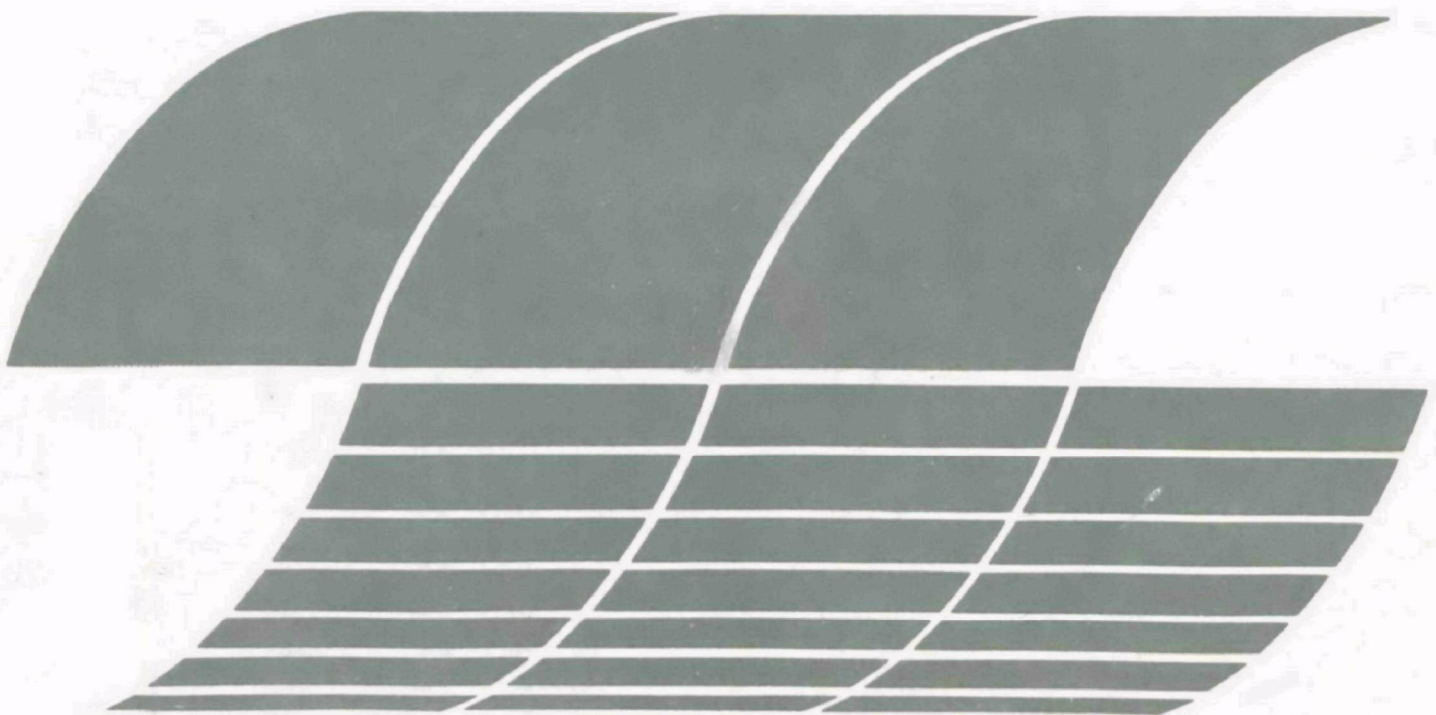




# Environmental Assessment of an Oil-fired Controlled Utility Boiler

Interagency  
Energy/Environment  
R&D Program Report



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**April 1980**

# **Environmental Assessment of an Oil-fired Controlled Utility Boiler**

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## ABSTRACT

A comprehensive emissions assessment was performed on the Haynes No. 5 boiler during oil firing. Level 1 and Level 2 procedures were utilized to characterize pollutant emissions. Results of the comprehensive assessment, in conjunction with assumed typical and worst case meteorological conditions, were utilized to estimate the environmental impact of emissions from this type of unit. Principal conclusions indicated are as follows: 1) The risk of violating National Ambient Air Quality Standards (NAAQS) due to criteria pollutant emissions is low. 2) Little adverse health effect is anticipated as a result of  $\text{SO}_2$ ,  $\text{SO}_4^{=}$ , and particulate emissions projected from widespread use of oil-fired units of the type tested. 3) The impact of trace element burdens in drinking water, plant tissue, soil and the atmosphere is negligible. 4) The risk of plant damage due to criteria pollutant emissions is remote. 5) The likelihood of plant damage due to trace element emissions is remote.

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# METRIC CONVERSION FACTORS AND PREFIXES

## CONVERSION FACTORS

<u>To convert from</u>	<u>To</u>	<u>Multiply by</u>
Degrees Celsius (°C)	Degrees Fahrenheit (°F)	$t(^{\circ}\text{F}) = 1.8 t(^{\circ}\text{C}) + 32$
Joule (J)	Btu	$9.478 \times 10^{-4}$
Kilogram (kg)	Pound-mass (avoirdupois)	2.205
Kilojoule/kilogram (kJ/kg)	Btu/lb <sub>m</sub>	$4.299 \times 10^{-1}$
Megagram (Mg)	Ton (2000 lb <sub>m</sub> )	1.102
Megawatt (MW)	Horsepower (HP)	$1.341 \times 10^3$
Meter (m)	Foot (ft)	3.281
Meter <sup>3</sup> (m <sup>3</sup> )	Barrel (bbl)	6.290
Meter <sup>3</sup> (m <sup>3</sup> )	Foot <sup>3</sup> (ft <sup>3</sup> )	$3.531 \times 10^1$
Meter <sup>3</sup> (m <sup>3</sup> )	Gallon (gal)	$2.642 \times 10^2$
Nanogram/joule (ng/J)	lb <sub>m</sub> /million Btu	$2.326 \times 10^{-3}$
Picogram/joule (pg/J)	lb <sub>m</sub> /million Btu	$2.326 \times 10^{-6}$

## PREFIXES

<u>Prefix</u>	<u>Symbol</u>	<u>Multiplication Factor</u>	<u>Example</u>
Peta	P	$10^{15}$	1 Pm = $1 \times 10^{15}$ meters
Tera	T	$10^{12}$	1 Tm = $1 \times 10^{12}$ meters
Giga	G	$10^9$	1 Gm = $1 \times 10^9$ meters
Mega	M	$10^6$	1 Mm = $1 \times 10^6$ meters
Kilo	k	$10^3$	1 km = $1 \times 10^3$ meters
Milli	m	$10^{-3}$	1 mm = $1 \times 10^{-3}$ meter
Micro	μ	$10^{-6}$	1 μm = $1 \times 10^{-6}$ meter
Nano	n	$10^{-9}$	1 nm = $1 \times 10^{-9}$ meter
Pico	p	$10^{-12}$	1 pm = $1 \times 10^{-12}$ meter

## SECTION 1

### INTRODUCTION

Conventional methods for conversion of fuels into usable forms of energy historically have impacted all segments of the environment. Most conventional combustion processes emit sulfur oxides, nitrogen oxides, carbon oxides, particulate matter and other potentially harmful pollutants to the air. Conventional fuel combustion processes are playing an increasing role in the movement toward national energy independence. As a result, the potential for adverse environmental impact is also increasing. In recognition of these facts, IERL-RTP established the Conventional Combustion Environmental Assessment program (CCEA) to conduct comprehensive assessments of the effects of combustion pollutants on human health, ecology, and the general environment. The assessments will result in recommendations for control technology and standards development to control adverse effects within acceptable limits.

This report details results of a comprehensive emissions assessment performed on the Haynes No. 5 utility boiler in Long Beach, California. The No. 5 unit is a once-through, supercritical boiler with a net electric generating capacity of 346 MW. Although either oil or gas may be burned in this unit, tests described herein were performed exclusively during oil firing. The unit has a horizontally-opposed wall fired furnace and is equipped with off-stoichiometric firing and flue gas recirculation for  $\text{NO}_x$  control. No particulate or  $\text{SO}_x$  controls are utilized.

Based on 1978 data, non-tangential units comprise 59% of all generating capacity for residual oil-fired utility boilers. The average size for non-tangential units is 100 MW which is a factor of three smaller than the tested unit. Only 18% of all non-tangential oil-fired generating capacity is associated with  $\text{NO}_x$  controls although 54% of the capacity provided by controlled horizontally-opposed firing is associated with some form of off-stoichiometric firing in conjunction with flue gas recirculation. Oil-fired utility boilers typically do not utilize particulate or  $\text{SO}_x$  controls. Since

the Haynes No. 5 unit is somewhat larger than the average non-tangential utility boiler, it may be considered typical of large horizontally-opposed units with NO<sub>x</sub> controls.

## SECTION 2

### SUMMARY AND CONCLUSIONS

A comprehensive emissions assessment was performed on the number 5 boiler at Haynes Power Plant in Long Beach, California. The plant is owned and operated by the Department of Water and Power of the City of Los Angeles. The number 5 boiler is a Babcock and Wilcox supercritical Universal-Pressure boiler with a net electrical generating capacity of 346 MW. Either low sulfur oil or natural gas may be fired in the horizontally-opposed wall fired furnace of the number 5 unit.  $\text{NO}_x$  emissions are controlled with off-stoichiometric firing and flue gas recirculation.

Emissions testing was performed during oil-fired operation. Level 1 and Level 2 (1) analyses were performed on the fuel oil and the flue gas. Level 1 analyses were performed to determine  $\text{NO}_x$  and hydrocarbon concentrations in the flue gas. Concentrations of  $\text{CO}$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{SO}_4^{=}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ , and total particulates in the flue gas were determined by Level 2 analyses. Trace element concentrations in the flue gas were estimated from Level 1 analysis of the fuel oil assuming all trace elements were emitted from the stack. No significant liquid or solid waste streams are produced by the boiler unit.

Results of the emissions assessment are presented in Table 2-1. Measured emissions of the criteria pollutants and  $\text{SO}_3$  correspond well with published AP-42 (2) emission data from oil-fired utility boilers although measured  $\text{NO}_x$  and total organic emissions were somewhat lower. Reduced  $\text{NO}_x$  emissions are the result of  $\text{NO}_x$  control systems on the number 5 unit.

Of the 39 trace elements studied during this effort, only the estimated flue gas concentrations of Cr and Ni were found to exceed their respective Discharge Multimedia Environmental Goal (DMEG) values. Hence, emission factors for these elements have been included in the emissions summary table.

Speciation of organic compounds present in the flue gas indicated the presence of aliphatic hydrocarbons, benzaldehyde, trimethyl cyclohexane-one,

TABLE 2-1. SUMMARY OF POLLUTANT EMISSIONS  
FROM AN OIL-FIRED UTILITY BOILER

Pollutant	Emission Factor, ng/J
NO <sub>x</sub> <sup>*</sup> (as NO <sub>2</sub> near full load)	116 ± 2.12 <sup>+++</sup>
CO <sup>†</sup>	6.6 ± 3.1 <sup>+++</sup>
SO <sub>2</sub> <sup>‡</sup>	98 ± 7.0 <sup>+++</sup>
SO <sub>3</sub> <sup>**</sup>	1.14
SO <sub>4</sub> <sup>=**</sup>	1.27
Total Organics <sup>††</sup>	0.42 - 0.58
Total Particulates <sup>**</sup>	7.5 ± 1.2 <sup>+++</sup>
Cl <sup>-**</sup>	1.34
F <sup>-**</sup>	0.061
Cr <sup>***</sup>	0.002
Ni <sup>***</sup>	0.2

\* NO<sub>x</sub> was determined by continuous chemiluminescent analysis (Level 1).

† CO was determined by continuous non-dispersive infrared analysis (Level 2).

‡ SO<sub>2</sub> was determined by continuous pulsed fluorescence analysis and by the CCS (Level 2).

\*\* SO<sub>3</sub>, SO<sub>4</sub><sup>=</sup>, Cl<sup>-</sup> and F<sup>-</sup> were determined by analysis of the CCS (Level 2).

†† C<sub>1</sub>- C<sub>16</sub> fractions were determined by gas chromatograph while the >C<sub>16</sub> fraction was determined gravimetrically (Level 1).

\*\* Total particulates were determined by a modified Method 5 procedure (Level 2).

\*\*\* Trace element emission factors were estimated from the SSMS fuel analysis under the assumption that all trace elements in fuel would be emitted from the stack. Only the estimated flue gas concentrations of Cr and Ni were found to exceed their respective DMEG values.

+++ The indicated uncertainty represents one standard deviation.

C<sub>2</sub> substituted acetophenone, methyl esters of benzoic acid and substituted benzoic acid, diethylphthalate, and ethylbenzaldehyde at concentrations between 0.02 µg/m<sup>3</sup> and 2 µg/m<sup>3</sup>. POM emissions consisted primarily of naphthalene. With the exception of the possible presence of benzo(a)-pyrene (benzopyrenes were detected but benzo(a)pyrene was not specifically identified), comparison of measured concentrations of organics with their respective DMEG values indicates that all POM compounds were present at levels too low to be of environmental concern.

An environmental impact assessment was performed based upon emission rates measured at the Haynes No. 5 boiler and assumed typical and worst case type meteorological parameters. Principal conclusions indicated by this assessment are as follows:

- The environmental acceptability of emissions from oil-fired boilers is largely dependent on site-specific factors such as background pollution levels and meteorology. However, the risk of violating NAAQS due to criteria pollutant emissions from an oil-fired boiler (353 MW gross output scale) like Haynes No. 5 appears low.
- Based on the Lundy-Grahn Model for health effects associated with suspended sulfate levels, limited adverse health effects would result from these emissions. Similar results were obtained with this model considering the effects of SO<sub>2</sub> and total particulate emissions on people older than 40 years of age.
- The impact of trace element burdens in drinking water, plant tissue, soil and the atmosphere as a result of measured emissions from this oil-fired utility boiler is generally orders of magnitude less than allowable exposure levels.
- The risk of plant damage due to criteria pollutant emissions from this oil-fired boiler appears to be remote. However, the effect of secondary pollutants formed by reactions between NO<sub>x</sub> and hydrocarbons, and the synergistic effects of SO<sub>2</sub> in the presence of ozone are uncertain.
- The likelihood of damage occurring in plants due to trace elements from oil firing at Haynes appears remote.

## REFERENCES FOR SECTION 2

1. Hamersma, J.W., D.G. Ackerman, M.M. Yamada, C.A. Zee, C.Y. Ung, K.T. McGregor, J.F. Clausen, M.L. Kraft, J.S. Shapiro, and E.L. Moon. Emissions Assessment of Conventional Stationary Combustion Systems, Methods and Procedures Manual for Sampling and Analysis. Report prepared by TRW Systems Group for the U.S. Environmental Protection Agency. EPA-600/7-79-029a. January 1979.
2. Compilation of Air Pollution Emission Factors, AP-42, Part A. Third Edition. U.S. Environmental Protection Agency. August 1977.

## SECTION 3

### TEST SETTING

#### PLANT DESCRIPTION

The oil-fired utility boiler tested was Boiler Number 5 at Haynes Power Plant, Long Beach, California. The boiler is owned and operated by the Department of Water & Power of the City of Los Angeles. Boiler Number 5 is one of six boiler units at the facility. It burns either natural gas or low sulfur oil, and utilizes off-stoichiometric firing and flue gas recirculation to control  $\text{NO}_x$  emissions.

The Haynes Power Plant is located in the urban Los Angeles Basin approximately 32 kilometers south of downtown Los Angeles. Figure 3-1 shows a general plot plan of the entire facility, and Figure 3-2 shows the general material flow diagram for the unit tested.

As shown in Figure 3-1 the facility has six boiler units. This number is made up of three identical pairs of boilers, that is units 1 and 2 are identical, units 3 and 4 are identical, and units 5 and 6 are identical.

Fuel for the facility is supplied by ARCO, Coastal States Marketing, and Asiatic Petroleum. It is usually transported to the facility by pipeline. There is approximately 1,000,000 barrels of oil storage capacity at the facility.

Water for boiler feed water makeup, fire fighting, and general usage is supplied by the City of Long Beach Water System. Waste water from general wash-down, and contaminated condensate is treated on site in settling ponds and ultimately discharged into the San Gabriel River. Metal cleaning waste solutions are removed via vacuum trucks and hauled to designated waste disposal areas.

