mixing or temperature "failure modes" that occur in practical turbulent diffusion flames rather than due to chemical limitations alone.

2.2. Experimental full-scale refinery burner tests

The results of an individual field emission test are subjected to many uncontrollable factors including process variations and ambient contamination, in addition to the general difficulty of making complex field measurements. Therefore, the uncertainty of measurements made in the field are greater than that may be achieved in a laboratory setting. Also, controlled variation of process parameters and fuel composition in the field are rarely implemented since it can impact process production and can be extremely costly. This is particularly true for oil refineries. The PERF full-scale burner testing program afforded an opportunity to vary the combustion process over a wide range of conditions while making high-quality organic HAP emission measurements.

The objective of the PERF testing program was to establish the level of HAP emissions from different full-scale burners used in petroleum industry heaters and boilers and to determine the impacts of different operating conditions and fuel properties on HAP emissions. The test matrix included:

- Conventional and low-NO$_x$ burners.
- Fuel property variations of heating value, fuel spikes (ethylene, propylene), and hydrogen to simulate a wide variety of refinery fuel gas compositions.
- Operating conditions with the variations of stoichiometric ratio (SR = actual air/theoretical air required for complete combustion), air staging, and mechanical burner failure modes.

The testing included operating conditions and fuel properties within the normal range of operation for these burners and at extreme "failure mode" conditions well outside the normal range of operation.

2.2.1. Approach

The full-scale burner testing was performed in the Burner Engineering Research Laboratory (BERL) furnace, located at the Sandia National Laboratories Combustion Research Facility in Livermore, California. The BERL is a two-story laboratory as shown in Fig. 1. The facility accommodates full-scale burners with firing

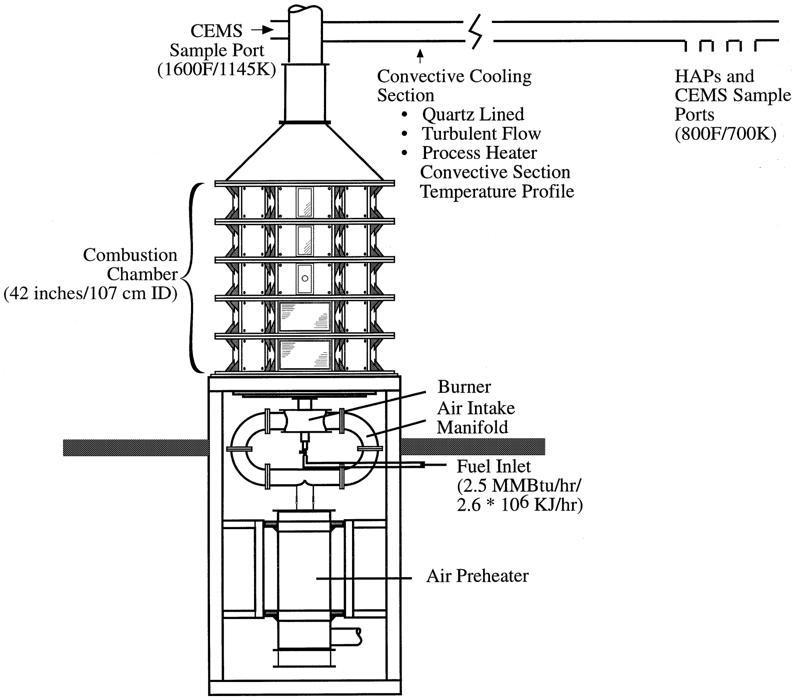


Fig. 1. BERL furnace at Sandia National Laboratory.

rates ranging from 0.1 to 2.6 MJ/h. The testing included a conventional diffusion flame burner (CDFB) and a low-NO_x diffusion flame burner (LDFB). The furnace enclosure has an octagonal cross-section and was assembled with six refractory-lined spool sections, each 33 cm tall and 110 cm inner diameter. This furnace configuration provided a furnace exit temperature of approximately 1100 K during the normal operating conditions for the burners. Window panels for optical diagnostics and small ports for sample probes' access were fitted into the spool sections as needed. The combustion air bypassed the preheater to the burner during these tests. Fuel was supplied from natural gas pipes which was mixed with bottled propane, nitrogen, hydrogen and/or fuel spikes (ethylene, propylene) to produce the desired fuel properties. The furnace exhaust was continuously monitored for carbon monoxide (CO), carbon dioxide (CO_2), oxygen (O_2), oxides of nitrogen (NO_x), nitrous oxide (N_2O). and unburnt total hydrocarbon (THC) concentrations. Furnace parameters were monitored and recorded by a PC-based data acquisition system (DAS).

Gases exited the furnace to a convective cooling section (CCS). Chemical kinetics calculations (Pitz et al., 1994) for a plug flow reactor have shown that significant oxidation of the light organic species (e.g., aldehydes, benzene) can be expected at the mean exhaust cool-down rates and residence times commonly encountered in refinery process heaters, convective heat transfer sections. Similar calculations for the destruction of the semi-volatile organics (e.g., PAH) were not available at the time of testing, but it was presumed that these species are more resistant to oxidation than the more volatile species. Thus, the rate of cooling of the exhaust gases was expected to have the potential to exert a strong influence on the level of emissions of some, if not all, of the air toxic species. The CCS was designed to provide a linear temperature/time history, variable over the range of mean cooling rates commonly encountered in refinery process heaters, 100–300 K/s, with BERL furnace exit/CCS entrance temperatures in the range of 1000–1500 K and HAP sampling location at 700 K. The CCS is a coflow heat exchanger and is quartz-lined so that the surface in contact with the furnace exhaust gases is noncatalytic. It has a turbulent gas flow to keep the exhaust gases well mixed.

The emission measurements focused on those HAPs expected to be present in measurable quantities. The HAP selection began with a review of the CAA HAP list and identification of those substances considered likely to be present at levels of concern in the fuel gas. Field test data and chemistry studies on HAP formation were used to guide the selection of target HAPs. Many of the substances, such as pesticides, are not produced in combustion processes and were eliminated from consideration since they were not present in the fuels. Chlorine is below measurable levels in natural gas (Chao and Attari, 1995) and since pure commercial gas mixtures were used for simulated process gas testing, chlorinated substances (e.g., polychlorinated dioxins and furans, hydrochloric acid) were not measured. Metallic HAPs, while some may be present in very small quantities in natural gas and other gases, are not transmuted during the combustion process. Thus, metal emissions are dependent mainly on the levels present in the fuel rather than on the combustion process variables of interest to the PERF project and metals were not selected for measurements. Other considerations in selecting target HAPs were: identification of those HAPs and other hydrocarbons which would be useful in elucidating HAP formation, consumption, and emission mechanisms; HAPs which may provide a link between the research furnace and actual field unit emission data; and HAPs believed to be of most significance on either a mass emission or health risk basis. As a result of this selection process, the measurements focused on volatile and semi-volatile organic compounds.

Four test methods were used to characterize the organic compounds targeted in the PERF study:

- Proposed draft EPA SW-846 method 0040 (EPA, 1995) was used to measure light volatile organics and hydrocarbons. Method 0040 uses integrated bag sampling with analysis by gas chromatography/flame ionization detector/photoionization detector with cryogenic pre-concentration to obtain lower detection limits.
- EPA method 0031/5040/5041/8240 (EPA, 1995) was used to measure volatile organics. Samples are concentrated by collection on Tenax sorbent with analysis by purge-and-trap gas chromatography/mass spectrometry.
- California air resources board (CARB) method 429 (CARB, 1992) was used to measure PAHs. CARB 429 samples are concentrated by collection on XAD-2 sorbent with analysis by high resolution gas chromatography/high resolution mass spectrometry. This method is similar to EPA SW846 methods 0010/8270, except that high (rather than low) resolution analytical techniques are used.
- CARB method 430 (CARB, 1991) was used to measure formaldehyde and acetaldehyde. CARB 430 samples are collected in impingers containing dinitrophenylhydrazine solution with subsequent analysis by high performance liquid chromatography with ultraviolet detection. The sampling and analysis procedures are similar to EPA SW-846 methods 0011/0011A, except that sampling is not isokinetic and screw-top midget impingers are used to reduce sample contamination, which is a chronic problem with this method.

The methods were carefully selected and represented the most sensitive and selective source test methods available for this application. Another methods, selection criterion was to provide a link between the research test and the field test results. Thus, it was desirable to use methods similar to those used to characterize actual field units so that results would be comparable and acceptable to regulatory agencies.