#### Boiler

Boiler Number 5 was built to the Department of Water and Power's specifications by Babcock and Wilcox. It is a double reheat, supercritical



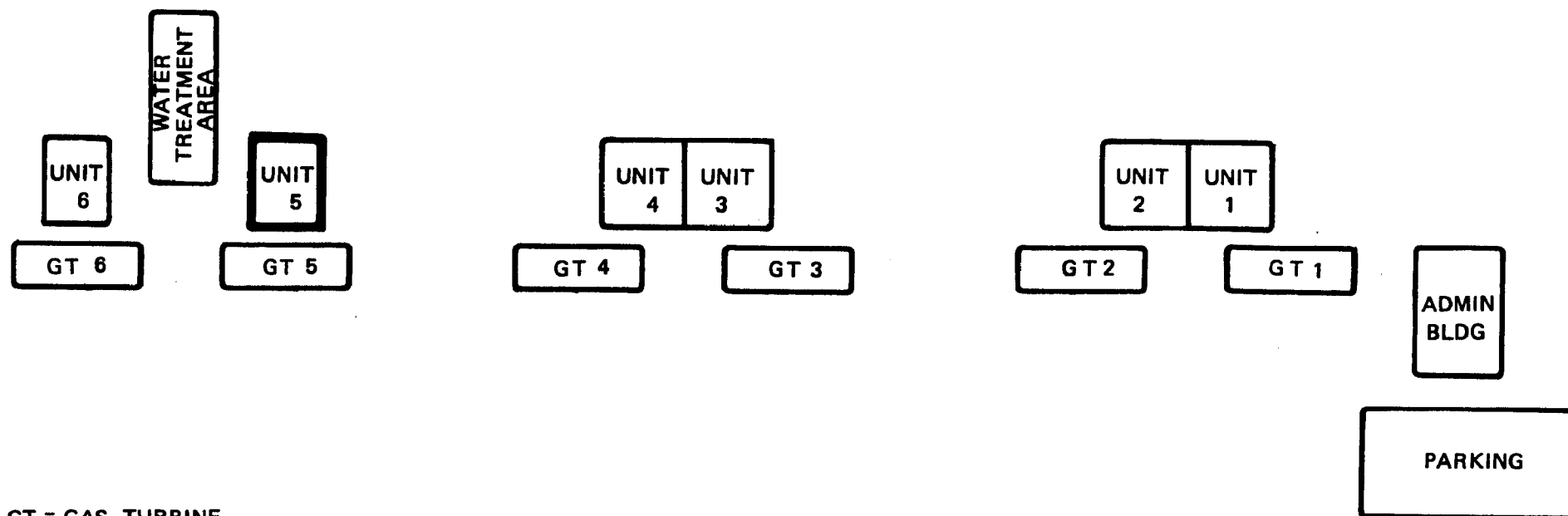


Figure 3-1. Plot Plant Haynes Power Plant

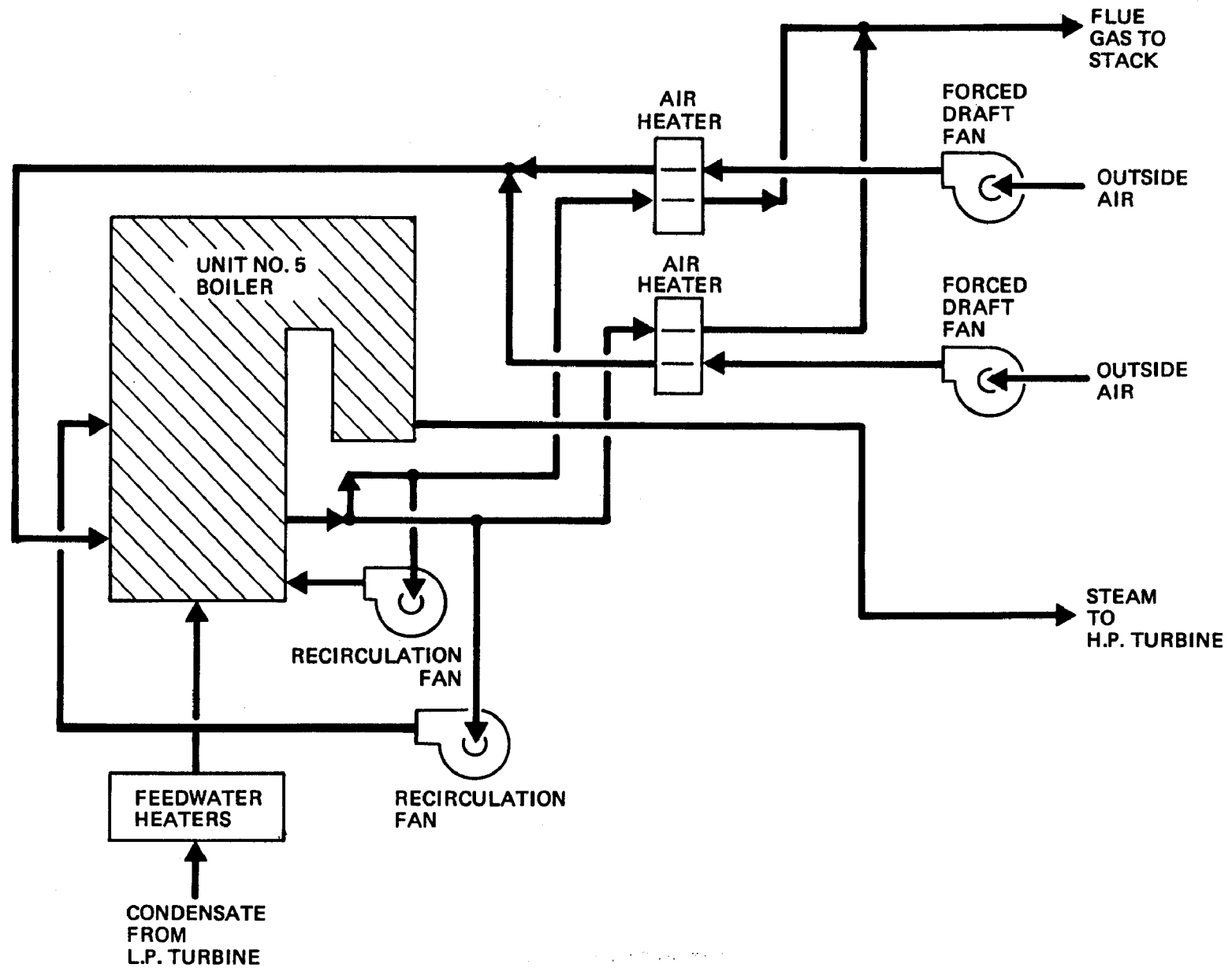


Figure 3-2. Schematic of the Oil Boiler

pressure, horizontally-opposed wall fired, Universal-Pressure boiler. The boiler can burn either natural gas or oil. Boiler number 5 was put into commercial operation in August 1966. Table 3-1 contains the boiler specification data. A schematic diagram of the boiler and ancillary equipment is given in Figure 3-2.

Combustion air is supplied to the unit by two forced draft fans. Prior to entering the combustion zone the temperature of the air is increased to approximately 550 K in the preheater section. The air preheaters recover heat from the flue gas and transfer it to the combustion air via heat exchangers.

Fuel is usually brought to the facility via natural gas and oil pipelines. The oil is continuously circulated through the system to avoid gumming and waxing due to settling of heavy hydrocarbons. The oil is pumped about the facility at a rate of  $0.024 \text{ m}^3/\text{s}$ .

Combustion air is supplied to the unit by two variable speed fluid drive, air foil blade fans. Each fan supplies  $10,100 \text{ m}^3$  of air at 300 K at a pressure of 113 kPa.

Recirculation of the flue gas to the boiler combustion zone is accomplished by two constant speed, damper controlled fans. Each flue gas recirculation fan delivers  $5500 \text{ m}^3$  at 648 K at a pressure rise of 4.16 kPa.

Figure 3-3 is a simplified schematic of the system showing the generalized flow through the system. Super heated steam leaves the boiler, passes through the high pressure turbine and is then routed back to the boiler where it passes through the 1st reheater. From the 1st reheater the steam is sent to the intermediate pressure turbine and is then routed back to the boiler where it passes through the 2nd reheater. From the 2nd reheater the steam is sent to the low pressure turbine. From the low pressure turbine the steam is sent to a condenser. From the condenser the liquid passes through a system of eleven heaters arranged in series where it is heated and returned to the boiler. The heaters are supplied with steam from various points in the system.

The boiler powers two generators. One is driven by the high and intermediate pressure turbines, the other by the low pressure turbines. The

TABLE 3-1. BOILER NUMBER 5 DESIGN DATA

Type	Oil/gas
Manufacturer	Babcock & Wilcox
Number of Burners	24
Burner Arrangement	Front and Rear Firing
Air Preheater	Yes
Combustion Air Temperature	572 K
Combustion Air Volume	6.02 m <sup>3</sup> /s (300 K)
Recirculation Gas	Yes
Volume	3.26 m <sup>3</sup> /s
Temperature	647 K
Reheat	Two Stage
Design Steam Rate	
Super Heat	16,200 Kg/s, 25 MPa, 811 K
First Reheat	13,700 Kg/s, 7.3 MPa, 835 K
Second Reheat	12,100 Kg/s, 2.6 MPa, 849 K
Design Generating Capacity	353 MW (gross)

combined generators have a capacity of 353 MW (i.e., maximum gross output is 353 MW as opposed to the salable or net output of 346 MW).

The fuel oil specifications are critical because burning of "clean" fuel constitutes the only SO<sub>2</sub> and particulate control mechanism. A typical fuel oil analysis is presented in Table 3-2. Because the boiler can burn gas, the oil tests were scheduled such that they occurred after the boiler had been burning only oil for at least a week.

#### Air Quality Control

Emissions of sulfur dioxide and particulates are controlled by burning low sulfur fuel oil, by the furnace design, and by rigorous maintenance and operational procedures.

Off-stoichiometric firing and flue gas recirculation are used to minimize NO<sub>x</sub> emissions. Off-stoichiometric firing consists of running each

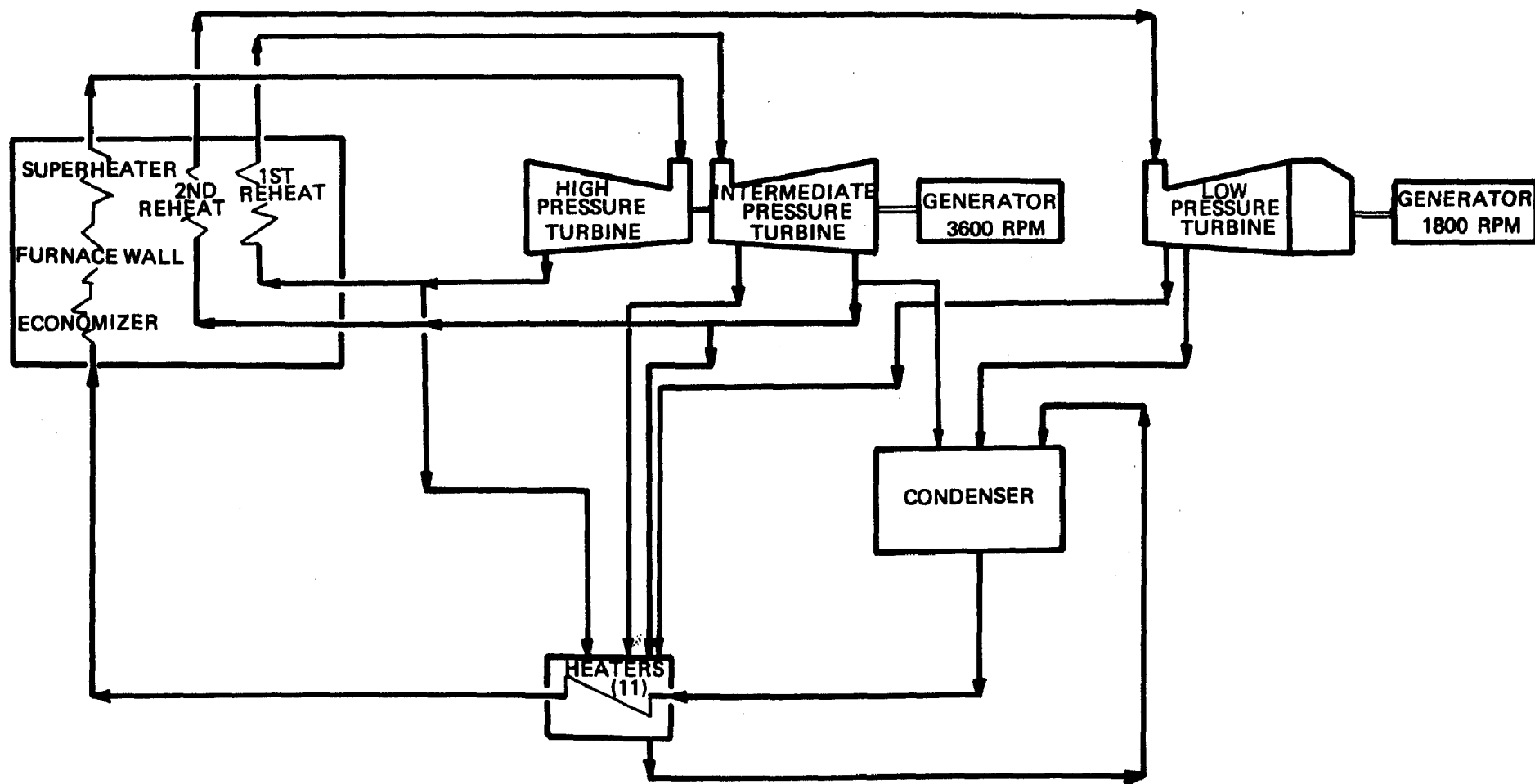


Figure 3-3. System Schematic

TABLE 3-2. TYPICAL FUEL OIL ANALYSIS\*

Heating Value	44,000 KJ/Kg
Viscosity, SUS at 333 K	112.9
Sulfur, % by Weight	0.18
Ash, Weight % of Oil	0.030
Specific Gravity of 289 K	0.9100
Water Content, %	0.21
Metal (ppm)	
Iron	9.3
Vanadium	3.9
Nickel	5.1
Sodium	30
Calcium	0.13
Magnesium	5.6
Copper	0.40
Potassium	1.85
Lead	2.3
Zinc	0.51
Aluminum	1.0

\* Data were provided by Haynes personnel. No information is available regarding the number of samples analyzed or standard deviations of analyses.

burner fuel rich (i.e., less than stoichiometric oxygen). The remainder of the oxygen necessary for complete combustion is added to the furnace either through burners to which the fuel feed has been terminated or through special air injection points called "NO<sub>x</sub> ports". Running the burners fuel rich stretches out each flame and causes it to burn cooler. NO<sub>x</sub> is formed two ways, by thermal fixation of atmospheric nitrogen and from the fuel nitrogen. Lowering the combustion temperature reduces the rate at which atmospheric nitrogen is converted to NO<sub>x</sub>. Also, fuel rich flames are oxygen deficient. Reduced availability of oxygen minimizes NO<sub>x</sub> formation from both of the mechanisms outlined above.

Flue gas recirculation consists of recirculating some part of flue gas through the burners. This procedure results in combustion air with a reduced oxygen concentration which in turn reduces the  $\text{NO}_x$  formation rates.

#### Liquid Effluents

No significant liquid streams are produced by the boiler.

#### Solid Waste

No significant solid wastes are produced by the boiler.

#### OIL-FIRED UTILITY TEST

The only major emission source at the oil-fired utility site is the stack. There are no emission controls other than rigid fuel specifications, except for  $\text{NO}_x$ . Control of  $\text{NO}_x$  is by off-stoichiometric firing and flue gas recirculation. Therefore, only two streams were sampled, the fuel oil feed and the stack emissions. No solid or liquid streams were sampled.

The stack emissions of criteria pollutants are very low. As a result, analysis of the particulates and organics was difficult because of small sample sizes.

Emissions were characterized using EPA's phased approach to sampling and analysis. This approach utilizes two separate levels of sampling and analytical effort (Level 1 and Level 2). Level 1 is a sampling and analysis procedure accurate within a factor of about 3. This level provides preliminary assessment data and identified problem areas and information gaps which are then utilized in the formulation of the Level 2 sampling and analysis effort. Level 2 provides more accurate detailed information that confirms and expands the information gathered in Level 1. The methods and procedures used are, in some instances, modified for Level 1 sampling and/or analysis procedures and are documented in the manual, "Combustion Source Assessment Methods and Procedures Manual for Sampling and Analysis", September 1977. The Level 2 methods and procedures included "state-of-the-art" techniques as adapted to the needs of this site. Normally all Level 1 samples are analyzed and evaluated before moving to Level 2. However, because of program time constraints, the Level 1 and Level 2 samples were obtained during the same test period.

The Source Assessment Sampling System (SASS) was used to collect both gaseous and particulate emission samples at the scrubber inlet and outlet for Level 1 organic and inorganic analysis. The train was run for 6 to 8 hours until a minimum of 30 cubic meters of gas had been collected.

Previous sampling and analysis efforts had indicated possible interference of SASS train materials on certain organic and inorganic analysis when at the lower detection limits of Level 2 methods. To avoid this possibility, all glass sampling trains were used to collect Level 2 samples. Two Method 5 sampling trains were modified for Level 2 organic and inorganic sample acquisition. Both trains sample approximately 10 cubic meters of flue gas during a 6- to 8-hour run time.

A controlled condensate train (Goksoyr-Ross) was used at each location to obtain samples for  $\text{SO}_2$ ,  $\text{SO}_3$  (as  $\text{H}_2\text{SO}_4$ ), particulate sulfate,  $\text{HCl}$  and  $\text{HF}$ .



## SECTION 4

### EMISSION ASSESSMENT OF AN OIL-FIRED UTILITY BOILER

#### TEST CONDITIONS

Four tests were performed firing residual fuel oil. Electrical output at this site ranged from 218 to 330 gross MW, corresponding to 62 to 94% of full-load capacity. These test conditions are tabulated in Table 4-1. Efficiencies and emission factors for oil firing are computed using the heat input from oil feed rates. The accuracy of tabulated steam production rates has been estimated to be about 13%, based on oil feed rates and gross electrical output. Oxygen concentrations presented are the averages obtained from continuous monitoring at the stack. Typical furnace oxygen levels for normal operation are 3 to 4%. Using fuel oil analyses, this oxygen range corresponds to an excess air input of approximately 16 to 22%. Flue gas flow rates were computed from the oxygen concentration at the stack, fuel analyses, and fuel feed rates (estimated from steam production rate data) using the following expression:

$$n_{FG} = \frac{4.762 (n_C + n_S + .45 n_N) + .9405 n_H - 3.762 n_{O_2}}{1 - 4.762 (O_2/100)}$$

where:

$n_{FG}$  = gram moles of dry effluent per gram of fuel

$n_j$  = gram moles of element j per gram of fuel

$O_2$  = volumetric  $O_2$  concentration in percent

Flue gas flow rates are expressed as dry standard cubic meters per second; standard temperature and pressure are defined as 293 K and 101.3 kPa, respectively.

Ultimate analyses of the fuel oil are presented in Table 4-2, along with averages and standard deviations. Analysis results indicate that the main fuel components and heat contents were essentially constant during the test period. Variation in oxygen contents is attributed to the low fuel oxygen content and the fact that oxygen is determined by difference.

TABLE 4-1. SUMMARY OF TEST CONDITIONS

Test No.	Electrical Output (Gross) MW	% of Maximum Load	Nominal Fuel Feed Rate, kg/hr	Steam Production Rate, kg/hr x 10 <sup>6</sup>	Overall Efficiency %	Average O <sub>2</sub> in Flue Gas %	Excess Air At Furnace %	Flue Gas Flow Rate dscm/s
141	330	94	69,000	0.781	39	6.35	16-22	300
142	218	62	54,900	0.536	32	5.76	16-22	230
143	325	92	66,300	0.860	40	5.66	16-22	280
144	310	88	61,700	0.717	40	5.98	16-22	270

TABLE 4-2. SUMMARY OF ULTIMATE FUEL ANALYSIS

Component	Test				Average	$\sigma^*$
	141	142	143	144		
Carbon	86.94	86.41	86.60	86.21	86.54	0.31
Hydrogen	12.41	12.40	12.33	12.43	12.39	0.04
Nitrogen	0.37	0.16	0.17	0.87	0.39	0.33
Sulfur	0.21	0.17	0.16	0.19	0.18	0.02
Ash	0.01	0.00	0.01	0.01	0.01	0.01
Oxygen <sup>†</sup>	0.06	0.86	0.73	0.98	0.66	0.41
Heating Value (kJ/kg)	43,994	44,224	44,131	44,035	44,096	103

\*  $\sigma$  = one standard deviation.

† Oxygen concentration by difference.

Additional analyses were performed on a composite oil sample (tests 141-144) to determine concentrations of trace and minor elements. The oil analysis was performed by spark source mass spectrometry (SSMS), except for mercury, which was performed by elemental sparging. These data are presented in Table 4-3. Typical ranges of some trace and minor elements in U.S. and foreign crude oils and in fuel oils are also presented for comparison. Analyses of most trace and minor elements for which typical oil values are available appear to be consistent with the literature values. However, several elements, notably Br, Cl, Cu, F, Fe, Ge, K, Pb, Rb, and V are somewhat lower than the cited literature values. The significance of these concentration differences is not apparent due to the limited quantity of published data. Comparison of SSMS data with typical oil analyses from the Haynes plant (Table 3-8) indicates excellent agreement for Cu, Fe, K, Ni, V, and Zn. However, Al, Ca, Na, and Mg were indicated to be major components by SSMS although they are normally present at the ppm level. Pb was detected at somewhat lower levels than normal for oil burned at this plant.

TABLE 4-3. CONCENTRATION OF MAJOR TRACE ELEMENTS IN OIL

Element	ppm in Fuel Oil*	Typical Concentration, ppm†	Reference	Element	ppm in Fuel Oil*	Typical Concentration, ppm†	Reference
Al	MC‡	4	2	Li	0.02	0.06	2
As	<0.01	0.0006-1.1	1	Mg	MC‡	13	2
B	0.5	0.4	2	Mn	0.04	0.001-6	1
Ba	0.5	1	2	Mo	0.1	0.9	2
Be	<0.01	0.08	2	Na	MC‡	31	2
Br	<0.01	0.1	2	Ni	8	14-68	2, 4
Ca	MC‡	14	2	P	1	1	2
Ce	<0.01	0.006	2	Pb	0.04	3	2
Cl	0.1	12	2	Pr	<0.01	No Data	
Co	0.5	2	2	Rb	<0.01	2	2
Cr	0.09	0.002-0.02	1	Sc	≤0.01	0.02	2
Cs	0.07	0.09	2	Se	0.02	0.03-1	1
Cu	0.1	3	2	Si	4	17	2
F	<0.01	0.1	2	Sr	0.09	0.1	2
Fe	2	0.003-14	1, 3	Th	≤0.2	No Data	
Ga	0.08	0.4	2	Ti	0.3	2	2
Ge	<0.01	0.2	2	U	≤0.2	0.7	2
Hg	0.07**	0.02-30	1	V	1	15-590	2, 4
K	3	34	2	Zn	0.2	1	2
La	0.01	No Data					

\* Composite sample analyzed by SSMS (Level 1).

† References 1 and 3 provided ranges for U.S. and foreign crude oils. References 2 and 4 provided either average values or ranges for residual oil.

‡ MC indicates a major component for which SSMS did not provide a numerical value.

\*\* Mercury was analyzed by elemental sparging (Level 1).

## FLUE GAS EMISSIONS

### Criteria Pollutants

Federal New Source Performance Standards (NSPS) currently in effect define allowable emission rates of  $\text{NO}_x$  (as  $\text{NO}_2$ ),  $\text{SO}_2$  and total particulates from fossil fuel fired utility boilers having 25 MW or greater output. More stringent limitations have been proposed by EPA for  $\text{NO}_x$ ,  $\text{SO}_2$  and total particulate emissions. Federal NSPS currently address neither CO nor total hydrocarbon emissions. Existing NSPS and corresponding proposed emission standards for oil-fired utility boilers are summarized in Table 4-4. It should be noted that this plant is not required to meet NSPS; they are provided for comparison only.

A total of 4 tests were performed. Criteria pollutant emissions data for these tests are summarized in Table 4-5 and compared with the EPA AP-42 emission factors for uncontrolled sources (5). In Table 4-6, average emissions data are presented. The emissions data are discussed by specific pollutant in the ensuing subsections.

#### Nitrogen Oxides--

$\text{NO}_x$  emissions were monitored continuously by chemiluminescent instrumentation. The  $\text{NO}_x$  emission factor near full load condition was 116 ng/J, which is 62% lower than the average  $\text{NO}_x$  emission factor of 309 ng/J tabulated in AP-42 (5). The lower  $\text{NO}_x$  emission factor was due to the use of flue gas recirculation and off-stoichiometric firing for  $\text{NO}_x$  control. Measured  $\text{NO}_x$  emissions are slightly below the NSPS limit of 130 ng/J for oil-fired utility boilers.

#### Carbon Monoxide--

Average CO emissions were 6.6 ng/J. This is in reasonable agreement with the AP-42 emission factor of 14.7 ng/J for oil-fired utility boilers, considering the normal scatter in reported CO data.

#### Sulfur Dioxide--

$\text{SO}_2$  emissions were monitored continuously by pulsed fluorescent analyzer for all tests. Additionally,  $\text{SO}_2$  was determined in conjunction with the Goksoyr-Ross Controlled Condensation System (CCS) for Test 143.

TABLE 4-4. EXISTING AND PROPOSED FEDERAL EMISSION STANDARDS  
FOR OIL-FIRED UTILITIES

Pollutant	NSPS	Proposed Standard
NO <sub>x</sub> (as NO <sub>2</sub> )	130 ng/J (0.30 lb/MM Btu)	130 ng/J (0.30 lb/MM Btu)
SO <sub>2</sub>	344 ng/J (0.80 lb/MM Btu)	520 ng/J (1.20 lb/MM Btu) max. with 85% reduction to 85 ng/J (0.20 lb/MM Btu)
Total Particulates	43 ng/J (0.10 lb/MM Btu)	13 ng/J (0.03 lb/MM Btu)

TABLE 4-5. COMPARISON OF AVERAGE CRITERIA POLLUTANT EMISSIONS WITH  
EPA AP-42 EMISSION FACTORS FOR OIL-FIRED UTILITY BOILERS

Pollutant	Emission Factor (ng/J)	
	Test Data	AP-42 Emission Factor
NO <sub>x</sub> <sup>*</sup> (as NO <sub>2</sub> near full load)	116	309
CO <sup>†</sup>	6.6	14.7
SO <sub>2</sub> <sup>‡</sup>	98	84
Total Organics <sup>**</sup>	0.42-0.58	2.94
Total Particulates <sup>††</sup>	7.5	14.2

\* NO<sub>x</sub> was determined by continuous chemiluminescent analysis (Level 1).

† CO was determined by continuous non-dispersive infrared analysis (Level 2).

‡ SO<sub>2</sub> was determined by continuous pulsed fluorescence analysis (Level 2).

\*\* C<sub>1</sub>-C<sub>16</sub> fractions were determined by gas chromatograph while the >C<sub>16</sub> fraction was determined gravimetrically (Level 1).

†† Total particulates were determined by a modified Method 5 procedure (Level 2).

TABLE 4-6. SUMMARY OF CRITERIA POLLUTANT EMISSIONS

Test No.	Emission Factor (ng/J)							
	NO <sub>x</sub> (as NO <sub>2</sub> )	CO	SO <sub>2</sub>	C <sub>1</sub> -C <sub>6</sub> Organics*	C <sub>7</sub> -C <sub>16</sub> Organics	>C <sub>16</sub> Organics	Total Organics	Total Particulates
141	114	11.3	105	0.35-0.56	ND <sup>†</sup>	ND <sup>†</sup>	ND <sup>†</sup>	ND <sup>†</sup>
142	91	5.2	95	0.29-0.43	0.02	0.16	0.47-0.61	8.3
143	117	5.6	90 <sup>±</sup>	0.11-0.22	0.02	0.14	0.27-0.38	6.6
144	98	4.5	103	ND <sup>†</sup>	ND <sup>†</sup>	ND <sup>†</sup>	ND <sup>†</sup>	ND <sup>†</sup>
Average	105	6.6	98	0.25-0.40	0.02	0.15	0.37-0.50	7.5

\* Upper limit values include detection limits.

† ND - data not available.

± Average of continuous monitoring (105 ng/J) and CCS (75.6 ng/J) data for Test 143.

Average  $\text{SO}_2$  emissions were 98 ng/J for oil firing. This uncontrolled emission factor is higher than the AP-42 emission factor of 84 ng/J for oil firing but is well below the NSPS limit of 344 ng/J for oil-fired utility boilers.

#### Total Organics--

In the determination of organic emissions, gas chromatographic analyses were performed on grab bag samples of flue gas and catches from the Level 1 sampling (SASS train). Additionally, gravimetric analyses were performed on Level 1 samples to quantify high molecular weight organics. Each bag sample was collected over an interval of 30 to 45 minutes, with a single sample being collected per test. These samples were utilized to measure  $\text{C}_1$  to  $\text{C}_6$  hydrocarbons. The SASS train collects approximately 30 cubic meters of flue gas which are drawn isokinetically during the test. Samples from the SASS train were analyzed to determine organics higher than  $\text{C}_6$ . The  $\text{C}_7$  to  $\text{C}_{16}$  fraction was determined by gas chromatograph while organics higher than  $\text{C}_{16}$  were determined gravimetrically.

Measured organics consisted primarily of the  $\text{C}_1$ - $\text{C}_6$  fraction. Average emissions of the  $\text{C}_1$ - $\text{C}_6$  fraction were 0.25 to 0.40 ng/J while those for the  $\text{C}_7$ - $\text{C}_{16}$  and higher molecular weight fractions were 0.02 ng/J and 0.15 ng/J, respectively.

Average organic emissions were 0.4-0.5 ng/J, which is only 15% of the reported AP-42 value of 2.94 ng/J for oil-fired utility boilers. The higher "measured" organic value includes the detection limit concentrations for fractions which were not detected and, as such, represents an upper limit.

#### Total Particulates--

Average emissions of total particulates were 7.5 ng/J. The measured particulate emission factor is only about half the reported AP-42 value of 14.2 ng/J, probably due to the extremely low ash content (0.01%) of the fuel oil burned. Measured emissions are well below the NSPS limit of 43 ng/J.



## Particulate Size Distribution

Due to the extremely light particulate loading, particulate size distribution data are not available. However, data available from the literature have indicated that generally 90 wt. % of emitted particulates are less than 7  $\mu\text{m}$  for oil-fired boilers (7).

In a recent draft document issued by the Health Effects Research Laboratory (HERL) of EPA (8), it is stated that larger particulates (from 3 to 15  $\mu\text{m}$ ) deposited in the upper respiratory system (in the nasopharynx and conducting airways) can also be associated with health problems. This is in contrast to the past belief that particulates of health consequence were those less than 3  $\mu\text{m}$  size and deep-lung penetrable. The area of concern now is particulates which are 15  $\mu\text{m}$  and less, which have been designated as "inhaled particulates" (IP). For oil firing, it can be reasonably assumed that almost all the particulates emitted are 15  $\mu\text{m}$  or less.

## Sulfur Compounds: $\text{SO}_2$ , $\text{SO}_3$ , and $\text{SO}_4^{=}$

Sulfur species were determined using several methods.  $\text{SO}_2$  at the stack was continuously monitored during all tests using a pulsed fluorescent analyzer. During test 143, the CCS was also used to collect  $\text{SO}_2$  (from the impinger),  $\text{SO}_3$  (condensed as  $\text{H}_2\text{SO}_4$ ), and  $\text{SO}_4^{=}$  (by anion analysis of the particulate catch). Sulfur speciation data are listed in Table 4-7. An average of 97.7% of the output sulfur is emitted as  $\text{SO}_2$ .

Particulate sulfate represented 1.1% of sulfur emissions. Sulfate emissions broken down into water- and acid-soluble fractions are presented in Table 4-8. The bulk (>87%) of the particulate sulfates was present in the water-soluble fraction.

Approximately 1.2% of the sulfur emitted was in the form of  $\text{SO}_3$ . The  $\text{SO}_3$  emissions were lower than typical values reported in the literature (9), probably because of the lower vanadium and nickel content of the fuel oil burned, and because of the use of flue gas recirculation which reduces the oxygen concentration and, therefore, reduces  $\text{SO}_3$  formation rate.

TABLE 4-7. SO<sub>2</sub>, SO<sub>3</sub>, AND SO<sub>4</sub><sup>=</sup> EMISSIONS\*

Sulfur Compound	Test No.	Sampling Method	Stack Gas ng/J	Mole % of Total Sulfur Species in Flue Gas
SO <sub>2</sub>	141	Continuous	105	
	142	"	95	
	143	"	105	
	144	"	103	
	143	CCS	75.6	97.7
	Average		98	
<hr/>				
SO <sub>3</sub>	143	CCS	1.14	1.2
<hr/>				
SO <sub>4</sub> <sup>=</sup>	143	CCS	1.27	1.1

\* Level 2 procedures were utilized.

TABLE 4-8. SUMMARY OF SULFATE EMISSIONS

Test No.	Sampling Point	Water Soluble Sulfates		Acid Soluble Sulfates		Total ng/J
		ng/J	% of Total	ng/J	% of Total	
143	Stack	1.27	>87.0	<0.19	<13	1.27-1.46

\* Level 2 procedures were utilized.

## Inorganics

Trace element concentrations in the flue gas were computed by assuming that all trace elements present in the fuel oil are emitted in the stack. Trace elements in the fuel oil were determined using spark source mass spectrometry (SSMS).

Concentrations of 39 major trace elements present in the flue gas are presented in Table 4-9. To assess the hazard potential of these emissions, the emission concentrations are compared with the DMEG values. The DMEG values are emission level goals developed under direction of EPA, and can be considered as concentrations of pollutants in undiluted emission streams that will not adversely affect those persons or ecological systems exposed for short periods of time (10). The DMEG values tabulated represent air concentrations which were derived from human health considerations based on the most hazardous compound formed by the element in question. Only chromium and nickel exceeded their DMEG values at the stack. Chromium and nickel have low DMEG values due to considerations of potential human carcinogenicity. Emission factors for the trace elements analyzed are presented in Table 4-10.