The PERF testing program was not subjected to regulatory constraints. The goal was to provide the highest-quality data, able to withstand regulatory and scientific scrutiny, within the resources available. A detailed quality assurance project plan (QAPP) was prepared based on EPA category II requirements (on a scale of I–IV, with I being the highest) – suitable for rulemaking/policy decisions in conjunction with other results (Simes, 1991). The QAPP was reviewed by the EPA office of air quality planning and standards staff and the EPA office of research and development staff. They provided many helpful comments which were incorporated in the final plan prior to testing. The test methods and quality assurance/quality control procedures used throughout the program are extensively documented in the final measurement report (McGrath et al., 1997).

2.2.2. Results: effect of operating and design parameters on HAP emissions

Fig. 2 shows the concentrations of key organic HAPs detected in all the PERF tests (McGrath et al., 1997). The data are divided into two broad categories according to operating conditions: "normal range" conditions, which duplicated the range of conditions normally encountered in actual process heaters at oil refineries, and "extreme failure mode" conditions, which are not considered representative of normal field operation but which were investigated in the research furnace to elucidate organic HAP emission mechanisms. The majority of detected data in normal operating conditions lies just above the limits of detection, with concentrations generally on the order of 1–100 parts per billion or less. With the exception of formaldehyde, significantly higher concentrations were encountered only in the extreme failure mode operating cases. This figure only shows measurements with detectable HAP levels, measurements with HAP levels below detection limits are not shown. For example, benzo[a]pyrene was not detected under normal operating conditions and was rarely detected even during tests at the extreme operating conditions.

A considerable range of excess air levels and simulated refinery fuel gas compositions and heating values was evaluated to encompass the range of operating conditions normally encountered in actual process heaters. These operating conditions included

- $1.1 \leqslant \mathrm{SR} \leqslant 1.5$;
- 30 000 kJ/Nm^3 $\leqslant$ fuel higher heating value (HHV) $\leqslant$ 56 000 kJ/Nm^3;
- 0% $\leqslant$ Hydrogen concentration $\leqslant$ 33%;
- propylene spike = 8%;
- ethylene spike = 18%.

Fig. 3 shows the results of the HAP measurements during the normal range operation tests. These normal range tests included a "baseline" operating condition (SR = 1.25, HHV = 39 000 kJ/Nm^3) that was repeated numerous times throughout the program to verify the absence of undesired changes in operating or measurement conditions and to define the inherent variability of the results. Thus, the baseline test results provide a sound basis for the comparison of other test conditions.

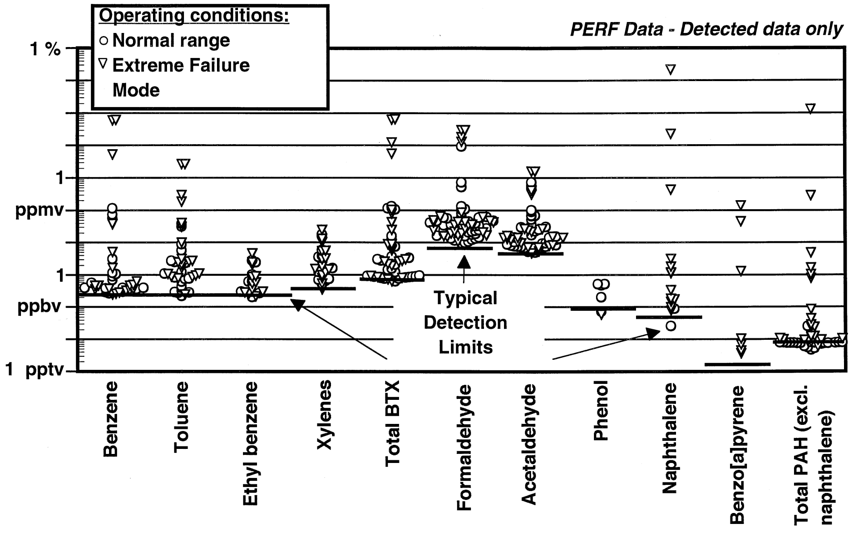


Fig. 2. Concentrations of HAPs detected during full scale refinery burner research tests.

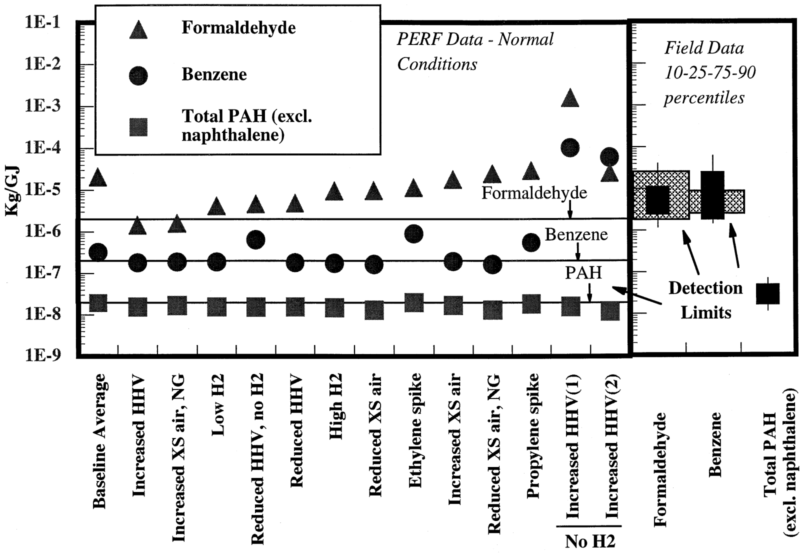


Fig. 3. HAP emissions during normal range operating conditions and comparison with field emission data.

Average emissions of benzene and PAH, at the baseline condition, were essentially at the detection limits and formaldehyde emissions were slightly above detection limits. Total PAH in Fig. 3 includes the sum of eighteen individual substances, excluding naphthalene. Naphthalene is a decomposition product of the sorbent used to collect PAH samples and therefore, a potential contaminant. It is often detected well above the analytical detection limits in both samples and in quality control blanks. It may appear in samples or in blanks even when the other samples are clean since decomposition of the sorbent is sometimes unavoidable. Therefore, naphthalene was excluded from the total in this and the following figure to enable a more valid comparison to field data. Undetected data are included individually or in average results at the full detection limit in Fig. 3 and the following charts, unless noted otherwise. Benzene, formaldehyde, and total PAH emissions generally remained near or below detection limits for the range of normal operating conditions. Generally, PAH other than naphthalene were not detected. Formaldehyde was detected but remained near detection levels in most tests. In one test (labeled "No H2, Increased HHV (1)"), benzene and formaldehyde showed an unexpected increase. Formaldehyde results were not reproduced when this test was repeated at an even higher fuel HHV (labeled "No H2, Increased HHV (2)"), but benzene results were consistent. This illustrates how formaldehyde measurements can occasionally be subjected to unexpected variability even under the best circumstances.

Fig. 3 also shows a comparison of the data from the pilot-scale furnace to actual field data. The figure illustrates the range of emissions measured in the field from the actual petroleum industry boilers and process heaters. Formaldehyde and total PAH data agree well, given the variability of the results. The field data indicate benzene emissions as somewhat higher than benzene measured in the pilot-scale tests. In most cases, this is the result of including undetected results in the field data at the full minimum detection limit. The test methods used for the PERF program were more sensitive than those used for most field tests.

A number of tests were conducted with the burner operating at extreme failure mode conditions that were well outside the normal operating range. These extreme conditions investigated organic HAP emission mechanisms and included:

- Extreme air quenching – $SR > 3$;
- Extreme air starvation – $SR < 1$;
- Mechanical failures: cold probe in flame and maldistribution of burner air;
- Fuel $HHV = 78\,000$ kJ/Nm^3;
- Poor air fuel mixing-burner $SR < 1$ and additional air injected from the sides of furnace.