## Chloride and Fluoride Emissions

Specific anion analysis was performed on extracts from particulate catches and impinger solutions from the Goksoyr-Ross sampling train (Test 143). Emissions of  $\text{Cl}^-$  and  $\text{F}^-$  were 1.34 ng/J and 0.061 ng/J, respectively. However, anticipated emissions based on SSMS analysis of a composite fuel sample from Tests 141-144 are 0.002 ng  $\text{Cl}^-$ /J and 0.0002 ng  $\text{F}^-$ /J. Whether this discrepancy is the result of analytical problems or due to significant variation in  $\text{Cl}^-$  and  $\text{F}^-$  contents of the different fuel samples cannot be conclusively determined from available data. Yet, ultimate fuel analyses indicate little variation among the fuel samples. Also, it is known that halogens are not determined well by SSMS. Fluorine is particularly difficult to analyze by SSMS. On the other hand, specific ion electrode analyses are generally accurate to within approximately 15%. Hence, it appears reasonable to conclude that the observed discrepancy is primarily the result of analytical problems associated with SSMS analyses of  $\text{Cl}^-$  and  $\text{F}^-$  in the fuel oil.

TABLE 4-9. EMISSION CONCENTRATIONS OF TRACE ELEMENTS

Element	Flue Gas Concentration* mg/m <sup>3</sup>	DMEG for Air (Health Basis) mg/m <sup>3</sup>	Discharge Severity†
Al‡	0.066	5.2	0.013
As	<0.0007	0.0020	<0.3
B	0.03	3.1	0.01
Ba	0.03	0.50	0.06
Be	<0.0007	0.0020	<0.3
Br	<0.0007	10	<0.00007
Ca‡	0.0086	16	0.0005
Ce	<0.0007	37	<0.00002
Cl	0.007††	No Data	---
Co	0.03	0.050	0.6
Cr	0.006	0.0010	6
Cs	0.005	82	0.00006
Cu	0.007	0.20	0.03
F	<0.0007††	2.5	<0.0003
Fe	0.1	1.0	0.1
Ga	0.005	5.0	0.001
Ge	<0.0007	0.56	<0.2
Hg**	0.005	0.050	0.1
K	0.2	2.0	0.1
La	0.0007	110	0.000006
Li	0.001	0.022	0.05
Mg‡	0.37	6.0	0.062
Mn	0.003	5.0	0.0006
Mo	0.007	5.0	0.001
Na‡	2.0	53	0.038
Ni	0.5	0.015	30
P	0.07	0.10	0.7
Pb	0.003	0.15	0.02
Pr	<0.0007	No Data	---
Rb	<0.0007	120	<0.000006
Sc	≤0.0007	53	≤0.00001
Se	0.001	0.20	0.005
Si	0.3	10	0.03
Sr	0.006	3.0	0.002
Th	0.01	No Data	---
Ti	0.02	6.0	0.003
U	≤0.01	0.009	≤1
V	0.07	0.50	0.1
Zn	0.01	4.0	0.002

- Continued -

TABLE 4-9. (Continued)

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- \* Estimates based on average trace element content of the fuel oil, as analyzed by SSMS.
- † Discharge severity is defined as the ratio of the discharge concentration to the DMEG value.
- ‡ Estimates based on typical trace element content of the fuel oil reported for this site. SSMS analyses performed on the fuel oil samples indicated Al, Ca, Mg, and Na as major components without specific numerical values being given.
- \*\* Mercury was determined by elemental sparging (Level 1).
- †† Specific ion analysis performed on the Goksoyr-Ross catch (test 143) indicate that the chloride and fluoride concentrations may be as high as 4.7 and 0.2 ng/m<sup>3</sup>, respectively. This discrepancy is considered to result primarily from analytical problems associated with SSMS analysis of these halides.

TABLE 4-10. EMISSION FACTORS FOR TRACE ELEMENTS\*

Element	Emission Factor, ng/J	Element	Emission Factor, ng/J
Al†	0.023	Li	0.0003
As	<0.0002	Mg†	0.13
B	0.01	Mn	0.001
Ba	0.01	Mo	0.002
Be	<0.0002	Na†	0.70
Br	<0.0002	Ni	0.2
Ca†	0.0030	P	0.02
Ce	<0.0002	Pb	0.02
Cl	0.002 (1.34)‡	Pr	<0.0002
Co	0.01	Rb	<0.0002
Cr	0.002	Sc	≤0.0002
Cs	0.002	Se	0.0003
Cu	0.002	Si	0.1
F	<0.0002 (0.061)‡	Sr	0.002
Fe	0.03	Th	0.003
Ga	0.002	Ti	0.007
Ge	<0.0002	U	≤0.003
Hg	0.002	V	0.02
K	0.7	Zn	0.003
La	0.0002		

\* Computed assuming that all trace elements in the fuel were emitted through the stack. Fuel trace elements were determined by SSMS with the exception of Hg which was determined by elemental sparging.

† Emission factors for Al, Ca, Mg, and Na are based on typical fuel concentrations of these elements for this site. SSMS analyses indicated these elements as major components without specific numerical values being given.

‡ Values in parentheses were obtained from specific ion analysis of the Goksoyr-Ross catch from Test 143.

### Specific Organic Compounds

Selected samples were analyzed by combined gas chromatography/mass spectrometry (GC/MS) for the identification of organic compounds present. The organic compounds identified include aliphatic hydrocarbons, benzaldehyde, trimethyl cyclohexane-one, C<sub>2</sub> substituted acetophenone, the methyl esters of benzoic acid and substituted benzoic acid, diethylphthalate, and ethylbenzaldehyde, at concentration levels between 0.02 and 2 µg/m<sup>3</sup>.

Emissions of polycyclic organic matter (POM) determined by GC/MS are summarized in Table 4-11. Naphthalene is the principal component of the POM emissions. Benzopyrenes were detected at low levels but specific isomers cannot be differentiated. Hence, it is not known whether benzo(a)-pyrene was present. With the exception of the possible presence of benzo(a)pyrene, all POM compounds from oil firing are at levels too low to be of environmental concern.

#### LIQUID WASTE

There are no significant wastewater streams associated with the oil-fired boiler tested.

#### SOLID WASTE

There are no significant solid wastes generated from the oil-fired boiler tested.

TABLE 4-11. POM EMISSIONS FROM OIL FIRING\*

Compound	Emission Concentration, $\mu\text{g}/\text{m}^3$		DMEG Value $\mu\text{g}/\text{m}^3$	Discharge Severity	
	Test 142	Test 143		Test 142	Test 143
Naphthalene	7	3	50,000	0.0001	<0.0001
Phenanthridine <sup>†</sup>	0.3	--	No data	ND	--
Dibenzothiophene <sup>‡</sup>	0.6	--	23,000	<0.0001	--
Anthracene/ phenanthrene	1	0.2	1,600	0.0006	0.0001
Fluoranthene	1	--	90,000	<0.0001	--
Pyrene	1	--	230,000	<0.0001	--
Chrysene/ benz(a)anthracene	0.1	--	45	0.0022	--
Benzopyrene <sup>**</sup> and perylene	0.04	--	0.02	2	--
Tetramethyl- phenanthrene <sup>††</sup>	--	0.6	1,600	--	0.0004
Total	11.0	3.8			

\* Level 2 procedures were utilized.

<sup>†</sup> Due to the low compound concentration, phenanthridene has not been positively identified.

<sup>‡</sup> Due to the low compound concentration, dibenzothiophene has not been positively identified. Also, the DMEG value for dibenzothiophene is assumed to be the same as that for benzothiophene.

<sup>\*\*</sup> The DMEG value for benzo(a)pyrene is used in the computation of the discharge severity.

<sup>††</sup> The DMEG value for tetramethyl phenanthrene is assumed to be the same as that for phenanthrene.



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## SECTION 5

### ENVIRONMENTAL IMPACT ASSESSMENT

This section presents an evaluation of impacts resulting from emissions from oil combustion in utility boilers similar to the emissions observed at the Haynes station. The evaluation is conducted in five parts. The first part introduces background information pertinent to the development of the environmental assessment, including a review of relevant studies, plant emissions, and air quality forecasts. In the succeeding parts, the major health, ecological, and economic impacts resulting from oil firing in controlled utility boilers of the type tested are estimated. The final section assesses the implications of the impacts for energy development by considering: 1) the additional controls which may be needed to mitigate the expected damage levels, and 2) the potential effect of such control needs on energy cost and energy resource development.

#### INTRODUCTION

Economic and environmental concerns over the nation's energy development policies have precipitated several research efforts to evaluate the consequences of all phases of energy development, from fuel production to fuel end use. To organize the various efforts into a systematic, coordinated, environmental assessment structure, the Environmental Protection Agency is implementing a Conventional Combustion Environmental Assessment (CCEA) Program. This program has been established for the purpose of integrating together separate data generated by past and current studies into a complete environmental assessment of conventional combustion processes. The integration procedure involves coordination and information exchange between EPA related studies to: 1) determine the extent to which the total environmental, economic, and energy impacts of conventional combustion process can be assessed, 2) identify additional information needed for complete assessment, 3) define the requirements for modifications or additional developments of control technology, and 4) define the requirements for modified or new standards to regulate pollutant emissions. The CCEA Program coordinates

and integrates current and future studies encompassing a wide spectrum of environmental assessment areas and conventional combustion processes. Integration of these studies, including the present effort, will provide the basis for energy policies which result in the expanded use of conventional combustion processes at reasonable environmental, economic, and energy costs.

## AIR QUALITY

### Model Plant Emissions

Air quality impacts of oil firing in utility boilers were estimated based on a hypothetical model plant. The model plant was characterized using emission factors derived from the Haynes plant test data and assumed meteorological parameters. The model plant was assumed to have the same fuel and boiler characteristics as the Haynes station. The criteria pollutant emission rates utilized are shown in Table 5-1. Comparison of the measured trace element emission concentrations with DMEG values revealed that the flue gas contained only 2 elements which exceed their DMEG values at the stack, Cr and Ni. Hence, only these trace elements were considered in the analysis.

TABLE 5-1. EMISSION RATES FROM A CONTROLLED 353 MW  
(GROSS) OIL-FIRED UTILITY BOILER

Pollutant	Emissions, gm/sec
NO <sub>x</sub>	95.2
CO	5.4
SO <sub>2</sub>	80
Total Organics	0.34 - 0.48
Total Particulates	6.2
Cr*	0.002
Ni*	0.2

\*Trace element concentration in the flue gas (based upon fuel analyses) exceeds DMEG value.

## Annual Emissions

Estimated annual emissions for oil-fired plants generating 353 MW (gross) are presented in Table 5-2. These estimates are based on the emission factors determined for the Haynes No. 5 boiler during oil firing. For annual emission computations, the plant was assumed to operate at 93% of its maximum load with 40% overall efficiency, for 7008 hours/year (80% of the year). These assumptions are based upon measurements made during the test period and operability data provided by Haynes personnel.

## Impact on Air Quality

The duration of exposure is important in determining effects of changing air quality. The highest concentrations occur for short periods (usually less than one hour) under meteorological conditions causing plume trapping. The stack emissions are trapped under an inversion layer, with the plume spreading downward. The frequency of occurrence and the severity of plume trapping conditions varies depending on the site. As a conservative worst case estimate in this study, plume trapping conditions were assumed to persist for periods as long as three hours.

TABLE 5-2. ANNUAL EMISSIONS\*

Pollutant	kg/yr
NO <sub>x</sub>	2.40 x 10 <sup>6</sup>
SO <sub>2</sub>	2.0 x 10 <sup>6</sup>
SO <sub>3</sub>	2.36 x 10 <sup>4</sup>
SO <sub>4</sub>	2.63 x 10 <sup>4</sup>
CO	1.4 x 10 <sup>5</sup>
Total Organics	7.7 x 10 <sup>3</sup> - 10 x 10 <sup>3</sup>
C <sub>1</sub> -C <sub>6</sub>	5.2 x 10 <sup>3</sup> - 8.3 x 10 <sup>3</sup>
C <sub>7</sub> -C <sub>16</sub>	4 x 10 <sup>2</sup>
>C <sub>16</sub>	3.1 x 10 <sup>3</sup>
Total Particulates	1.5 x 10 <sup>5</sup>

\*Oil-fired plants generating 353 MW operating 7008 hours/year.

Typical 24 hour maximum concentrations were estimated assuming Gaussian steady state plume dispersion under conditions of low wind speed and stable atmosphere. Typical 24 hour levels were translated to annual expected concentrations by applying ratios for the one day maximum and annual mean as empirically derived from the Continuous Air Monitoring Project (1, 2, 3, 4). The effective stack height was estimated based on assumed meteorological conditions, and the actual stack height of the Haynes unit.

Maximum predicted levels for criteria pollutants in the vicinity of the model plant are presented in Table 5-3. Ambient concentrations resulting from oil firing are in conformance with all tabulated air quality standards. The short term maximum concentrations present the most significant air pollution problem. For any of the pollutants, it should be noted that the short term maximum concentrations generally occur infrequently, depending on site meteorology, and are usually of very brief duration (about 1 hour or less). The maximum concentration levels are localized within a distance of about one-half to four miles from the boiler stack. These concentrations diminish to about one-half the peak level another one to eight miles further downwind. Concentrations of CO and total organics are seen to be insignificant with respect to short term NAAQS. Hence, these compounds will not be considered further.

Federal standards limiting deterioration of air quality are generally more restrictive than the NAAQS. Included in Table 5-3 is a list of the allowable increments of deterioration for the three classes of growth and development areas. Allowable emissions may depend primarily on the existing air quality and the allowable deterioration increment. Consequently, siting of the plants would be a major consideration in their environmental acceptability, since areas which already experience marginally acceptable air quality may not tolerate the increases projected to occur.

#### HEALTH IMPACT

The health effects of exposure to high concentrations of the various pollutants are well known and have been tabulated throughout the literature (5). However, the specific extent to which health is affected by ambient pollutant exposure levels (dose-response relationships) is unclear. Moreover,

TABLE 5-3. COMPARISON OF FEDERAL AIR QUALITY STANDARDS  
WITH AIR QUALITY PREDICTED TO RESULT FROM OIL  
COMBUSTION IN A 353 MW (GROSS) UTILITY BOILER

Pollutant	Concentration, $\mu\text{g}/\text{m}^3$				
	Model Plant	NAAQS	PSD Increments**		
			Class I	Class II	Class III
Annual Mean*					
NO <sub>x</sub>	2	100	---	---	---
CO	0.1	---	---	---	---
SO <sub>2</sub>	2	80	2	20	40
Total Organics	0.01	---	---	---	---
Total Particulates	0.1	75	5	19	37
24 Hour†					
NO <sub>x</sub>	8	---	---	---	---
CO	0.4	--- <sup>††</sup>	---	---	---
SO <sub>2</sub>	6	365	5	91	182
Total Organics	0.04	---	---	---	---
Total Particulates	0.5	260	10	37	75
1-3 Hour‡					
NO <sub>x</sub>	260	---	---	---	---
CO	15	40,000 <sup>††</sup>	---	---	---
SO <sub>2</sub>	230	1,300	25	512	700
Total Organics	1	160	---	---	---
Total Particulates	18	---	---	---	---

\* The expected annual average levels were estimated based on the conservative end of the range of typical ratios for 24 hour maximum to annual as reported in the Air Quality Criteria Documents (1, 2, 3, 4).

† Based on typical meteorological conditions for 24 hour period.

‡ Based on worst case meteorological conditions (plume trapping).

\*\* Prevention of significant deterioration standards (PSD).

†† The NAAQS for CO are 40,000  $\mu\text{g}/\text{m}^3$  for a 1 hour period and 10,000  $\mu\text{g}/\text{m}^3$  for an 8 hour period.

it is unclear how pollutant specific dose-response curves may be related to the overall health effects of the gas-aerosol complex associated with fossil fuel combustion products.

Most attempts to establish dose-response functions for ambient pollution levels involve the formulation of some indicator which is then assumed to represent the entire spectrum of primary and secondary pollutants present. The indicator (usually sulfur dioxide, total particulates, or sulfates) is then related to mortality or morbidity data for various areas by various statistical approaches designed to factor out effects of other variables (e.g., population age, climatology, etc.). Dose-response curves derived from these studies are then employed to estimate health effects of air quality changes resulting from proposed projects.

Recently, the health effects model by Lundy and Grahn (6) has been developed for application in the National Coal Utilization Assessment Studies being conducted at Argonne National Laboratories. The model combines mortality functions for suspended sulfates as developed by Finch and Morris (7) and age-dependent and established response curves for cigarette smoke. The mortality dose-response functions for suspended sulfates are based on statistical studies of various populations experiencing different sulfate exposures. Unlike the dose-response air pollution studies, investigations of smokers have been relatively well controlled with respect to age, degree of exposure, and effect. Thus, to expand the predictability of the sulfate dose-response curves to populations of different age distribution (e.g., future populations), the cigarette response curves are adjusted to fit the observed mortality/sulfate data, resulting in a model which predicts age-specific death rates. This elaboration is important because death rates vary exponentially with age, and shifts in the age distribution of a population will result in substantial shifts in total mortality. Accordingly, the Lundy-Grahn Model utilizes projections of the population age distribution to estimate the age-specific and total death rates due to air pollution at any specific time in the future. The basic relationship of the model is:

$$B(X, X_0) = \frac{ae^{bX}}{1 + ce^{-d(X-X_0)}} S$$

where B is the number of excess deaths per year for the population of age X which was exposed to the sulfate concentration S (in  $\mu\text{g}/\text{m}^3$ ) since age  $X_0$ . The constants a,b,c and d are coefficients to fit the model to cigarette smoking mortality data and response data for a specific population subgroup exposed to air pollution.

The Lundy-Grahn Model is being used in the ongoing National Coal Utilization Assessment Program to estimate excess mortality resulting from increased coal utilization. Air diffusion modeling was conducted first to predict a population-weighted exposure increase for suspended sulfates. The Lagrangian Statistical Trajectory Model of Argonne National Laboratory (8), which assumes a constant transformation of  $\text{SO}_2$  to sulfate, is employed in the estimation procedure. This technique has been applied to oil firing; based on the predicted exposure increase and projections of the population age distribution, excess death rates are calculated for each age and summed to yield the expected mortality associated with oil combustion. Figure 5-1 presents the adjusted projections for an oil firing scenario through the year 2020. The figure indicates that the expected health effects caused by air pollution (as indexed by suspended sulfates) from oil-firing of controlled utility boilers are minimal. The maximum impact is expected to occur in the year 2000, when the proportion of population in the highest risk age groups will be greatest. For each million persons, the expected increase in death rate when oil firing of utility boilers is prevalent is 49 persons per million.

Health effects caused by sulfate levels may also be expressed in terms of morbidity. Table 5-4 presents data for increases in incidents of health disorders due to ambient sulfate exposures. In those areas which already experience high sulfate levels, respiratory disease may increase significantly with increases of suspended sulfates due to increased fuel consumption. For example, in areas where the threshold level  $10 \mu\text{g}/\text{m}^3$  is exceeded regularly, the contribution of  $2.4 \mu\text{g}/\text{m}^3$  of sulfate concentration associated with controlled oil-fired boilers would be estimated to produce a 32% increase in the incidence of chronic respiratory disease caused at the threshold level.



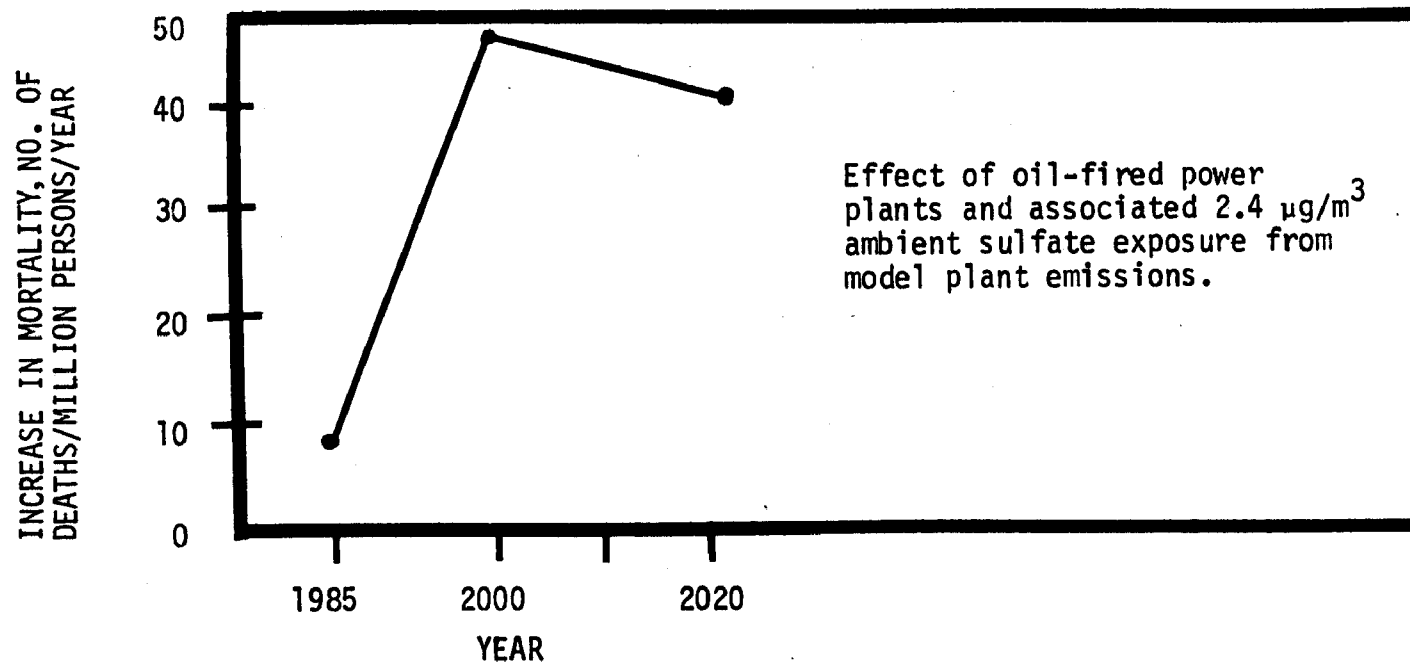


Figure 5-1. Health Effects From Sulfate Levels Resulting From Oil Combustion in Utility Boilers.

TABLE 5-4. HEALTH IMPACTS OF SULFATE AEROSOL \*

Pollutant and Health Effect	Population at Risk	Assumed Baseline Frequency of Disorder within Population at Risk	Pollutant Concentration Threshold For Effect	Effect Increase as % of Baseline Per Pollutant Unit Above Threshold
<u>Sulfates</u> Mortality	Total Population	Daily death rate of 2.58 per 100,000	25 $\mu\text{g}/\text{m}^3$ for one day or more	2.5% per 10 $\mu\text{g}/\text{m}^3$
Aggravation of Heart and Lung Disease in Elderly	Same as above for oxidants function	Same	9 $\mu\text{g}/\text{m}^3$ for one day or more	14.1% per 10 $\mu\text{g}/\text{m}^3$
Aggravation of Asthma	Same as above for oxidants function	Same	6 $\mu\text{g}/\text{m}^3$ for one day or more	33.5% per 10 $\mu\text{g}/\text{m}^3$
Lower Respiratory Disease in Children	Same as above for nitrogen dioxide function	Same	13 $\mu\text{g}/\text{m}^3$ for several years	76.9% per 10 $\mu\text{g}/\text{m}^3$
Chronic Respiratory Disease Nonsmokers	62 percent of population age 21 or older	Two percent prevalence	10 $\mu\text{g}/\text{m}^3$ for several years	134% per 10 $\mu\text{g}/\text{m}^3$
Smokers	38 percent of population age 21 or older	Ten percent prevalence	15 $\mu\text{g}/\text{m}^3$ for several years	73.8% per 10 $\mu\text{g}/\text{m}^3$

\* Reference 9.

In addition to potential health effects created by long range sulfate levels from utility boilers, high concentrations of pollutants in the proximity of the power plant pose a potentially serious health problem. The Lundy-Grahn model may also be applied to estimate mortality effects caused by ambient levels of  $\text{SO}_2$  and total suspended particulates. The model gives the following relationships when fitted to Lave and Seskin dose-response data (6) for  $\text{SO}_2$  and total suspended particulate (TSP):

$$\text{per } 10^6 \text{ males: } \frac{.823e^{-.064X}}{1 + 100e^{-.2(X - X_0)}} \quad (.835 \text{ TSP} + .715 \text{ SO}_2)$$

$$\text{per } 10^6 \text{ females: } \frac{.056e^{-.088X}}{1 + 100e^{-.2(X - X_0)}} \quad (.835 \text{ TSP} + .715 \text{ SO}_2)$$

If the model is applied for average concentrations expected to occur in the vicinity of a power plant (Table 5-3), the expected increase in mortality is appreciable. Figure 5-2 illustrates the estimated impact on mortality. When boilers are fired with oil, the increased death rate is about 19 male and 9 female deaths per million persons per year, at age 50.

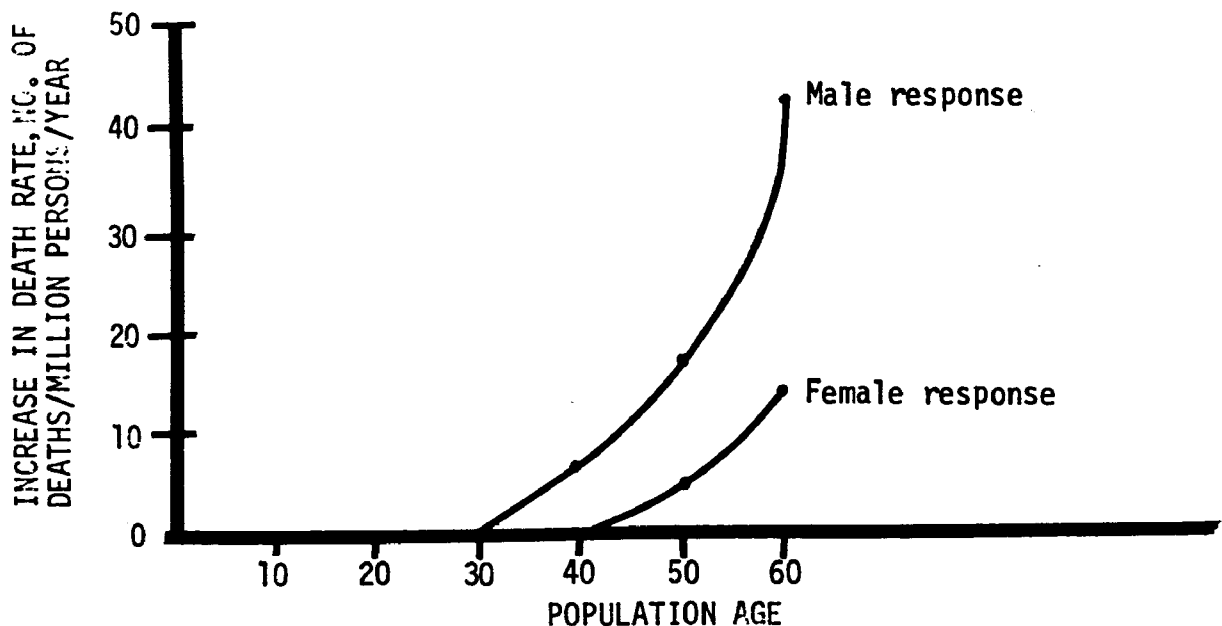


Figure 5-2. Increase in Mortality Rates in Vicinity of Oil-fired Utility Boilers as a Result of  $\text{SO}_2$  and Total Particulate Emissions.

## Effect of Trace Elements--

Trace elements from combustion emissions enter the atmosphere and are then dispersed to the upper atmosphere or deposited in the environment around the sources. The principal routes of entry to man are by inhalation, drinking water, and food.

Table 5-5 summarizes estimates of the annual average atmospheric concentrations of Cr and Ni expected in the vicinity of a single oil-fired utility boiler of 353 MW gross capacity. These elements were examined because their stack concentrations exceeded their respective DMEG values. Also included in Table 5-5 is a listing of concentrations considered acceptable for continuous ambient exposure. The allowable concentrations are based on proposed regulations for control of air pollution from hazardous waste management facilities, as required by Section 3004 of the Resource Conservation and Recovery Act. It is clear that the air concentrations of trace elements resulting from operation of the utility boiler are several orders of magnitude below either the allowable exposure level or typical urban air concentrations.

TABLE 5-5. EXPECTED TRACE ELEMENT CONCENTRATIONS IN VICINITY OF A 353 MW (GROSS) OIL-FIRED UTILITY BOILER

Element	Annual Ambient Concentration $\mu\text{g}/\text{m}^3$	Typical Urban Air Concentration* $\mu\text{g}/\text{m}^3$	Allowable Exposure Level† $\mu\text{g}/\text{m}^3$
Cr	0.00003	.010	50
Ni	0.004	1.40	100

\* Based on data reported in References 10, 11, and 12.

† Based on ambient air objectives proposed for hazardous waste management facilities (13).

A primary concern in emissions of trace elements is the contribution of these elements to body burden due to exposure to water and food. To estimate this contribution, pollutant deposition rates are approximated by the product of the ambient concentrations and the deposition velocity of the pollutant. The deposition rate is dependent on particle size. As discussed previously particles emitted from an oil-fired boiler are predominantly less than 7  $\mu\text{m}$  in diameter. Available data indicate that the median particle size is in the 1  $\mu\text{m}$  to 3  $\mu\text{m}$  range. The deposition velocity of particles this size over grass surfaces is approximately 0.1 to 0.2 cm/sec (14). Accordingly, the deposition rates of the various trace elements were approximated and are shown in Table 5-6.

The significance of the deposition rates is evaluated by considering the associated effect on drinking water and diet. The pathway to drinking water is by run-off of soil particles containing deposits of trace elements, and the pathway to the diet is by plant uptake from trace elements in the soil. In either pathway, the incremental concentration of elements in the soil determines the extent of the potential impact. Table 5-7 summarizes the maximum predicted soil concentration in the vicinity of the oil-fired model plant. The concentrations are estimated by assuming mixing of the deposited elements to a depth of 10 cm, and over a period of 40 years. For these trace elements, only minor increases over the background soil levels would be expected. The significance of elevated soil concentrations is evaluated by considering the associated increase in trace element concentration in plant tissues and drinking water.

The concentration of elements in plant tissues is related to the biologically available fraction of the elements in the soil. This is often expressed as the soluble concentration in the soil, and is some fraction of the total concentration reported in Table 5-7. Plants possess the ability to concentrate elements from dilute soil solutions. This ability is dependent on the concentration of elements in the soil, and usually increases with decreasing soil concentrations. The ratio of concentration of elements in plants to the concentration in the soil is known as the concentration ratio. Table 5-8 lists average plant concentration ratios for various elements. The data are based on various published data as compiled in a study by

TABLE 5-6. ANNUAL DEPOSITION OF TRACE ELEMENTS IN VICINITY OF CONTROLLED OIL-FIRED POWER PLANTS

Element	Annual Deposition Rate*, g/m <sup>2</sup> -yr.
Cr	$1.9 \times 10^{-6}$
Ni	$2.5 \times 10^{-4}$

\* Calculated by assuming a particulate deposition velocity of 0.2 cm/sec. The deposition velocity is multiplied by the annual average concentration to estimate the total deposition rate. The deposition rate is calculated for the location where the maximum average annual concentration occurs.

TABLE 5-7. LONG TERM EFFECT OF CONTROLLED OIL-FIRED UTILITY BOILER EMISSIONS ON SOIL CONCENTRATIONS OF TRACE ELEMENTS

Element	Increased Soil Concentration After 40 Years*, mg/kg	Typical Soil Concentration† mg/kg	Increase Over Average Soil Concentrations, %
Cr	0.001	40	0.003
Ni	0.07	40	0.2

\* Based on deposition rate (Table 5-6), an assumed mixing depth of 10 cm and soil density of 1.5 gm/cm<sup>3</sup>.

† Based on data compiled in Reference 15.

TABLE 5-8. LONG TERM EFFECT OF CONTROLLED OIL-FIRED BOILER EMISSIONS ON CONCENTRATIONS OF ELEMENTS IN PLANTS

Element	Concentration Ratios*	Solubility of Elements %	Typical Concentration in Plants,* mg/kg	Increase in Concentration of Plants,† mg/kg
Cr	250	0.004	.23	0.00001
Ni	331	0.1	3	0.02

\* Extracted from Reference 15.

† Calculated by multiplying concentration ratio by the incremental increase in soil concentration (Table 5-7) by the fraction of the element which is soluble.

Battelle (15). The effect of increased trace element soil loadings (caused by 40 years of boiler emissions) on concentration of the elements in plants is then estimated by assuming that the soluble portion of the loadings is available for plant take-up. The estimates reveal that oil firing produces less than a 1% increase in concentrations of chromium and nickel in plants. The actual impact of trace element emissions on plant burden depends greatly on many site-specific variables, such as temperature, precipitation, soil type, water chemistry, and plant species at a given site.

Trace elements also enter the plant via foliar absorption. Intake from the leaf surface to the interior occurs through stomatal openings, walls of epidermal cells, and leaf hairs. Although relatively little is known regarding the efficiency of foliar intake, it would appear that the plant burden produced by soils containing long term deposits is several orders of magnitude greater than that which could be transferred from foliar interception of trace elements in the atmosphere. Soil concentrations are the result of accumulation of elements over the long-term, and crops raised in these soils tend to concentrate the trace elements in the plant tissue.

By contrast, the foliar intake rate can be no greater than the deposition rate on the plant surface, and there is much uncertainty regarding the efficiency of the plant in absorbing the deposited particles. Thus, it is clear that the soil uptake scenario (Table 5-8) represents the more adverse case for plant uptake of trace elements. This scenario assumes no interference (e.g., animal or crop uptake) with trace element buildup in soils over a 40 year period, and a fixed concentration of elements in the soil despite crop uptake.

Trace elements emissions could also affect the quality of drinking water. The impact of trace element particle deposition on runoff water concentration will be related to the relative increase in soil concentration due to long term atmospheric deposition of elements. The actual runoff concentrations may be estimated by applying average sediment burden rates for representative runoff per unit of watershed area. The sediment is assumed to carry the cumulative deposits of metals originating from the boiler emissions. Table 5-9 summarizes estimates of increased soluble metals concentrations for runoff waters in the vicinity of the model plant. Runoff water in this vicinity contains trace elements at levels from six to nine orders of magnitude less than the potable water standard.