Fig. 4 shows the results of HAP measurements from tests under extreme operating conditions. The average baseline levels are shown in this figure as reference values. The data show that organic HAP emissions were the same as baseline levels with poor fuel/air mixing (including simulated air staging conditions) or simulated mechanical failures. Organic HAP emissions increased only under conditions of extreme air starvation (i.e., $SR < 1$, insufficient air was added for complete combustion) or extreme air quenching (i.e., at very high excess air levels approaching the lean extinction limits of the burner). Fig. 4 also shows "smoke spot" readings

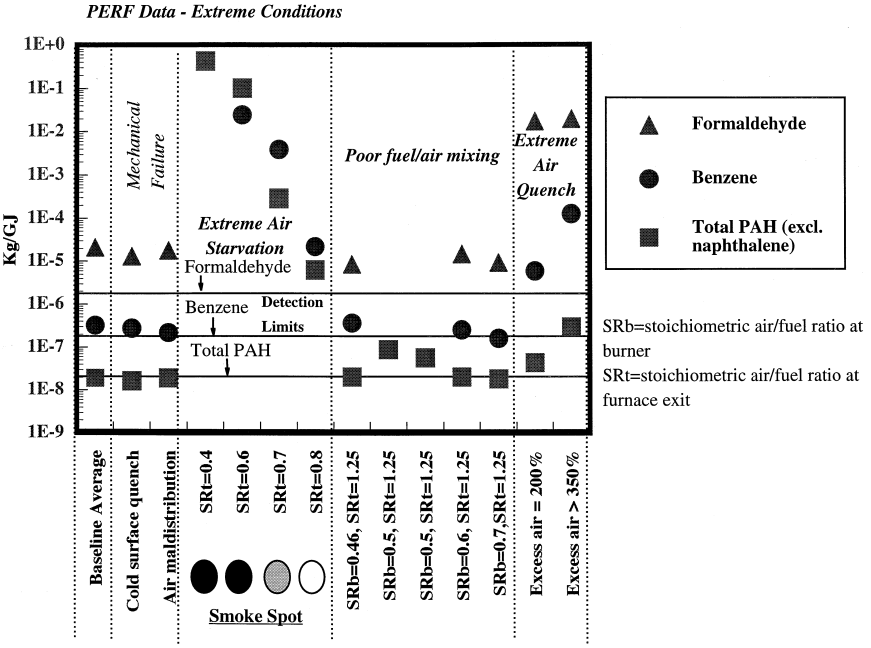


Fig. 4. HAP emissions during extreme failure mode operating conditions.

taken from the PAH sampling trains particulate filters from the starved air test conditions. The smoke spots' darkness is an indicator of the sooting levels during these test conditions. The starved air data shows soot and PAH levels increasing as the stoichiometric ratio is reduced below one. The 78 000 kJ/Nm^3 fuel HHV test data are shown in Fig. 3 and labeled "No H2, Increased HHV (2)".

NO$_x$, CO and THC were measured concurrently with the organic HAP measurements during the PERF tests. The low-NO$_x$ burner produced substantially lower NO$_x$ emissions than the conventional burner without impacting organic HAP, CO or THC emissions. Organic HAP emissions from the low-NO$_x$ burner lie within the range seen with the conventional burner as shown in Fig. 5.

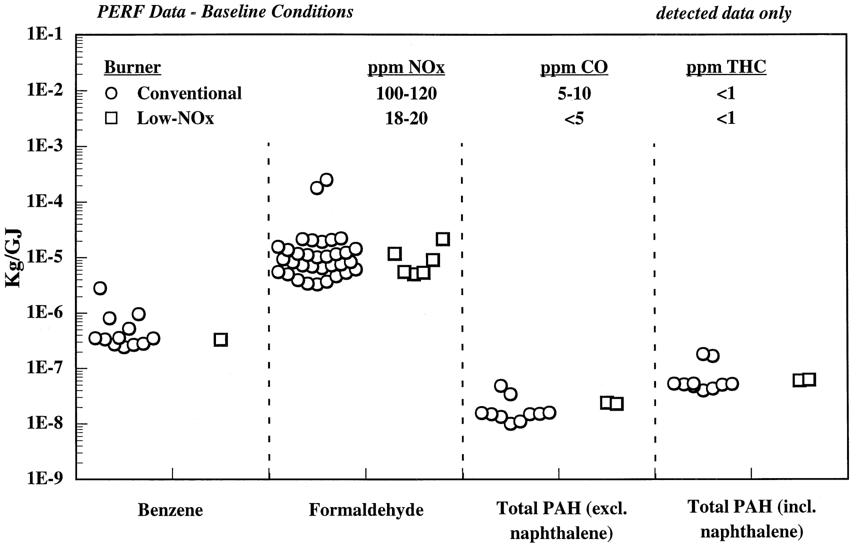


Fig. 5. Comparison of HAP emissions from conventional and low-NO$_x$ burners.

3. HAP emission factors development

In 1988, the California state legislature passed the Assembly Bill 2588 (AB2588), entitled the *Air toxics "hot spots" information and assessment Act of 1988*. This California law required the industry to make an inventory of the emissions of more than 300 (which later grew to more than 700) "air toxics" for the purposes of assessing potential health risk to communities surrounding emission sources. These air toxics include most of the 188 HAPs listed in Section 112 of the CAA. Source testing to characterize air toxics emissions was required for sources where reliable emission factors or engineering estimating techniques did not exist. All source testing was performed under strict guidelines for test methodology specified by the CARB. In 1989, the Western States Petroleum Association (WSPA) initiated development of industry-wide air toxics emission factors with a pooled source testing program for combustion devices. Two rounds of testing were performed, in 1990 and 1992. The results of this testing program were organized into a common database of air toxics emission factors to provide common and consistent emission factors for petroleum industry combustion devices. This database has become known as the WSPA database (Hansell et al., 1992). The source types included in the database (Table 1) are:

- Externally fired combustion devices (boilers and process heaters, with and without NO_x emissions controls, and glycol reboilers).
- Internal combustion engines (reciprocating and gas turbines), with and without NO_x and other air emission controls.
- Direct-fired combustion devices (asphalt blowers, coke calciners).

The database includes units firing a variety of gaseous and liquid fuels, including natural gas and petroleum industry process gases (e.g., refinery gas, field gas, production gases). It is important to note that the field test emission database only includes information on sources located in California. California generally has more stringent air pollutant emission regulations than other states and some sources included in the database probably have more stringent controls for criteria pollutants (e.g., NO_x, SO_2, particulate) than those in the rest of the US. Therefore, some data may not be representative of emissions for sources outside of California.

3.1. Field HAP emission measurements

The process heaters' and boilers' HAP emissions data contained in the WSPA database reflect field tests on petroleum industry units in California which were performed to comply with AB2588. CARB specified the substances to be measured and the corresponding test methods for AB2588 compliance. CARB required the affected companies to submit test protocols before performing the tests, which were reviewed by CARB (or local agencies to which CARB delegated this responsibility) for appropriate test methodology and approved before tests were performed. If a company failed to receive CARB approval prior to testing, they risked having the results rejected by CARB (which occurred in cases where an appropriate methodology was not followed).

CARB recognized that testing of air toxics would be very costly and a heavy burden on the affected plant owners. For each source category, CARB specified exactly which air toxics should be measured. CARB's list of 300 + (later 700 +) air toxics included most, but not all, of the HAPs included in title III of the CAA plus many more substances. Since the law was directed at identifying health risk, it is likely that their intent was to prioritize industry's resources by characterizing those air toxics which CARB's engineering and scientific staff judged as being the most significant contributors to health risk from each source category.

CARB determined that validated test methods for many pollutants did not exist for many of the sources to be tested. Therefore, CARB embarked on a program to develop and/or validate many air toxics test methods so that the law would be enforceable. Many of these methods (Table 2) were still evolving when the AB2588 testing was initiated and they improved over the ensuing years as analytical techniques were improved, providing lower minimum detectable HAP concentrations, and/or field experience revealed data quality problems.