#### IMPACT ON ECOLOGY

The ecological environment will be affected by air emissions and by solid waste residuals generated by air pollution control equipment.

##### Effect of Air Emissions

A major ecological impact category most likely to be affected by utility boiler emissions is plant life. Of the major gaseous pollutants emitted by fossil fuel combustion, plant life is most affected by  $\text{SO}_2$  and  $\text{NO}_x$  in the concentration ranges expected. Concentrations of CO and hydrocarbons produced by oil firing of utility boilers would be expected to cause negligible impact on vegetation (4, 16). The maximum levels of  $\text{NO}_x$  and  $\text{SO}_2$  expected to occur in the vicinity of utility boilers may exceed the threshold injury values for these pollutants. Sensitive plants in the vicinity of the utility boiler could suffer injury, although such injury would be limited to a downwind sector a few miles from the plant.



TABLE 5-9. TRACE ELEMENT CONCENTRATION IN RUNOFF WATER IN VICINITY OF CONTROLLED OIL-FIRED UTILITY BOILER

Element	Typical Background Concentration of Soluble Metals In Runoff Water* mg/l	Increase in Soluble Metals Concentration in Soil After 40 Years† mg/kg	Increase in Soluble Metals Concentration In Runoff Water‡ After 40 Years mg/l	EPA Proposed Maximum Acceptable Concentration for Livestock mg/l	Standard As Critical Concentration in Potable Water mg/l
Cr	$1 \times 10^{-5}$	$4 \times 10^{-8}$	$4 \times 10^{-11}$	1	$2 \times 10^{-2}$
Ni	$1 \times 10^{-4}$	$7 \times 10^{-5}$	$7 \times 10^{-8}$	---	$5 \times 10^{-2}$

\* Based on average soil particulate runoff rate of 1000 mg/l of runoff water, and soluble endogenous concentration of metals in soils (15).

† Based on increase in trace element concentration (Table 5-7) and solubility of elements (Table 5-8).

‡ Based on average soil particle runoff rate of 1000 mg/l of runoff water, and increased soluble metals concentration in soil after 40 years.

The secondary pollutants (ozone and peroxyacetylnitrates) formed by reaction of hydrocarbons and nitrogen oxides are considerably more toxic than either of the precursors alone. The formation of secondary compounds in boiler stack plumes and the impact of the boiler nitrogen oxides emissions on urban photochemical smog depend on complex relationships which are not yet totally understood. Therefore, it is not possible to reliably estimate the effect of  $\text{NO}_x$  emissions levels on levels of photochemical compounds. However, based on typical regional emissions figures, it appears that emissions from power plant fuel combustion provide a significant source of the regional emissions of  $\text{NO}_x$  necessary for photochemical smog. Approximately 28% of the nation's  $\text{NO}_x$  emissions are produced by combustion in power plants (17).

If  $\text{NO}_x$  emissions from utility boilers are a significant contributor to photochemical smog, then there is valid concern that boiler emissions may contribute to plant injury. The effects of photochemical air pollution on plant life have been observed frequently at various different severities throughout the United States. In addition, the effect of the major constituents of photochemical smog (products of nitrogen oxides and organic compounds) on plants has been investigated separately. The pigmentation of small areas of palisade cells is characteristic of ozone injury, and a bronzing of the undersurface of leaves is typical for peroxyacetylnitrate injury. Table 5-10 illustrates the relatively low levels of ozone which will produce significant plant injury to crops. The concentrations shown are typical of many areas experiencing photochemical air pollution, and suggest the necessity for concern over sources emitting high levels of  $\text{NO}_x$ .

Nitrogen oxides may also cause injury to vegetation by direct contact. The significant oxides of nitrogen are  $\text{NO}$  and  $\text{NO}_x$ . The major oxide in combustion emissions is  $\text{NO}$ . However, after residence in the atmosphere,  $\text{NO}$  is converted to  $\text{NO}_2$  by photolysis and by photochemical interaction with hydrocarbons. The effect of  $\text{NO}_2$  on plant life has been studied under controlled laboratory conditions. Acute injury is characterized by collapse of cells and subsequent development of necrotic patterns. Chronic injury, caused by exposure to low concentrations over long periods, is characterized by chlorotic or other pigmented patterns in leaf tissue. Such injury results

TABLE 5-10. PROJECTED OZONE CONCENTRATIONS WHICH WILL PRODUCE, FOR SHORT TERM EXPOSURES, 20 PERCENT INJURY TO ECONOMICALLY IMPORTANT VEGETATION GROWN UNDER SENSITIVE CONDITIONS\*

Concentrations producing injury in three types of plants, ppm			
Time, Hr	Sensitive	Intermediate	Resistant
0.2	0.40-0.90	0.80-1.10	1.00 and up
0.5	0.20-0.40	0.35-0.70	0.60 and up
1.0	0.15-0.30	0.25-0.55	0.50 and up
2.0	0.10-0.25	0.20-0.45	0.40 and up
4.0	0.07-0.20	0.15-0.40	0.35 and up
8.0	0.05-0.15	0.10-0.35	0.30 and up

\* Reference 18.

in reduction of growth and reproduction. Only limited data are available to characterize the effect of NO on plants. Generally, it appears that NO leads to effects somewhat similar to those observed for NO<sub>2</sub>, but at slightly higher threshold concentrations. Therefore, for worst case evaluations of the impact of ambient NO<sub>x</sub> levels, it is assumed that NO<sub>x</sub> exists as NO<sub>2</sub>, and that the NO<sub>x</sub> levels are not depleted by the photochemical reactions which typically occur in urban areas.

Figure 5-3 illustrates the threshold concentrations at which various degrees of damage result from exposure to NO<sub>2</sub>. As the long term concentration of NO<sub>x</sub> in the vicinity of the model plant is estimated at 2 µg/m<sup>3</sup>, injury to plants from oil firing is not likely to occur. Even the maximum short term ambient concentration of NO<sub>x</sub> near the oil-fired boiler, which is estimated to be 260 µg/m<sup>3</sup>, is below the threshold levels which induce plant injury.

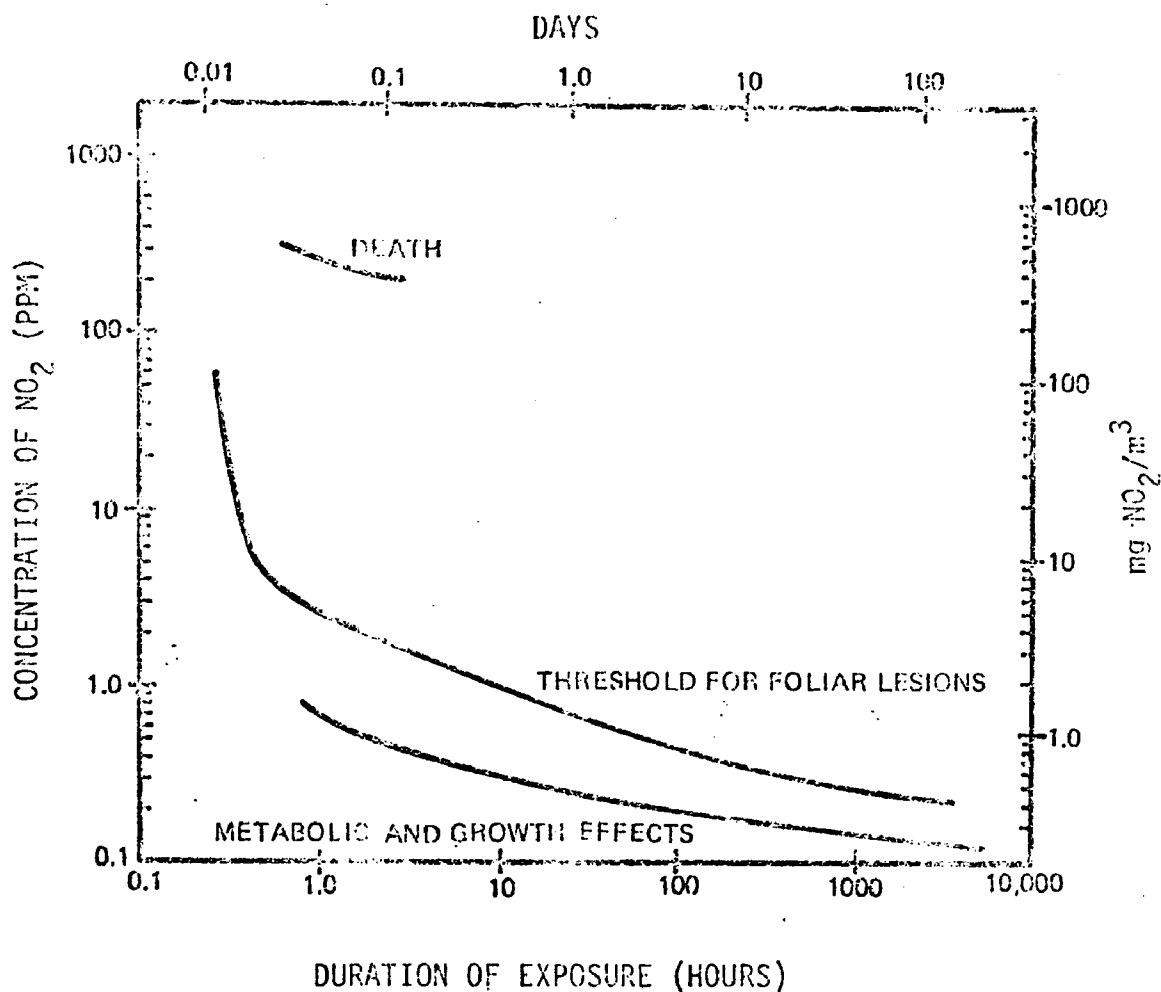


Figure 5-3. NO<sub>2</sub> Threshold Concentrations for Various Degrees of Plant Injury (19).

Acute short term injury to vegetation by SO<sub>2</sub> exposure is characterized by damaged leaf areas which first appear as water soaked spots, and later appear as bleached white areas or darkened reddish areas. Chronic SO<sub>2</sub> injury is usually characterized by chlorosis (yellowing) which develops from lower concentrations over extended periods of time. Either acute or chronic SO<sub>2</sub> injury may result in death or reduced yield of the plant if the extent of the damaged tissue exceeds 5 to 30 percent of the total amount of foliage.

The impact of the expected  $\text{SO}_2$  concentrations varies with the plant species. Threshold injury in sensitive plants may be caused by short-term  $\text{SO}_2$  levels as low as  $30 \mu\text{g}/\text{m}^3$  (20). Table 5-11 summarizes the broad categories of sensitivity for different plants. Grain, vegetable, pasture, and forage crops are susceptible to  $\text{SO}_2$  damage for most of the growing season. These crops may suffer yield reductions in areas where power plants such as that of the present study are located, although the damage would be relatively localized. Data presented in Figure 5-4 indicate that the peak short term  $\text{SO}_2$  concentration of  $230 \mu\text{g}/\text{m}^3$  near the oil-fired boiler may exceed the injury threshold of sensitive plants, although the damage would be slight.

It should be noted that the plant damage thresholds illustrated by Figure 5-4 apply to conditions of temperature, humidity, soil moisture, light intensity, nutrient supply, and plant age which cause maximum susceptibility to injury. The occurrence of such conditions are rare. In fact, in the unlikely event that all such conditions are met, the dose-response curves indicate that plant injury could occur without a violation of the federal air quality standard for the 3 hour or 24 hour concentration of  $\text{SO}_2$ . Additional susceptibility may also result from synergistic effects of sulfur dioxide and other pollutants. Particularly relevant to the urban environment are combinations of sulfur dioxide and ozone. Moderate to severe injury of tobacco plants have been observed for four hour exposures to concentrations of 0.1 ppm ( $262 \mu\text{g}/\text{m}^3$ )  $\text{SO}_2$  in combination with 0.03 ppm ozone. Because high ozone levels are a frequent problem in the vicinity of urban areas, susceptibility to plant injury by  $\text{SO}_2$  pollution is greater when utility boilers are also sited in urban areas. One of the major concerns associated with fossil fuel utilization is acid precipitation resulting from wet deposition of suspended sulfur and nitrate compounds. Data show that there has been an intensification of acidity in the northeastern region of the U.S. since the mid 1950's. Precipitation in a large portion of the eastern U.S. averages between pH 4.0 and 4.2 annually. Values between pH 2.1 and 3.6 have been measured for individual storms at distances several hundred miles downwind of urban centers. The areas experiencing highest acidity are typically downwind of the areas where sulfur emissions are highest (19, 22).

TABLE 5-11. SENSITIVITY OF COMMON PLANTS TO SO<sub>2</sub> INJURY\*

Vegetation			Crops		
Sensitive	Intermediate	Resistant	Sensitive	Intermediate	Resistant
White pine	Maple	Sugar maple	Alfalfa	Irish Potato	Corn
Goldenrod	Virginia creeper	Phlox	Barley	Clover	Sorghum
Cottonwood	White oak	Oak	Oats	Sweet clover	
Virginia creeper	Elm	Maple	Eye		
Aster	Shortleaf pine	Shrubby willow	Wheat		
Gooseberry	Aster		Sweet potato		
Elm	Linden		Soybean		
Wild grape			Sweet clover		
American elm			Cotton Tobacco		
White ash			Clover		
Virginia pine					
Tulip tree					

\* Reference 21.

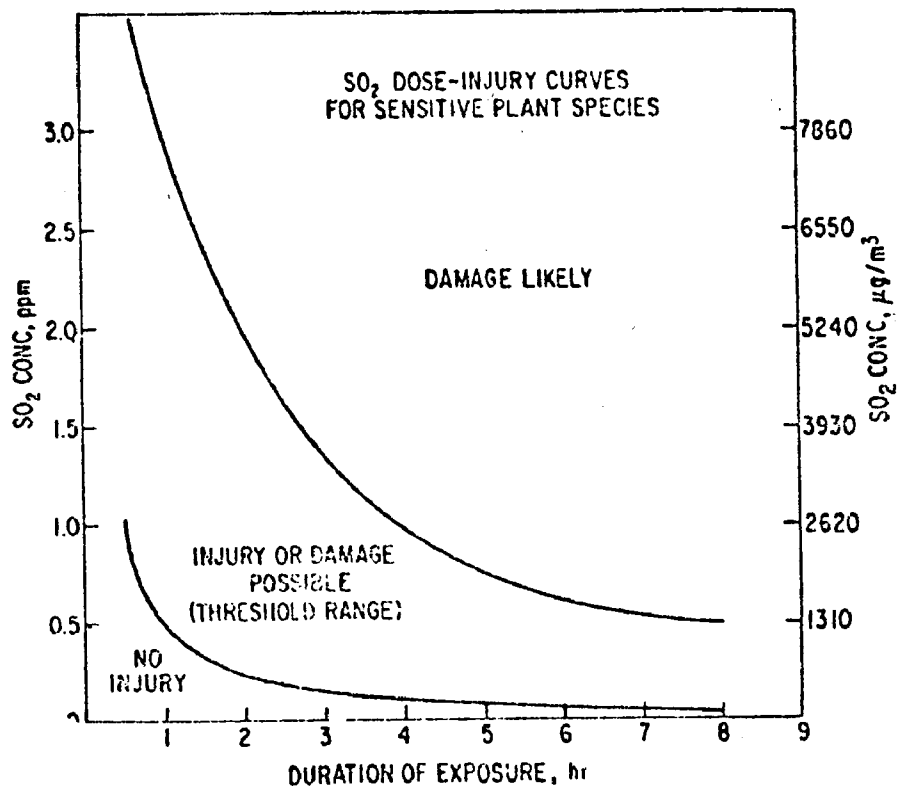


Figure 5-4. SO<sub>2</sub> Dose-Injury Curves for Sensitive Plant Species (20).

Acid rain affects plant life in varying degrees depending on the pH and the type of plant species. Experiments show that the effects on plants may include reduction in growth or yield, leaf damage, death, and chlorosis. Acid rain also has been shown to affect aquatic organisms, and it is believed that thousands of lakes are now experiencing reductions in fish population due to acidification between pH 5.0 and 6.0 (19). The level of sulfates estimated to result from oil firing is about  $2.4 \mu\text{g}/\text{m}^3$ , a level not expected to result in significant acid precipitation. Based on tests of the utility boiler of this study, it appears that emissions from oil firing are not apt to cause adverse plant burdens of either chromium or nickel.

#### ECONOMIC IMPACT

The direct economic impacts associated with residuals of fuel combustion involve the costs of damages (or benefits) sustained when the residuals enter the environment. Second order economic impacts associated with the residuals involve the alterations that occur in employment, the tax base, energy prices, income, and land values due to the damages (or benefits) resulting from combustion residuals. The quantification of direct economic impacts involves the difficult task of ascribing economic values to environmental changes. Quantification of second order economic effects are yet more difficult because of gaps in knowledge which make it impossible to determine the complex relationships between cost and the numerous socio-economic factors involved.