3.2. Data screening and quality assurance procedures

The WSPA database was one of the first attempts to organize industry-specific air toxics emission data in a manner that enabled test results to be evaluated in a systematic manner. The database development also included a strong emphasis on the evaluation of data quality. Field data from the first round of pooled source testing exhibited high variability among tests of similar source types. Closer examination of these data revealed that many of the anomalous results were generally associated with inferior or superseded measurement methods, leading to high minimum detection limits and/or quality problems such as sample contamination. Considering that many of the test methods for measuring air toxics emissions are complex and were newly developed (or still evolving) over this testing period, these data quality issues were not entirely unexpected. Recognizing the need for more reliable emission factors, WSPA developed a guidance manual for performing air toxics tests to ensure high quality data in the second round of pooled source tests and for any subsequent tests performed by its individual member companies

Table 1
Petroleum industry combustion devices included in California air resources emission factor database[a]

Description	Number of tests						
	Boiler	Heater	Reciprocating internal combustion engine	Gas turbine	Asphalt blowing	Coke calcining	Reboiler
Total tests–all	17	19	22	8	2	1	2
Number of units tested	16	16	22	7	1	1	2
Fuel type							
Asphalt fumes	–	–	–	–	2	–	–
Natural gas/production gas	6	0	0	0	–	0	–
Crude oil	3	0	–	–	–	–	–
Natural gas	1	1	13	3	–	1	–
No. 6 fuel oil	2	0	–	–	–	–	–
Refinery gas	5	16	0	1	–	0	–
Natural/refinery gas	0	1	0	3	–	0	–
Pipeline oil	0	1	–	–	–	–	–
Ethylene glycol	–	–	–	–	–	–	1
Triethylene glycol	–	–	–	–	–	–	1
Diesel oil	0	0	3	0	–	0	–
Field gas	0	0	6	0	–	0	–
Natural/liquified propane/refinery gas	0	0	–	1	–	0	–
Burner type							
Unknown	7	3	–	–	–	–	–
Low NO_x	5	8	–	–	–	–	–
Conventional	5	8	–	–	–	–	–
Duct burners							
No	–	–	–	3	–	–	–
Yes	–	–	–	5	–	–	–
Post-combustion air pollution controls							
Thermal oxidizer	0	0	0	0	2	0	0
None	14	16	22	1	0	0	2
SO_2 scrubber	2	0	–	–	0	0	–
Selective catalytic NO_x reduction	1	2	0	1	0	0	–
Spray drier/Fabric filter	0	0	–	–	0	1	–
Selective non-catalytic NO_x reduction (Thermal $DeNO_x$)	0	1	–	–	–	–	–
Selective catalytic NO_x reduction/CO catalyst	0	0	0	5	0	0	–
CO catalyst	0	0	0	1	0	0	–
Cycles							
4-stroke	–	–	19	–	–	–	–
2-stroke	–	–	3	–	–	–	–
Engine design							
Lean burn	–	–	19	–	–	–	–
Rich burn	–	–	3	–	–	–	–
Capacity							
>650 Hp (>490 kW)	–	–	3	–	–	–	–
<650 Hp (<490 kW)	–	–	19	–	–	–	–
Load							
Unknown	9	3	–	–	–	–	–
>80%	3	7	–	–	–	–	–
<80%	5	9	–	–	–	–	–

[a] Hansell, (1997).

Table 2
Test methods used for organic air toxics emission measurements

Substance	Sampling principle	Sampling reference	Analytical principle	Analytical reference	AB2588 (field)	PERF (pilot-scale)
Aldehydes	Integrated-DNPH midget impingers	CARB 430	HPLC	CARB 430	×	×
Benzene, toluene, xylene (BTX)	Integrated-tenax/ charcoal sorbent traps	EPA 0030	GC/MS	EPA 5040, 5041, 8240	×	
BTX	Integrated-tedlar bag	CARB 410A	GC/PID	CARB 410A	×	
Dioxins/furans	Integrated- XAD sorbent trap	CARB 428	HRGC/HRMS	CARB 428	×	
PAH	Integrated-XAD-2 sorbent trap	CARB 429	HRGC/HRMS	CARB 429	×	×
Phenol	Integrated-XAD sorbent trap	EPA 0010	GC/MS	EPA 8270		×
VOC (low MW compounds)	Integrated-tedlar bag	EPA 0040	GC/FID/PID	EPA 18		×
VOC (low MW compounds)	Integrated-tedlar bag	CARB 422	GC/FID/PID/ ECD/MS	CARB 422	×	
VOC (high MW compounds – BTX)	Integrated-tenax/ anasorb sorbent traps	EPA 0031	GC/MS	EPA 5040, 5041, 8240		×

(Soelberg et al., 1994). As additional tests were performed by the industry over the ensuing years, the database has been periodically updated to provide more reliable and representative emission factors.

Recently, the WSPA database was updated for inclusion in a broader database being developed by CARB. The first release of the California air toxics emission factors (CATEF) database was compiled from results of air toxics emission tests on approximately 400 sources of all types throughout California performed under California's AB2588 program (Hansell, 1996a). Since the CATEF and WSPA databases originate from virtually the same source test reports, the WSPA database was updated following CARB's rigorous data screening and validation process to ensure that the emission data were of sufficient quality for emission factor development. These data will be incorporated in the next release of the CATEF database. Results from 161 petroleum industry tests were screened for inclusion in the database. Screening included a review of each report for the presence of key process data (e.g., process descriptions or fuel flow rate for determination of heat input rate), measurement quality control results (e.g., matrix spike recoveries used to assess analytical results' quality), and appropriate test methods necessary to develop reliable emission factors. Those reports passing the screening step were further reviewed to validate the data. Validation included verification of acceptable HAP measurement method procedures and quality assurance/quality control (QA/QC) results (blank results, surrogate spike recoveries, etc.), calculation, and other checks. Many of the test reports did not pass this rigorous screening and validation due to incomplete information or lack of appropriate air toxics data. 71 tests (usually in triplicate) of 65 different petroleum industry sources for approximately 80 toxic air contaminants are now represented in the WSPA-CATEF database (Hansell, 1996b). The petroleum industry now considers this to be the most reliable and comprehensive compilation of emission data and factors available for petroleum industry combustion sources.

3.3. Calculation of emission factors

The WSPA-CATEF database of air emission test results for petroleum industry boilers and process heaters has been used to develop HAP emission factors which allow extrapolation of the test results to other like devices. It also allows analysis of emission trends over a range of different design and operating parameters. Due to the complexity of HAP measurement methods and the importance of good accompanying QA/QC, HAP measurements are very costly. Therefore, representative units are typically tested and the results extrapolated to other units of similar design and operation by using emission factors. An emission factor is defined as the pollutant mass emission rate divided by a characteristic process production rate. For example, the benzene emission factor measured during a refinery gas-fired boiler test may be simply derived as follows:

$$\text{Benzene emission factor (kg/GJ)} = 10^6\,(\text{kJ/GJ}) \times \frac{\text{Benzene concentration (kg/Nm}^3) \times \text{Stack gas flow rate (Nm}^3/\text{h})}{\text{Fuel flow rate (Nm}^3/\text{h}) \times \text{Fuel heating value (kJ/Nm}^3)}$$

In this case, the fuel heat input, rather than the volume of gas-fired, is the appropriate characteristic process production rate since the refinery gas heating value itself may vary significantly with time. Thus, the fuel gas flow rate and the heating value must be determined concurrently with HAP emission measurements to facilitate the emission factor calculation.

3.3.1. Emission factors' data variability

Emission factors are developed from the emission data from facilities having similar design and operating parameters. Still, there will be variability in the emission data due to inherent differences between different facilities, use of different sampling and/or analytical procedures, measurement errors, different data reduction procedures, and/or other factors.

There is often more than one test method to choose from for each HAP, and if a HAP is measured by several different methods, the results may be neither comparable nor of the same quality. The selectivity and sensitivity may vary, for example, if different test methods were used or if the same method was not applied in the same manner at different sites. HAP emission measurements are generally very complex, relying on advanced analytical methods often pushing the state-of-the-art. The low concentrations of individual HAPs of concern, ranging from a few parts per million to less than a part per trillion, inherently make such complex measurements subjected to errors, which create uncertainty in the results. For example, measurement of benzene emissions in combustion gases at the ten parts per billion level is generally accomplished by stripping benzene from a large volume of stack gas sample onto a sorbent, then taking the sample on the sorbent to a laboratory where the concentrated benzene is desorbed onto another sorbent and then into a gas chromatograph with a mass spectrometer detector. Along the way, there are several opportunities for the sample to become compromised at the parts per billion level. Contamination may occur from ambient levels of benzene which may be in the air at the site or in the laboratory, or from other samples carried in the same container after field tests are completed. Conversely, some of the benzene may be lost during sample handling. Analytical interferences may also impact test results. Since combustion products generally contain not just a single HAP but many other gases as well, other gases may interfere with the sample analysis for the HAP of interest, possibly raising the detection levels above the ideal level or biasing the analytical instrument response high or low. Adherence to a rigorous QA/QC protocol and the experience and skill level of the field and laboratory personnel in handling unusual circumstances play major roles in the reliability of the final results.

Data reduction and handling procedures are also important considerations in developing emission factors. If a HAP is not detected during a test, it is impossible to discern whether it is absent from the sample altogether or present at levels below the ability of the method to detect them. For conservatism in health risk assessments, an arbitrary value of one-half the minimum detection limit is frequently used. However, this may yield erroneously high emission factors when minimum detection limits for tests of the same HAP at different sites vary significantly and many results are undetected. Other important considerations include accounting for different reporting conventions for different methods and whether results are corrected for QC samples (blank contamination, spiked samples, etc.) which might be collected.

All test results, regardless of methods and QA/QC procedures, are subjected to statistical uncertainty due to measurement and process variability and measurement bias (error). This may be expressed in statistical terms (ASME, 1990; EPA, 1996). For HAPs of interest for gas-fired boilers and process heaters, the statistical uncertainty may range from a few percent to several hundred percent (or more) of the average result. This becomes an important consideration when comparing sets of results to determine if differences are significant (e.g., to compare emissions from boilers and process heaters).

3.4. Selection of emission factors' categories

The data from the updated WSPA-CATEF database were analyzed to determine if design and operating parameters, fuel gas type, and criteria pollutant controls, significantly influenced HAP emissions (Hansell, 1997). The results of 36 field tests on petroleum industry boilers (including steam generators) and process heaters were sufficiently complete and valid to develop reliable emission factors. For inclusion in the CATEF database, CARB specified the extent to which subcategories of sources could be combined to produce average emission factors, using standard source classification codes (SCC). In many cases, this produced categories in which only a few tests on a single petroleum industry source were included. Therefore, the goal of the analysis was to determine whether source subcategories could be combined to develop emission factors for the petroleum industry sources based on a larger number of facilities and emission tests; thus creating a more "robust" emission factor by increasing the confidence that the variation in the emission data is indicative of the population of sources and reducing the chance that an emission factor is biased due to outlier data. Engineering judgement and a knowledge of the potential impact on emission behavior were used to select potential subcategories. Statistical tests were then applied to screen for significant differences between source subcategories (*t*-test at 95% confidence level using both normal and log-normal distributions), with the consideration that strong conclusions should not be drawn from small data sets and/or data from single sources (EPA, 1996). This approach follows EPA's guidance that engineering judgement, as well as statistical tests, should be applied when analyzing data sets.

The pollutants of most concern for gas-fired boilers and process heaters are volatile organic HAPs, formaldehyde, and PAH. One limitation of the database is that all HAPs of concern were not measured in all tests. Therefore, the analysis was performed on a subset of the measured HAPs common to all tests so that a comparative analysis would be valid. Benzene and the sum of benzene plus toluene plus xylene (BTX) were used as indicators of volatile organic HAPs. Benzene (which is formed in fuel-rich flame pockets) and formaldehyde (which is a combustion intermediate emitted when rapid flame quenching occurs) are indicators of HAPs formed in different parts of the flame and thus provide a clue to flame "failure modes". Total PAHs (the sum of sixteen individual substances common to all tests), and the individual PAHs anthracene and benzo[a]pyrene were used to represent PAH and polycyclic organic matter (POM). POM is listed as a HAP in the CAA. Three definitions of POM are currently under consideration by the EPA. One definition considers POM as the sum of seven PAHs, the second considers POM to be the sum of sixteen PAHs, and the third defines POM as a total extractable organic matter. Naphthalene, which can be biased high due to sorbent contamination/decomposition issues, was included in the PAH total for this analysis to yield a conservative emission factor.

3.4.1. Comparison of organic HAP emission factors for boilers and process heaters

Fig. 6 compares BTX, formaldehyde, and total PAH emission factors in kilograms per gigajoule (kg/GJ) for boilers and process heaters. The central tendency of the data population (i.e., the 25th to 75th percentile) is represented in the figure by the vertical bar, and the range of data is expressed by the vertical line which shows the 10th to 90th percentile. Also shown in the figure is the range of detection limits achieved in the various tests. The height of the horizontal bars represents the 25th to 75th percentile of the detection limits. There are 36 records in the database for BTX for 32 different units tested. A comparison of the BTX results for boilers and process heaters shows there is no significant difference. The range of BTX emissions is broader for process heaters than for boilers. However, a statistical *t*-test suggests that the difference is not significant at the 95 percent confidence level. Thus, the data for boilers and process heaters were combined to produce a single, more robust emission factor. The combined data for heaters and boilers are also shown in the figure.

The ranges of the formaldehyde emissions shown in Fig. 6 are considerably broader than the BTX or PAH emissions. This is due in large part to the difficulty in making reliable formaldehyde measurements due to contamination. Formaldehyde is present at low concentrations in the ambient air as a natural product of transpiration and respiration. Many common materials such as carpeting and wood paneling are known to emit small amounts of formaldehyde. Thus, it is present in many environments and contamination is sometimes unavoidable even with the best field and laboratory QA practices. Nevertheless, formaldehyde is an intermediate combustion product that may escape complete destruction in combustion systems. The central tendency of the formaldehyde data shown in Fig. 6 is at the same level as the detection limits, but there are a small number of

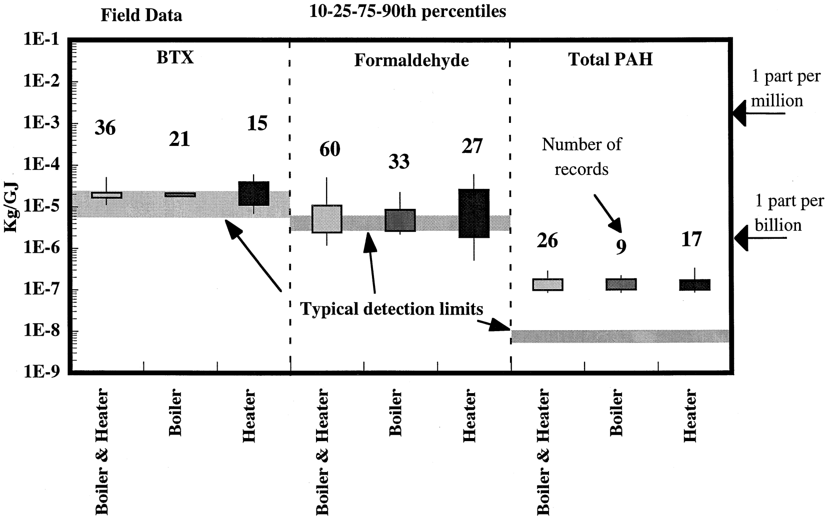


Fig. 6. Comparison of HAP emissions for gas-fired process heaters and boilers.

results at considerably higher levels. These high results may be due to unidentified combustion conditions and/or equipment design parameters which enhance formaldehyde emissions or may be due to measurement artifacts, such as sample contamination. As with the BTX results, there is no significant difference between boilers and process heaters with respect to formaldehyde emission factors.

Fig. 6 also presents the total PAH results obtained from twenty-six tests. The PAH detection limits shown in the figure are the sum of detection limits for the sixteen individual PAH included in the total. Total PAHs are usually dominated almost entirely by naphthalene. Total PAH emission factors are approximately an order of magnitude higher than detection limits, but one and a half to two orders of magnitude lower than BTX and formaldehyde emission factors. There are no statistically significant differences between emissions from boilers and process heaters. Therefore, an aggregate emission factor was used.

3.4.2. Comparison of organic HAP emission factors for natural gas and process gases

In addition to natural gas, process gases are frequently used as a primary or supplemental fuel in boilers and heaters. Process gases vary in heating value depending on the gas source and other process operations. Fig. 7 shows the fuel heating value for several common process gases and a comparison to natural gas. Natural gas usually varies in gross heating value from approximately 35,000 to 39,000 kJ/Nm^3 with an average of approximately 38,000 kJ/Nm^3. It consists of a high percentage of methane (generally above 85 percent) and varying amounts of ethane, propane, butane and inerts (typically nitrogen, carbon dioxide and helium) (EPA, 1997). For the process gas samples shown, heating value ranges from approximately 23,000 to nearly 75,000 kJ/Nm^3. Refinery gas may vary in composition and hence heating value from hour-to-hour depending on refinery process operations. The broad range of refinery gas composition is illustrated in Fig. 8. These data were collected from nineteen gas streams in five southern California refineries (Edwards and Goix, 1995). The hydrogen content of these samples ranged from about one to 70 percent, which is perhaps its most distinguishing feature when compared to natural gas. The balance of the gas is primarily methane and ethane, with smaller amounts of other hydrocarbons.