A number of ongoing energy related studies are attempting to develop sophisticated economic models which will predict the cost of environmental damages (6, 21, 23). The models address the cost of visibility reduction, health effects (morbidity and mortality), and certain second order effects. Utilization of the models requires substantial input data involving regional demography and emission source distributions. The models require further refinement and are currently under continuing development. The data base or scope of the present program did not permit the adaption and utilization of such models.

The extent of the economic impacts resulting from residuals of 353 MW oil-fired utility boilers is proportional to the extent of the environmental damages which occur. The analyses have shown that while some impact of emissions from the oil-fired boiler tested in this study may occur, federal ambient air quality standards for sulfur oxides and nitrogen oxides will probably not be violated in the vicinity of the model plant. However, in spite of conformance with air quality standards, the economic cost of plant emissions in the affected areas may be significant. These costs include medical expenses, loss of productivity, cost of cleanup and maintenance for soiling damages, and reduced crop revenues.

Whatever the extent to which additional controls may be required for oil-fired boilers, the cost of such controls will probably be relatively minor compared to the overall operating cost of a boiler and other factors affecting the overall costs. Even when predicted pollutant loadings meet environmental standards, it is not entirely clear whether the increasing use of fossil fuels may be continued at the forecasted levels of control technology without potential long term environmental damages. If it is found that long term effects of pollution (e.g., trace metals accumulation, lake acidity, land use) are unacceptable, then more stringent environmental regulations can be expected, and it is clear that energy cost will increase with increasing control requirements.



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## APPENDIX A

### SIMPLIFIED AIR QUALITY MODEL

Simple ambient air quality models were used to estimate the maximum expected ground level concentrations of criteria pollutants. It is important to recognize that these air quality values are estimates only, based upon several simplified assumptions, as discussed below. Two sets of meteorological conditions were considered: worst case and typical. Conditions were selected that are representative of what could reasonably be expected to occur almost anywhere in the country but are not specific to the area of the plant from which the pollutant emission rates were obtained. It was assumed that all species were inert. No photochemical reactions were considered.

There are several meteorological conditions which can produce high ground level pollutant concentrations. These conditions can result in plume coning, looping, fumigation, and trapping, all of which can cause high ambient concentrations. In the case of coning, high levels occur along the plume centerline. Looping causes high ground level concentrations at points where the plume impacts the ground. Fumigation causes high ground level concentrations which are generally lower than those from plume trapping. For this study it was assumed that plume trapping constituted the worst case in terms of ground level concentrations.

Trapping conditions occur when an inversion layer or stable air aloft inhibits upward dispersion of the plume. Although the plume is trapped by the capping stable layer at height L, the plume distribution is still Gaussian in the horizontal and uniform in the vertical directions. Ambient concentrations can be estimated by the following equation (1):

$$\begin{aligned}
 X(x, 0, z; H) = & \frac{Q}{2\pi u \sigma_y \sigma_z} \left\{ \exp \left[ -\frac{1}{2} \left( \frac{z-H}{\sigma_z} \right)^2 \right] + \exp \left[ -\frac{1}{2} \left( \frac{z+H}{\sigma_z} \right)^2 \right] \right. \\
 & \left. + \sum_{N=1}^J \left[ \exp \left[ -\frac{1}{2} \left( \frac{z-H-2NL}{\sigma_z} \right)^2 \right] + \exp \left[ -\frac{1}{2} \left( \frac{z+H-2NL}{\sigma_z} \right)^2 \right] \right] \right\} \quad (1)
 \end{aligned}$$

$$+ \exp - 1/2 \left( \frac{z-H+2NL}{\sigma_z} \right)^2 + \exp - 1/2 \left( \frac{z+H+2NL}{\sigma_z} \right)^2 \Big] \Big\}$$

Where:  $X(x,y,z;H)$  = Concentration at point  $(x,y,z)$  assuming an effective stack height of  $H$ ,  $\mu\text{g}/\text{m}^3$

$H$  = Effective stack height, m

$Q$  = Pollutant emission rate, kg/hr

$\mu$  = Mean wind speed, m/s

$\sigma$  = Concentration distribution within the plume in the horizontal ( $\sigma_y$ ) and vertical ( $\sigma_z$ ) directions, m

$z$  = Height above the ground, m

$J$  = Maximum wind speed class index, unitless

$N$  = Wind speed class index, unitless

$L$  = Height of the stable layer, m

At ground level ( $z=0$ ) and at the plume center line ( $y=0$ )

Equation (1) reduces to:

$$X(x,0,0;H) = \frac{Q}{\pi u \sigma_y \sigma_z} \left\{ \exp \left[ -1/2 \left( \frac{H}{\sigma_z} \right)^2 \right] + \sum_{N=1}^J \left[ \exp - 1/2 \left( \frac{H+2NL}{\sigma_z} \right)^2 + \exp - 1/2 \left( \frac{H-2NL}{\sigma_z} \right)^2 \right] \right\} \quad (2)$$

For typical conditions, ground level concentrations were calculated using a Gaussian solution to the convective diffusion equation (2):

$$X(x,y,0) = \frac{Q}{\pi \sigma_y \sigma_z \bar{u}_s} \exp - \left\{ (H^2/2\sigma_z^2) + (y^2/2\sigma_y^2) \right\} \quad (3)$$

Where:  $X$  = Concentration,  $\text{g}/\text{m}^3$

$Q$  = Pollutant release rate, g/s

$\sigma_y, \sigma_z$  = Crosswind and vertical plume standard deviations, m

$\bar{u}_s$  = Mean wind speed, m/s

$H$  = Effective stack height, m

$x, y$  = Downwind and crosswind distances, m.

At the plume centerline, Equation (3) reduces to:

$$X(x,0,0) = \frac{Q}{\pi \sigma_y \sigma_z \bar{u}} \exp - \frac{H^2}{2\sigma_z^2} \quad (4)$$

The maximum value of this equation occurs at the distance where

$$\sigma_z = H / \sqrt{2}.$$

In Equations (3) and (4), H is defined by:

$$H = H_s + \Delta H \quad (5)$$

Where  $H_s$  = physical height of the stack and  $H$  = plume rise, both expressed in meters. There are more than 30 plume-rise formulas in the literature, all of which require empirical determination of one or more constants. For the purpose of this study, the Briggs plume rise formula was chosen to calculate the final plume rise in stable conditions.

$$\Delta H = 2.6 \left( \frac{F}{\mu s} \right)^{1/3} \quad (6)$$

Where:  $\Delta H$  = Plume rise, m  
 $\mu$  = Wind speed, m/s  
 $s$  = Stability parameter, unitless  
 $F$  = Buoyancy flux.

The stability parameter,  $s$ , is defined as:

$$s = \frac{g}{\theta} \frac{\partial \theta}{\partial z} \quad (7)$$

Where:  $g$  = Gravitational constant,  $m/s^2$ ;  
 $\theta$  = Potential air temperature, K  
 $\partial \theta / \partial z = (\partial T / \partial z) + 0.0098$  K/m, the potential temperature gradient. Based on the normal lapse rate,  $\partial T / \partial z$ , of temperature in the atmosphere of  $-0.0065$  K/m, a value of  $.0033$  K/m was employed for  $\frac{\partial \theta}{\partial z}$  in this study.

The buoyancy flux, F, is defined as:

$$F = \frac{\Delta T}{T_s} g w r^2 \quad (8)$$

Where  $\Delta T$  = Stack temperature minus the ambient air temperature, K  
 $T_s$  = Stack temperature, K  
 $g$  = Gravitational constant,  $m/s^2$   
 $w$  = Stack exit velocity, m/s  
 $r$  = Inside radius of the stack, m.

The plume rise was calculated using Equation (6). The data used for the calculations are shown in Table A-1. The values selected for wind speed are discussed below.

TABLE A-1. STACK PARAMETERS AND PLUME RISE

Stack temperature, K	394
Ambient temperature, K	293
Stack exit velocity, m/s	24
Stack area, $m^2$	26
Stack height, m	73

Equation (2) was used to estimate maximum ambient concentrations resulting from short term meteorological conditions causing plume trapping. As a worst case estimate for this study, plume trapping conditions were assumed to persist for periods as long as three hours. Equation (4) was used to estimate maximum ambient concentrations for conditions which could typically persist over a 24 hour period. For the 24 hour concentration forecasts, typical conditions of wind speed (4 m/sec) and atmosphere stability (Class D stability) were assumed to persist. For the short-term plume trapping, conditions of low wind speed (1 m/sec) and a moderately unstable atmosphere (Class B stability) were assumed to persist throughout the applicable averaging period. These conditions were selected because

they produce high ground level concentrations. The inversion inducing plume trapping was assumed to be at an elevation equivalent to the effective stack height (504 m). Results of these calculations are presented in Table A-2.

TABLE A-2. PREDICTED MAXIMUM AMBIENT CONCENTRATIONS OF CRITERIA POLLUTANTS

Pollutant	Pollutant Concentration, $\mu\text{g}/\text{m}^3$
24 hour period:	
NO <sub>x</sub>	8
CO	0.4
SO <sub>2</sub>	6
Particulates	0.5
Total organics	0.04
Plume trapping:	
NO <sub>x</sub>	260
CO	15
SO <sub>2</sub>	230
Particulates	18
Total Organics	1

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APPENDIX B  
ORGANIC ANALYSES - OIL FIRING

Sample Preparation

Emissions from the stack at the oil-fired utility boiler were sampled both while the unit was operating at 62 and 92% of full load. The test run at 62% of full load conditions will be referred to as test 142; the run at 92% of full load will be called test 143.

Two additional test runs were made, using the SASS train, which were not analyzed. All samples from the four tests were prepared for analysis using procedures detailed in Reference B-2, with modifications whenever necessary to ensure Level 2 quality data would be produced. The steps involved for each sample type are summarized below.

XAD-2 resins: Each sample was extracted in a Soxhlet apparatus for 24 hours with methylene chloride.

Filters: Each sample was extracted in a Soxhlet apparatus for 24 hours with methylene chloride.

XAD-2 module condensates: Each sample was extracted three times with methylene chloride at adjusted pH condition to first 11, and then 2. The volume of methylene chloride used for each extraction was ten percent of the condensate volume.

Organic rinses: No preparation required.

One milliliter aliquots were taken of all these samples for subsequent TCO analysis. Then the solutions were concentrated to 10 ml in Kuderna-Danish evaporators. Aliquots taken for analyses included 1 ml for TCO, 1 ml for GRAV/IR and a composite for GC/MS prepared as follows:

CD-LEA-KD	1 ml	CDB-LEA-KD	1 ml
CD-LEB-KD	1 ml	CDB-LEB-KD	1 ml
XR-SE-KD	2 ml	XR-SE-KD	2 ml
PF-SE-KD	2 ml	PFB-SE-KD	2 ml
PR-O-KD	2 ml	MAB-O-KD	4 ml
MR-O-KD	2 ml		

The flow diagram in Figure B-1 shows the sample handling and analysis scheme used. The sample code is explained in Table B-1.

### Summary

#### Level 1--

The total amounts of organics found in the stack emissions during these two tests are shown below:

<u>Test</u>	<u>C<sub>1</sub>-C<sub>6</sub></u>	<u>C<sub>7</sub>-C<sub>16</sub></u>	<u>&gt; C<sub>16</sub></u>	<u>Total Organics</u>
142	850-1241 $\mu\text{g}/\text{m}^3$	61.1 $\mu\text{g}/\text{m}^3$	478 $\mu\text{g}/\text{m}^3$	1389-1780 $\mu\text{g}/\text{m}^3$
143	327-652	54.6	397	779-1104

The field GC analysis showed measurable amounts of only C<sub>1</sub>, i.e., methane. The laboratory GC analysis indicated about fifty percent of the less volatile materials were in the C<sub>8</sub> boiling range. The other 20  $\mu\text{g}/\text{m}^3$  were reasonably well distributed throughout the entire 200°C boiling point range being examined.

A peak-by-peak evaluation of the chromatograms of the C<sub>7</sub>-C<sub>16</sub> compounds shows no signs of the acetone condensation products mesityl oxide (a C<sub>8</sub>) or diacetone alcohol (a C<sub>9</sub>).

The amount of material less volatile than n-heptane in individual samples was too low to trigger the Level 1 liquid chromatographic separation procedure. Also, the infrared spectra of XAD-2 resin samples were indistinguishable from the resin blank.

#### Level 2--

Results of the analysis of the combined SASS train extracts and the controls are summarized as follows:

- 1) The compounds found in the combined SASS train extracts and which are believed to have been present in the gas sample are present at 2  $\mu\text{g}/\text{m}^3$  or less. Many of the compounds identified in the total sample are sorbent resin artifacts.
- 2) Some compounds could not be identified by computerized data reduction techniques. These are believed to be silicone artifacts, for the most part.

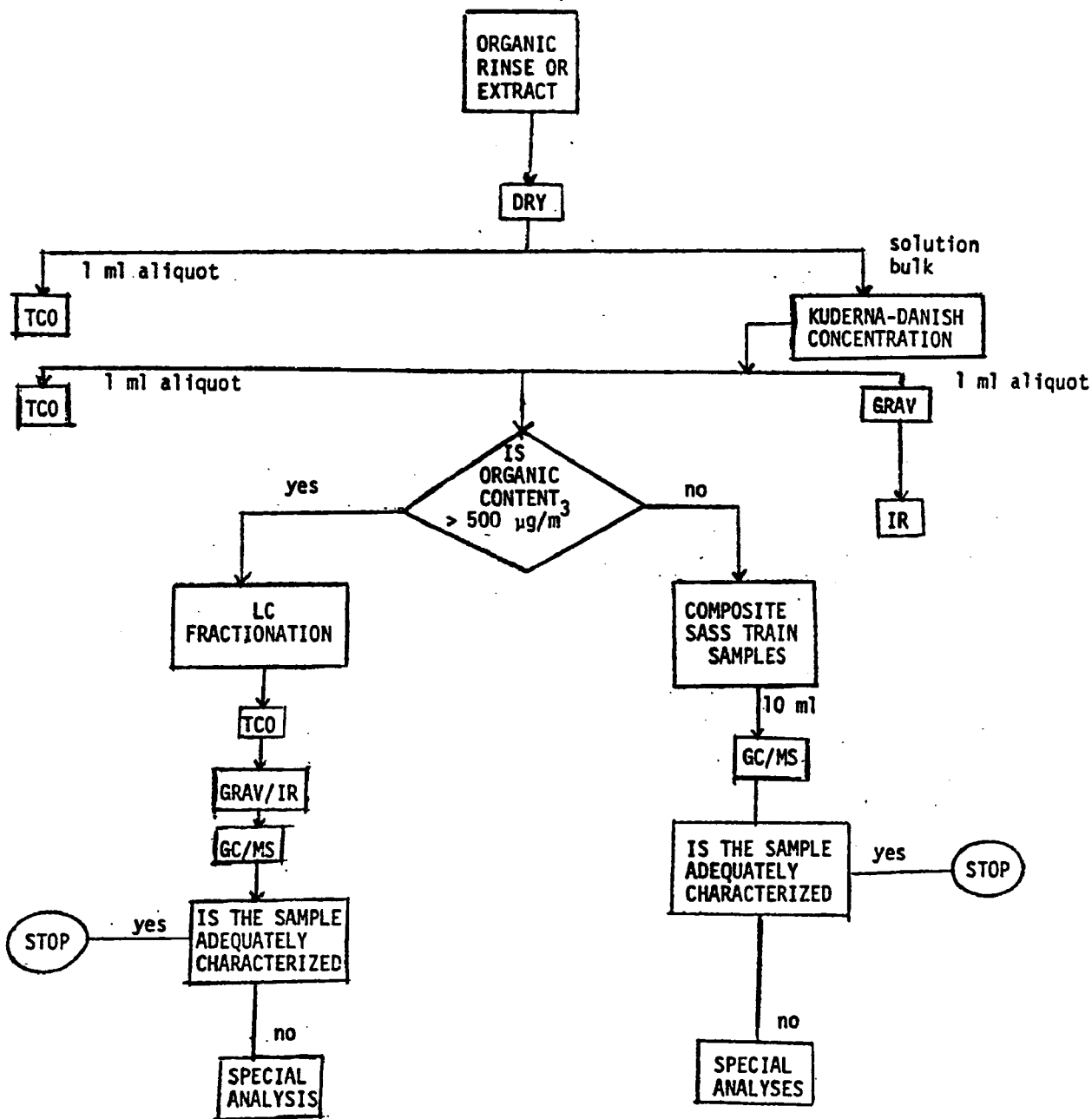


Figure B-1. Flow Chart of Sample Handling and Analysis Procedures

TABLE B-1. SAMPLE CODE FOR ORGANIC SAMPLES ANALYZED

SAMPLE CODE				
XXX-XX-XX-XX-XX				
Site Identification	Sample Type	Sample Preparation	First Level Analysis	Second Level Analysis
141	CD-condensate from XAD-2 module	0-no preparation		GC-C <sub>7</sub> -C <sub>16</sub> GI-GRAV/IR
142	PR-solvent probe rinse	LEA-liquid-liquid extraction, acidified sample		MS-GC/MS
143	MR-solvent XAD-2 module rinse XR-XAD-2 resin		KD-K-D concentration	LC-LC separation
144	PF-filters XM-composite of SASS train component samples	LEB-liquid-liquid extraction, basic sample SE-Soxhlet solvent extraction		

- 3) Some POM were found in the samples at levels ranging from less than 0.05 to 10  $\mu\text{g}/\text{m}^3$  of sampled gas.