BTX, formaldehyde, and total PAH emissions for different fuel gases including natural gas-fired in process heaters and boilers are compared in Fig. 9. BTX and formaldehyde emissions are not significantly different for the different fuels, although the emission variability observed for refinery gas is somewhat greater than for the other fuel gases. Both the magnitude and variability of PAH emissions were similar for all fuel gases. Some of

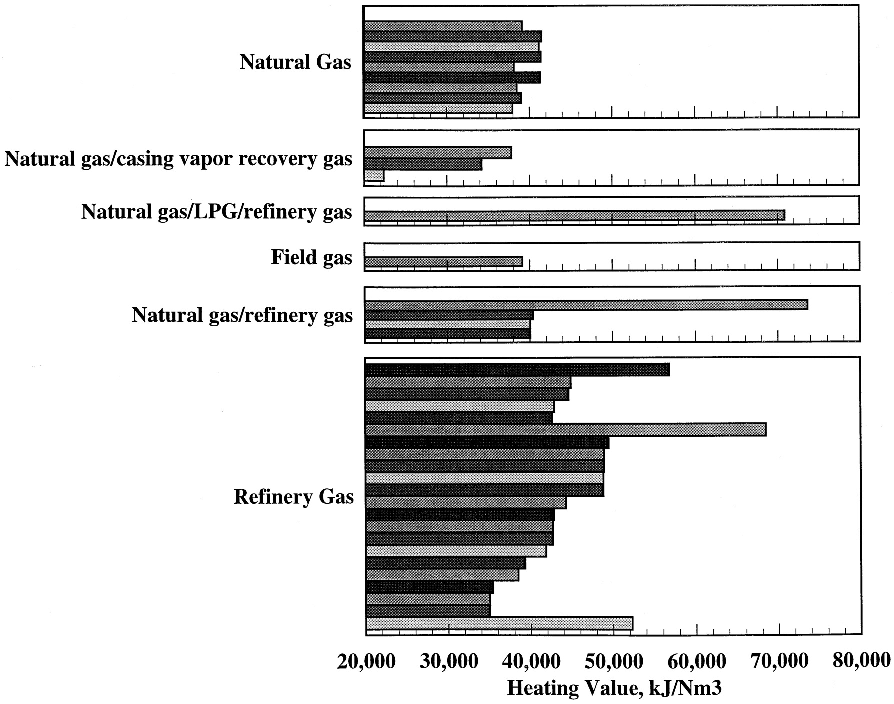


Fig. 7. Range of heating values for petroleum industry process gases (Hansell, 1997).

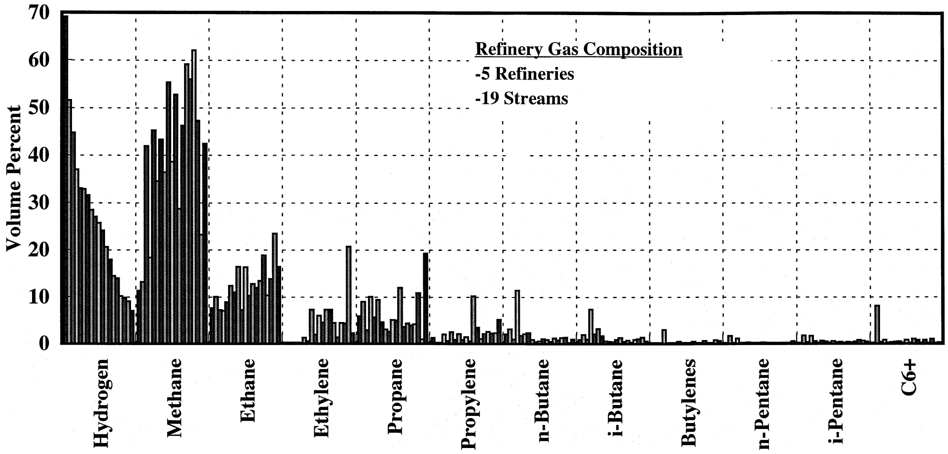
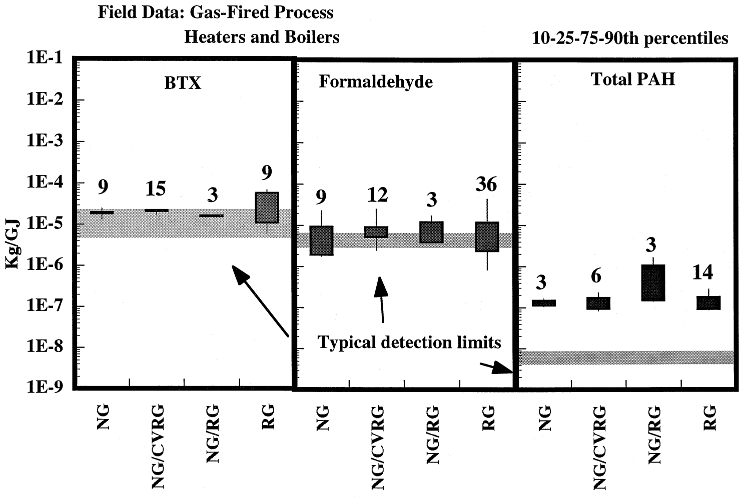


Fig. 8. Refinery gas compositions from five California refineries (Edwards and Goix, 1995).



NG-natural gas
RG-refinery gas
CVRG-casing vapor recovery gas

Fig. 9. HAP emissions from gas-fired process heaters and boilers firing fuel gases of varying composition and heating value.

the data sets are small but are consistent with emissions for other fuels. Statistically significant differences in emissions for the different fuels were not found. Therefore, combined emission factors for all gaseous fuels were developed for process heaters and boilers.

3.4.3. Impact of NO_x controls on organic HAP emissions

NO_x emission controls have been installed in many petroleum industry boilers and process heaters, and are especially common to these sources in California due to stringent air quality regulations. It has been speculated that NO_x emission controls may increase or decrease organic HAP emissions. Field data (Fig. 10) were obtained from process heaters and boilers with no NO_x controls and from units with different NO_x control equipment including low-NO_x burners (LNB), selective catalytic NO_x reduction (SCR) and selective non-catalytic NO_x reduction (SNCR). Several of the data sets are small, so conclusions drawn from these results may be tenuous and require further investigation.

BTX emissions from units with and without low-NO_x burners are not significantly different and a combined emission factor for units with and without NO_x controls was developed. The data from one unit with both LNB and SNCR (Thermal DeNOx) show higher emissions than the others. However, these data repre-

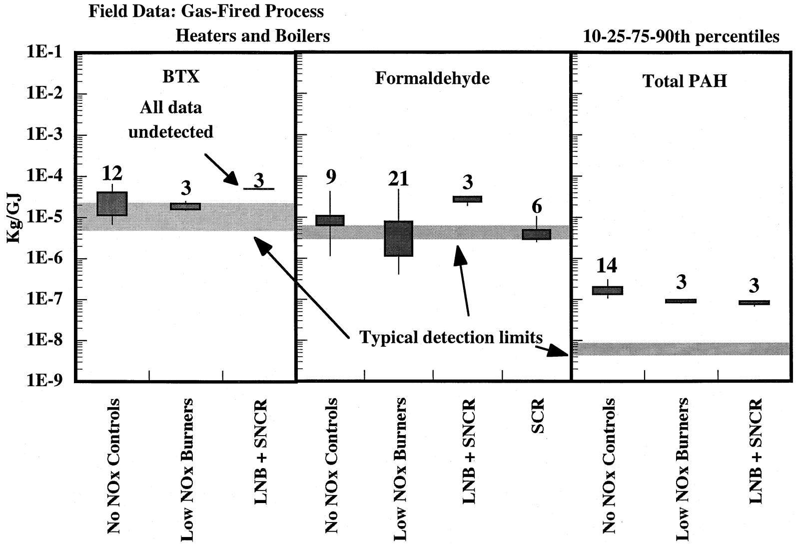


Fig. 10. Comparison of HAP emissions from gas-fired process heaters and boilers with and without NO_x emission controls.

sent detection limits for undetected results and hence are an upper bound for emissions rather than a true measurement.

Formaldehyde emissions again showed the characteristic variability both within and among subcategories with tests of units with low-NO_x burners having the greatest variability. There are no statistically significant differences in formaldehyde emissions among units equipped with LNB, SCR, and no NO_x controls. Formaldehyde emissions from the unit with both LNB and SNCR are not statistically significantly different than those units with no NO_x controls. The LNB/SNCR unit does appear to have higher emissions than those from the low-NO_x burners units and SCR units. However, the data represent three tests of a single unit, and great reliance should not be placed on the small data set. More data are needed to determine if units with LNB and SNCR truly have higher formaldehyde emissions.

PAH results are relatively scarce for units with NO_x controls. The PAH emissions appear to be slightly lower for units with LNB or LNB and SCR than for units with no controls. Statistical *t*-test results indicate a significant difference between units with low-NO_x burners and conventional burners. However, again the small data set leads to high uncertainty and the difference should not be viewed as significant. Additional data is needed to determine if units equipped with LNB and LNB and SNCR actually emit less PAHs.

In summary, additional data are needed to determine if NO_x controls impact HAP emissions. Based on the available data, no significant differences between units with NO_x controls and those without were found and aggregate emission factors were used.

3.5. Calculation of emission factors for gas-fired petroleum industry process heaters and boilers

The above analysis of organic HAP emission factors derived from field tests of gas-fired petroleum industry boilers and process heaters revealed no significant differences due to process design or fuel gas type. Therefore, the data were combined to achieve more robust emission factors applicable to all gas-fired boilers and process heaters. Table 3 summarizes the combined organic HAP emission factors for gas-fired boilers and process heaters derived from data included in the WSPA-CATEF database. Emission factors for these organic HAPs range from approximately 1 μg/GJ to 0.1 g/GJ. Note, undetected results generally have been included in the average emission factors at the full value of the minimum detection limit to provide a conservative estimate of emissions. Some undetected results were not included if the detection limits were significantly higher than other results detected at lower concentrations. Table 3 also lists the emission factors in the English units of pound per million British thermal unit (lb/MMBtu).

The upper and lower 95 percent confidence intervals are also shown as an indication of the uncertainty in the emission factors. The emission factor is generally based on 26 test runs or more, which reduces the uncertainty substantially compared to smaller data sets consisting of three or six samples. Nevertheless, the range from the lower to the upper 95 percent confidence interval represents approximately 50 to 300 percent of the mean organic HAP emission factors. This is a consequence of the fact that organic HAP emissions are very low and lie very close to the limits of detection, resulting in inherently large measurement variabilities. This is typical of

Table 3
Organic emission factors for petroleum industry gas-fired boilers and process heaters[a]

Substance	Test runs	Detect ratio	Estimation factor, Kg/GJ				Emission factor, lb/MMBtu			
			Arithmetic mean	Median	Upper confidence interval at 95% confidence	Lower confidence interval at 95% confidence	Arithmetic mean	Median	Upper confidence interval at 95% confidence	Lower confidence interval at 95% confidence
POM (acenaphthene)	26	0.79	1.0E−9	6.4E−10	1.4E−9	6.9E−10	2.4E−9	1.5E−9	3.3E−9	1.6E−9
POM (acenaphthylene)	26	0.89	2.8E−9	5.6E−10	6.0E−9	(−4.1E−10)	6.5E−9	1.3E−9	1.4E−8	(−9.6E−10)
POM (acenaphthene)	26	0.79	1.0E−9	6.4E−10	1.4E−9	6.9E−10	2.4E−9	1.5E−9	3.3E−9	1.6E−9
POM (anthracene*)	26	0.97	2.0E−9	1.1E−9	3.2E−9	8.2E−10	4.7E−9	2.6E−9	7.5E−9	1.9E−9
POM (benzo[a]anthracene)	41	0.99	9.5E−9	1.0E−9	1.8E−8	4.7E−10	2.2E−8	2.4E−9	4.3E−8	1.1E−9
POM (benzo[a]pyrene*]	41	0.98	2.5E−8	6.0E−10	5.6E−8	(−8.6E−9)	5.7E−8	1.4E−9	1.3E−7	(−2.0E−8)
POM (benzo[b]fluoranthene)	41	0.98	1.2E−8	1.0E−9	2.5E−8	(−2.1E−9)	2.7E−8	2.4E−9	5.8E−8	(−4.8E−9)
POM (benzo[g,h,i]perylene)	26	0.39	5.6E−10	4.7E−10	6.9E−10	3.9E−10	1.3E−9	1.1E−9	1.6E−9	9.0E−10
POM (benzo[k]fluoranthene	41	0.94	6.9E−9	6.0E−10	1.5E−8	(−1.2E−9)	1.6E−8	1.4E−9	3.4E−8	(−2.7E−9)
POM (chrysene)	26	0.51	6.9E−10	5.6E−10	8.6E−10	5.2E−10	1.6E−9	1.3E−9	2.0E−9	1.2E−9
POM (dibenz[a,h]anthracene)	41	0.00	(2.9E−9)	(5.6E−10)	(6.0E−9)	(−1.0E−10)	(6.8E−9)	(1.3E−9)	(1.4E−8)	(−2.4E−10)
POM (fluoranthene)	26	1.00	3.7E−9	1.5E−9	6.0E−9	1.5E−9	8.7E−9	3.5E−9	1.4E−8	3.6E−9
POM (fluorene)	26	1.00	2.1E−8	3.0E−9	5.2E−8	(−1.0E−8)	4.8E−8	6.9E−9	1.2E−7	(−2.4E−8)
POM (indeno[1,2,3-cd]pyrene)	41	0.99	2.8E−8	6.0E−10	6.4E−8	(−9.0E−9)	6.6E−8	1.4E−9	1.5E−7	(−2.1E−8)
POM (naphthalene)	26	1.00	1.7E−7	9.0E−8	2.8E−7	6.0E−8	3.9E−7	2.1E−7	6.4E−7	1.4EE−7
POM (phenanthrene)	26	1.00	1.4E−8	8.2E−9	2.1E−8	6.0E−9	3.2E−8	1.9E−8	5.0E−8	1.4E−8
POM (pyrene)	26	1.00	4.2E−9	1.4E−9	6.9E−9	1.4E−9	9.8E−9	3.2E−9	1.6E−8	3.2E−9
Ethylbenzene	21	0.54	8.6E−6	3.1E−6	1.4E−5	3.6E−6	2.0E−5	7.2E−6	3.2E−5	8.3E−6
Phenol	36	0.95	1.7E−6	5.6E−7	2.5E−6	9.5E−7	4.0E−6	1.3E−6	5.7E−6	2.2E−6
Acetaldehyde	60	0.88	5.2E−6	2.8E−6	6.9E−6	3.6E−6	1.2E−5	6.4E−6	1.6E−5	8.3E−6
Acrolein	21	0.88	5.6E−6	7.3E−6	7.3E−6	4.0E−6	1.3E−5	1.7E−5	1.7E−5	9.2E−6
Benzene*	49	0.79	2.6E−5	1.9E−6	5.2E−5	2.1E−6	6.0E−5	4.5E−6	1.2E−4	4.8E−6
Formaldehyde*	60	0.97	2.2E−5	6.4E−6	4.1E−5	3.0E−6	5.2E−5	1.5E−5	9.6E−5	7.0E−6
Toluene	69	0.81	6.4E−5	1.5E−5	1.2E−4	1.1E−5	1.5E−4	3.4E−5	2.8E−4	2.5E−5
Xylene (total)	39	0.37	1.2E−5	1.2E−5	1.5E−5	9.5E−6	2.9E−5	2.9E−5	3.6E−5	2.2E−5

[a] Notes:

- Values in parentheses are considered unreliable due to undetected data or negative lower confidence bounds.
- Undetected results are included at the full value of reported detection limits.
- Detect ratio is the fractional contribution of undetected data to mean emission factors. A detect ratio of zero means all results were below detection limits. A detect ratio of one means all data were detected.
- Emission factors include process heaters and boilers fired on natural gas and process gases (e.g., refinery fuel gas, casing gas, etc.).
- Confidence bounds calculated using *z*-distribution except for data sets with less than 30 test runs, for which the *t*-distribution was used (Hansell, 1997).

* Some data were excluded if undetected at levels significantly greater than levels in other data with detected results, indicating inferior test methods.

other HAP emission factor data sets where emission levels are low, and highlights that factors of two or three in organic HAP emissions at this level should be considered insignificant.

Emission factors may be derived as the arithmetic mean or median of the sample set. For some organic HAPs, the arithmetic mean is higher than the median by approximately an order of magnitude. The arithmetic means are often dominated by one or two outliers; thereby representing more conservative emissions factors. Median emission factors generally better represent the distribution of emissions from the population and are sometimes more appropriate estimates of actual emissions.

4. HAP emission data for similar non-petroleum industry sources

Tests outside of the petroleum industry have also been performed. The Gas Research Institute (GRI) and the Electric Power Research Institute (EPRI) co-sponsored tests of two gas-fired electric utility boilers (Rossi-Lane et al., 1996). EPRI also performed limited tests on six other gas-fired utility boilers (EPRI, 1994). These tests were designed to encompass a wide range of utility boiler designs and emission controls, and were performed according to a uniform test protocol to ensure high quality data. GRI recently performed tests on a process heater similar to those used in oil production (Lott, 1997).