#### Level 1 Data

##### Total Chromatographable Organics Analysis (TCO)--

TCOs were performed as described earlier. All samples were analyzed both prior to and after the Kuderna-Danish concentration step. The results of the  $\text{C}_7$ - $\text{C}_{16}$  analyses on the K-D concentrates are given in Table B-2. The unconcentrated samples did not contain any detectable quantity of hydrocarbons, and are, therefore, not listed.

##### Field Gas Chromatographic Analyses--

The chromatographic analyses performed in the field make use of a Shimadzu GC-Min 1 gas chromatograph with dual flame ionization detectors. Separations are made on a 183 cm x 0.32 cm stainless steel Poropak Q packed column.

Calibration and quantitation is accomplished using the same techniques as in the laboratory. The n-alkanes and the data reporting ranges are listed below.

$\text{C}_1$	-160 to -100°C	$\text{C}_4$	0 to 30°C
$\text{C}_2$	-100 to - 50°C	$\text{C}_5$	30 to 60°C
$\text{C}_3$	- 50 to 0°C	$\text{C}_6$	60 to 90°C

The detection limits for the field GC analyses, properly calibrated with  $\text{C}_1$ - $\text{C}_6$  standards, are 0.1 ppm or 65  $\mu\text{g}/\text{m}^3$  hydrocarbon as methane.

Results of the field analysis are summarized in Table B-3.

##### Gravimetry for $\text{C}_{13}$ and Higher Hydrocarbons--

Gravimetric determinations were performed on the concentrates of solvent rinses and extracts in accordance with the procedure in Reference B-2: a one milliliter aliquot was taken from each sample and evaporated to dryness in an aluminum pan. The residues were then weighed on a micro-balance. The results are presented in Table B-4.

TABLE B-2. RESULTS OF TCO ANALYSIS OF UNCONCENTRATED AND CONCENTRATED SAMPLES

Sample	Hydrocarbon Content, $\mu\text{g}/\text{m}^3$										Total
	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>14</sub>	C <sub>15</sub>	C <sub>16</sub>	
142-CD-LEA-KD-GC	LB	0	0	0	0	0	0	0	0	0	LB
142-CD-LEB-KD-GC	LB	0	0	0	0	0	0	0	0	0	LB
143-CD-LEA-KD-GC	LB	0	0	0	0	0	0	0	0	0	LB
143-CD-LEB-KD-KC	< 0.1	0	0	0	0	0	0	0	0	0	< 0.1
142-XR-SE-KD-GC	0.4	26.5	1.0	2.5	6.9	13.7	1.9	0	0.2	0.5	53.6
143-XR-SE-KD-GC	0.4	28.1	2.2	2.7	4.4	LB	2.4	2.8	LB	0.1	43.1
142-PF-SE-KD-GC	0	LB	0	0	0	0	0	0	0	0	LB
143-PF-SE-KD-GC	0	0	0.9	0	3.2	0	0	0	0	0	4.1
142-PR-O-KD-GC	0	0	2.9	0	0	0	0	0	0	0	2.9
143-PR-O-KD-GC	0	0.2	3.6	0	0	0	0	0	0	0	3.8
142-MR-O-KD-GC	0	0	4.6	0	0	0	0	0	0	0	4.6
143-MR-O-KD-GC	0	0	3.6	0	0	0	0	0	0	0	3.6

All values corrected for blanks.

Value of 0 given whenever no material was detected. Instrument detection limit stated in text.

LB means less material found in sample than in blank.

TABLE B-3. RESULTS OF FIELD GC ANALYSIS

Sample	Hydrocarbon Content, $\mu\text{g}/\text{m}^3$						Total
	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	
141	981	< 65	< 262	< 131	< 65	< 65	981 - 1569
142	850	< 65	< 131	< 65	< 65	< 65	850 - 1241
143	327	< 65	< 65	< 65	< 65	< 65	327 - 652
144 (no data)							

TABLE B-4. GRAVIMETRY OF SAMPLE CONCENTRATES

Sample	Weight mg/ml	Correction for Blank, mg/ml	Aliquot Factor	Sample Volume, m <sup>3</sup>	Net Grav, μg/m <sup>3</sup>
142-CD-LEA-KD-GI	0.078	LB	X10	24.4	0
142-CD-LEB-KD-GI	0.051	LB	X10	24.4	0
143-CD-LEA-KD-GI	0.103	0.028	X10	30.6	9.2
143-CD-LEB-KD-GI	0.050	0.013	X10	30.6	4.2
142-XR-SE-KD-GI	1.470	0.954	X10	24.4	396
143-XR-SE-KD-GI	1.582	1.104	X10	30.6	361
142-PF-SE-KD-GI	0.135	0.014	X10	24.4	5.7
143-PF-SE-KD-GI	0.093	LB	X10	30.6	0
142-PR-O-KD-GI	0.159	0.110	X10	24.4	45.1
143-PR-O-KD-GI	0	0	X10	30.6	0
142-MR-O-KD-GI	0.142	0.077	X10	24.4	31.5
143-MR-O-KD-GI	0.138	0.070	X10	30.6	22.9
141-CDB-LEA-KD-GI	0.075				
141-CDB-LEB-KD-GI	0.036				
141-XRB-SE-KD-GI	0.582				
141-PFB-SE-KD-GI	0.121				
141-MCB-O-KD-GI	0.075				
141-MAB-O-KD-GI	0.109				



## Infrared Analyses (IR) on Samples Concentrated in Kuderna-Danish Evaporators--

Each of the concentrates weighing more than 0,5 mg was also scanned by infrared (IR) spectroscopy. After the final weighing, the residue in each weighing pan was redissolved in methylene chloride and smeared onto a NaCl window. The resulting spectra and the compound classes whose presence was identified are summarized in Table B-5. The spectra of the samples were indistinguishable from those of the blanks.

## Other Analyses--

No sample contained more than 0.5 mg/m<sup>3</sup> of organic material. Applying stated Level 1 decision criteria, the organic analysis was halted. A composite sample of all the SASS train components was prepared for Level 2 organic work.

## Level 2 Data

Two different GC/MS analyses were performed. GC/MS was performed using parameters as similar as possible to those used in the Total Chromatographable Organics (TCO) analysis. The objective of this approach was to identify peaks seen in the TCO chromatograms. In addition, several of the samples in this study were also subjected to a specific POM analysis using a Dexsil 300 column. Both of these techniques are described in Reference B-2. A total of three samples was submitted for this effort. A description of the samples analyzed is presented in Table B-6.

Tables B-7 through B-9 present the results of the GC/MS analyses as source concentrations. DMEG values are also given. Compounds marked with an asterisk were not found in the blank, as described in the next paragraph. Except for the possible benzopyrene in the 142 SASS composite, DMEG values for compounds in Tables B-8 and B-9 were at least 1600 times larger than the concentrations found. Benzopyrene was not positively identified, but if the compound was benzopyrene, it is present at a level 32% above its DMEG value.

The results for the blank sample (Table B-7) are included in this document because chemical compound contribution from the blank is substantial when compared to the samples. Furthermore subtraction of the blank levels from the sample levels could lead to misinterpretation of the data.

TABLE B-5. INTERPRETATION OF INFRARED  
SPECTRA OF SAMPLE CONCENTRATES

Sample Identifica- tion	Band Location, cm <sup>-1</sup>	Band Intensity	Compound Classification
141-XRB-SE-KD- GI	3400	W	OH, NH or C = O overtone
	3060	W	CH stretch-aromatic
	2920, 2860	S	CH stretch-aliphatic
	1720	M	C = O
	1690, 1670, 1640, 1630	W	C = C
	1600	W	Benzene ring
	1550	W	NO <sub>2</sub> antisym stretch
	1530	W	Benzene ring
	1510, 1480	W	Benzene ring
	1460	M	CH <sub>2</sub>
	1450	M	CH <sub>2</sub>
	1410	W	Carboxylic acid
	1370	M	CH <sub>3</sub>
	1345	M	NO <sub>2</sub> sym stretch
	1270	M	C-O-C
	1110	S	C-O-H
	930	W	Carboxylic acid
	700	W	Benzene ring substitution
			Indicates esters, poly- ethylene oxide with alcohol possible, i.e., resin
			N.B. Samples 142-XR-SE-KD- GI and 143-XR-SE-KD-GI indistinguishable from blank

- Continued -

TABLE B-5 (Continued)

Sample Identification	Band Location, $\text{cm}^{-1}$	Band Intensity	Compound Classification
142-XR-SE-KD-GI	3560-3140	W	OH, NH or C = O overtone
	3060	W	CH stretch-aromatic
	2920, 2860	S	CH stretch-aliphatic
	1720	S	C = O
	1710	S	C = O
	1640, 1630	W	C = C
	1600	W	Benzene ring
	1550	W	NO <sub>2</sub> antisym stretch
	1500, 1495, 1480, 1470	W	Benzene ring
	1460, 1450	M	CH <sub>2</sub>
	1410	W	Carboxylic acid
	1370	W	CH <sub>3</sub>
	1345	W	NO <sub>2</sub> sym stretch
	1270	M	C-O-C
	1175	W	Unassigned
	1105	S	C-O-H
	1025, 1015	W	Unassigned
	940	W	Carboxylic acid
	855	W	Benzene ring substitution
	835	W	
	800	W	
	755	W	
	710	W	

- Continued -

TABLE B-5 (Continued)

Sample Identification	Band Location, $\text{cm}^{-1}$	Band Intensity	Compound Classification
143-XR-SE-KD-GI	3600-3150	W	OH, NH or C = O overtone
	3060	W	CH stretch-aromatic
	2960, 2920, 2870	M	CH stretch-aliphatic
	1720	M	C = O
	1710	M	C = O
	1640, 1630, 1600, 1530, 1510, 1500, 1490, 1470	W	Unsaturation; 1600 in benzene ring
	1550	W	NO <sub>2</sub> antisym stretch
	1460	W	CH <sub>2</sub>
	1450	W	CH <sub>2</sub>
	1410	W	Carboxylic acid
	1370	W	CH <sub>3</sub>
	1275	M	C-O-C
	1250	M	C-O-C
	1175	W	Unassigned
	1100	M	C-O-H
	1030	W	Unassigned
	940	W	Carboxylic acid
	850, 800, 760, 710	W	Benzene ring substitution

TABLE B-6. SUMMARY OF GC/MS SAMPLES AND ANALYSES  
FROM THE OIL-FIRED SITE

Sample No.	Description
142-XM-SE-KD	Composite of SASS Train Extract and Rinse Concentrates
143-XM-SE-KD	Composite of SASS Train Extract and Rinse Concentrates
141-XMB-SE-KD	Composite of Blank Samples Related to SASS Train Sampling; Also Concentrated

TABLE B-7. GC/MS ANALYSIS OF 141-XMB-SE-KD  
(BLANK) COMBINED EXTRACTS

Compound	Concentration In Extract µg/ml	Simulated Concentration In Sampled Gas µg/m <sup>3</sup> *
<u>Level 2 Analysis</u>		
Diethylbenzene	26	3
Ethylstyrene	60	7
Methylindene	3	0.4
Naphthalene	44	5
Chloronaphthalene (Internal Standard)	20	2
Ethylbiphenyl or Diphenylethane	16	2
Unknown	1	0.1
Two Components believed to be Trimethylpropenylnaphthalene and Dihydromethylphenylbenzofuran	29	3
Unknown Silicone Compound	13	2
C <sub>18</sub> H <sub>22</sub>	9	1
Mixture believed to contain Hexadecyloxypentadecyl - 1, 3-Dioxane and an alcohol >C <sub>14</sub> .	73	9
Butylisobutylphthalate	17	2
Unknown Silicone	2	0.2
Unknown Silicone	5	0.6
Unknown Silicone	4	0.5
Diethylphthalate	34	4
<u>POM Analysis</u>		
Naphthalene	24	3
Possible Trimethylpropenylnaphthalene	11	1.3

\* Theoretical Sample Volume of 30 m<sup>3</sup> used.

TABLE B-8. GC/MS ANALYSIS OF 142 SASS COMPOSITE

Compound	Concentration In Sampled Gas $\mu\text{g}/\text{m}^3$	DMEG Value $\mu\text{g}/\text{m}^3$
<u>Level 2 Analysis</u>		
Ethylstyrene	4	---
Methylindene	0.3	---
Naphthalene	4	---
*Benzaldehyde	2	5.9E4
*Trimethylcyclohexene-one	0.4	No Data
*C <sub>2</sub> Substituted Acetophenone	0.3	4.1E4+
*Substituted Benzoic Acid, Methyl Ester	0.4	6.1E4
Chloronaphthalene (Internal Standard)	3	---
Ethylbiphenyl or Diphenylethane	0.7	---
Unknown Silicone	0.7	---
*Diethylphthalate	0.7	5E3
Unknown	0.3	---
Two compounds believed to be Trimethylpropenylnaphthalene and Dihydromethylphenylbenzofuran	2	---
Unknown Silicone	0.6	---
Unknown Silicone	3	---
Unknown	0.4	---
Hexadecyloxypentadecyl - 1, 3-Dioxane	2	---
Butylisobutylphthalate	1	---
*Fluoranthene	2	9E4
*Pyrene	0.6	2.3E5
Unknown Silicone	0.7	---
Diethylphthalate	25	---
<u>POM Analysis</u>		
Naphthalene	10	---
*Possible Phenanthridene      MW179	0.3	No Data
Possible Trimethylpropenylnaphthalene	2	---
*Probable POM MW184	0.6	Unknown
*Phenanthrene	1	1.6E3
*Fluoranthene	1	9E4
*Pyrene	1	2.3E5
*Chrysene or other MW228 POM	0.1	2.2E3
*Benzopyrene or other MW252 POM	0.01	2E-2

\* Detected compounds not found in blank sample: 141-XMB-SE-KD.  
These are presumed to be in the gas sample.

+ Value is for acetophenone.

TABLE B-9. GC/MS ANALYSIS OF 143 SASS COMPOSITE

Compound	Concentration In Sampled Gas $\mu\text{g}/\text{m}^3$	DMEG Value $\mu\text{g}/\text{m}^3$
<u>Level 2 Analysis</u>		
Possible trans Chlorocyclohexanol	0.5	---
Diethylbenzene	2	---
Ethylstyrene	2	---
*Benzoic Acid, methyl ester	0.02	6.1E4
Possible Methylindene	0.07	---
Methylindene (isomer)	0.1	---
*Ethylbenzaldehyde	0.4	5.9E4+
Naphthalene	2	---
*Trimethylcyclohexene-one	0.5	No Data
*C <sub>2</sub> Substituted Acetophenone	0.2	4.1E4+
*Possible C <sub>3</sub> Substituted Phenol	0.5	1.5E4‡
Chloronaphthalene (Internal Standard)	2	---
Ethylbiphenyl or Diphenylethane	0.1	---
*Unknown (apparent mole wt 180)	0.4	---
*Diethylphthalate	0.2	5E3
Unknown Silicone	0.4	---
Two Compounds believed to be Trimethylpropenyl naphthalene and Dihydromethylphenylbenzofuran	2	---
Unknown Silicone	0.5	---
Unknown Silicone	0.4	---
Unknown Silicone	3	---
Unknown Silicone	0.4	---
Unknown Silicone	0.4	---
Unknown; Apparent mole wt 343	1	---
Butylisobutylphthalate	0.8	---
Unknown Silicone	1	---
*Tetramethylphenanthrene	0.6	1.6E3
Unknown Silicone	0.4	---
Dioctylphthalate	2	---
<u>POM Analysis</u>		
Naphthalene	6	---
Possible Trimethylpropenyl naphthalene	0.5	---
*Anthracene or Phenanthrene or Other MW178 POM.	0.2	1.6E3

\* Detected compounds not found in blank sample: 141-XMB-SE-KD.  
Presumed to exist in sample gas.

+ Value given is for parent compound.

‡ Value is for ethylphenol.

The compounds which have been found in the two samples (Tables B-8 and B-9) and which are absent in the mixture of blank resin artifacts have been designated by an asterisk preceding their name. One will notice that only 7 to 8 compounds have been so designated. None of these compounds have been determined to be in the sample gas at levels exceeding  $2 \mu\text{g}/\text{m}^3$ .

The lower portions of Tables B-7, B-8, and B-9 present the results of the specific POM analysis performed. Several POM compounds were found in the 142-XM-SE-KD sample when the computerized search techniques for POM were used. Three of the compounds were also found by the nonspecific Level 2 technique. In sample 143-XM-SE-KD, only one compound was found by specific POM analysis which was not found in the blank.



## REFERENCES FOR APPENDIX B

- B-1. Leavitt, C., et al. Environmental Assessment of Coal and Oil Firing in a Controlled Industrial Boiler. Appendix B. Report prepared by TRW for the U.S. Environmental Protection Agency. EPA-600/7-78-164a. August 1978.
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