The emission factors shown in Table 3 compare well to emission factors developed for natural gas-fired external combustion sources reported by EPRI (part of the EPA's utility boiler HAPs docket for utility boilers), by CARB based on tests reported for natural gas-fired utility boilers in the CATEF database, and by EPA for natural gas-fired external combustion sources in the most recent AP-42 emission factor draft update (EPA, 1997). HAP emissions from electric utility boilers have been the subject of several recent studies (EPRI, 1994; Rossi-Lane et al., 1996). Fig. 11 compares reported mean emission factors from tests of eight gas-fired utility boilers tested by EPRI and four gas-fired utility boilers reported in the CATEF database to those for petroleum industry boilers and process heaters. The general agreement in emission levels is quite good. EPRI reported emission factors for formaldehyde, benzene, toluene, and PAH emissions which were expressed as benzo[a]pyrene equivalent using relative potencies developed by the California department of health services (Collins et al., 1991). EPRI reported benzo[a]pyrene equivalent emissions as not detected. However, they did not report what detection limit was achieved in their tests. Benzo[a]pyrene equivalent emissions for petroleum industry boilers and heaters calculated on the same basis for comparative purposes were at the same level as detection limits. Presuming similar detection limits were achieved in the EPRI tests, these data should be very comparable.

5. Discussion

HAP emissions from gas-fired process heaters and boilers are very low. Fig. 12 shows calculated organic

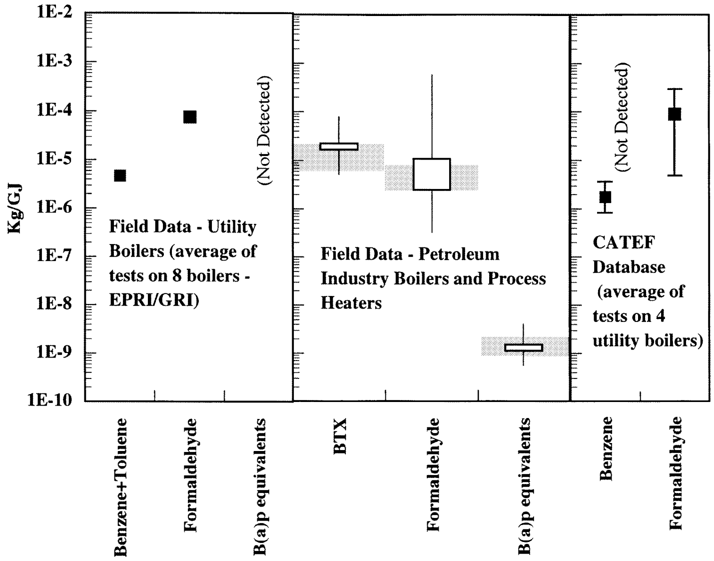


Fig. 11. HAP emission factors for gas-fired utility boilers and petroleum industry boilers and process heaters.

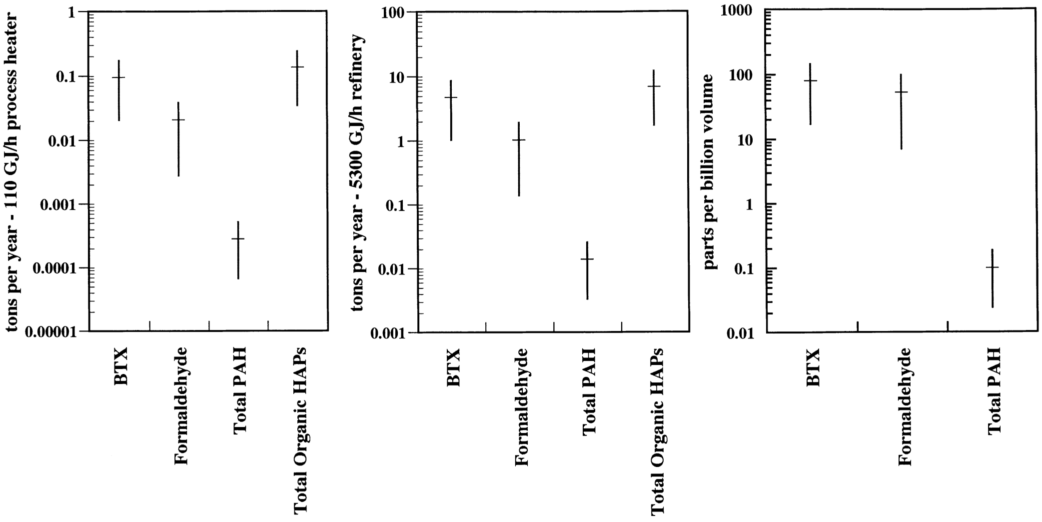


Fig. 12. Annual organic HAP emissions for a hypothetical 110 GJ/h process heater and a hypothetical 5300 GJ/h refinery.

HAP mass emissions in tons per year for a hypothetical process heater or boiler with a fuel heat input value of 110 GJ/h, which is in the same order of magnitude as those commonly found in petroleum industry facilities such as refineries and natural gas processing plants. BTX, formaldehyde, and PAH emissions for a source of this magnitude are below one tenth of a ton, one tenth of a ton and one thousandth of a ton per year, respectively The figure compares these emission levels to the equivalent gas concentrations and show that these mass emission rates correspond to very low concentrations. The figure also shows estimated total organic HAP emissions for all the HAPs listed in Table 3, using the sum of the mean emission factors to represent mean emissions and the sum of the 95 percent confidence intervals to represent the range of emissions. Total organic HAP emissions from a 110 GJ/h source are below one ton per year.

The total heat input to gas-fired combustion equipment in a typical oil refinery is on the order of 5,300 GJ/h. Organic HAP mass emissions from a refinery of this magnitude may be estimated using the same approach applied above. Emissions of BTX, formaldehyde, and total PAH are less than five tons, two tons, and 0.02 tons per year, respectively. Total organic HAP emissions from such a refinery are less than ten tons per year, based on the sum of mean emission factors from Table 3 (Fig. 12).

6. Conclusions

- Organic HAP emissions from normally operated gas-fired external combustion systems are low, typically below or near the detection limit of current source testing methods.
- Operation of gas-fired burners at sub-stoichiometric or high excess air levels can result in increased HAP emissions.
- No differences in organic HAP emissions from gas-fired process heaters and boilers were determined.
- No differences in organic HAP emissions from process heaters and boilers firing gases having wide varieties in composition and heating value were determined.
- Significant differences in HAP emissions between units with NO_x controls and those without were not found. However, there are limited data for units with NO_x controls and additional data are needed to determine if NO_x controls impact HAP emissions.

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Appendix A. List of symbols and acronyms

ASME	American Society of Mechanical Engineers
BERL	Burner Engineering Research Laboratory
BTX	benzene, toluene and xylene
CAA	Clean air Act
CARB	California air resources board
CATEF	California air toxics emission factors
CCS	Convective cooling section
CDFB	Conventional diffusion flame burner
CO	Carbon monoxide
CO_2	Carbon dioxide
CRADA	Cooperative research and development agreement
DAS	Data acquisition system
DNPH	Dinitrophenylhydrazine
ECD	Electron captive detection
EPRI	Electric Power Research Institute
FID	Flame ionization detection
g/GJ	Grams per gigajoule
GC	Gas chromatography
GRI	Gas Research Institute
HAP	Hazardous air pollutant
HHV	Higher heating value
HPLC	High-Performance Liquid Chromatography
HRGC	High-Resolution Gas Chromatography
HRMS	High-Resolution Mass Spectrometry
K	degrees Kelvin
kg/GJ	Kilograms per gigajoule
kJ/h	Kilojoules per hour
kJ/Nm^3	kilojoules per normal cubic meter
K/s	degrees Kelvin per second
kW	Kilowatt
lb/MMBtu	Pounds per million british thermal units
LLNL	Lawrence Livermore National Laboratory
LNB	Low-NO_x burner
MACT	Maximum achievable control technology
MS	Mass spectrometry
MW	Molecular weight
μg/GJ	Micrograms per gigajoule
N_2O	Nitrous oxide
NO_x	Oxides of nitrogen
PERF	Petroleum Environmental Research Forum
PID	Photoionization detection
POM	Polycyclic organic matter
QAPP	Quality assurance project plan
QA/QC	Quality assurance/quality control
SCC	Source classification code
SCR	Selective catalytic reduction
SNCR	Selective non-catalytic reduction
SNL	Sandia National Laboratory
SR	Stoichiometric ratio
THC	Total hydrocarbons
UCLA	University of California at Los Angeles
VOC	Volatile organic compound
WSPA	Western States Petroleum Association

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