

MODDERFONTEIN
KOPPERS-TOTZEK
SOURCE TEST RESULTS

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ABSTRACT

A source test program was conducted at a Koppers-Totzek (K-T) coal gasification facility operated by AECI Limited at Modderfontein, Republic of South Africa. The EPA's interest in the K-T process stems from the fact that the process economics and demonstrated commercial reliability make it a very viable prospect for some U.S. applications. The responsibilities for sampling, analysis, and engineering descriptions of the Modderfontein plant were shared between TRW and GKT, Gesellschaft für Kohle-Technologie mbH of Essen, Federal Republic of Germany. GKT is the wholly owned subsidiary of the German-based parent company which is the developer and licensor of the K-T process. EPA's phased approach for environmental assessment was followed. Level 1 and Level 2 data were collected along with priority pollutant screening data. Much of the effort was focused on wastewater streams. The wastewater treatment, consisting of a clarifier and settling pond, was adequate to produce a final discharge that had lower pollutant levels than the fresh input waters supplied to the plant. The complete data are presented in this paper along with brief descriptions of the K-T process and the Modderfontein plant. The purpose of the Source Test and Evaluation was intended as an initial effort and was somewhat limited in scope.

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INTRODUCTION AND SUMMARY

TRW, under contract 68-02-2635 to the Environmental Protection Agency, and at the direction of Project Officer William J. Rhodes, is performing the environmental assessment of high-BTU gasification and indirect liquefaction technologies. A major portion of this environmental assessment project is to obtain data on commercial operating facilities through Source Test and Evaluation (STE) programs. The ultimate objective of each STE program is to obtain the data necessary to: 1) evaluate environmental and health effects of waste streams or streams that may potentially be discharged in plants designed for U.S. sites, and 2) allow subsequent evaluation of the equipment available or required for controlling these streams. This paper describes an STE program that was conducted on a Koppers-Totzek (K-T) coal gasifier plant operated by AECI Limited in Modderfontein, Republic of South Africa. The EPA's interest in the K-T process stems from two principal factors: first, in the national drive to supplement liquid and gaseous fossil fuels through coal conversion, process economics dictate that the more viable conversion products will be those having the highest unit retail value. The K-T process represents one of the prime candidates for converting raw coal into the intermediate synthesis gas needed to produce these high-value products. Secondly, the K-T process has a lengthy history of successful application to a variety of foreign coals and promises to be equally adaptable over the range of American coals. This factor is particularly important in view of the contrasting lack of demonstrated commercial reliability on the part of the developmental U.S. gasifiers, and is viewed in a very positive light by both conversion project financiers and program managers.

The K-T process operates on an entrained bed principle. It utilizes a high temperature, atmospheric pressure reaction fueled by a continuous co-current input stream of coal, oxygen, and steam. The gasification

reactor vessel is a horizontal, ellipsoidal, double-walled steel chamber with a refractory lining. Two gasifier designs are available. The two-burner gasifier design utilized at Modderfontein has a burner head located on each end of the ellipsoid as illustrated in Figure 1. The four-burner gasifier resembles two of the two-burner gasifiers which intersect one another at a 90° angle. A burner head is located at each of the ends of the two intersecting ellipsoids. The gasifier operates with a flame temperature of 2000°C (3650°F) or more and a gas outlet temperature of about 1400° to 1600°C (2550° to 2900°F). The major constituents of the gasifier output stream are carbon monoxide and hydrogen.

All of the K-T gasification facilities in operation as of 1978 were used entirely to make synthesis gas as an input stream for the production of ammonia. The Modderfontein plant, illustrated in Figure 2, was commissioned in 1974 and has a design production rate of 1000 tonnes per day of ammonia. It utilizes a High Volatile B, Bituminous coal that is high in ash content (20%) and low in sulfur (1.0%).

The STE program was carried out as a joint effort between TRW and GKT. TRW's initial review of the Modderfontein plant resulted in the identification of 25 streams as necessary to the comprehensive STE goals. Of these 25 streams, nine were selected for testing as a result of discussions between GKT and TRW in which streams considered proprietary, not applicable, or otherwise restricted were eliminated from the list. The STE thus became limited in scope and focused on the nine available streams. Further STE programs are anticipated in the future which will serve to provide basic characterization data on K-T generated wastes so that control technology requirements for facilities built in the U.S. can be identified early in the planning stages. It is not intended that any data presented in this paper or future data resulting from tests at Modderfontein be used for the purpose of either promoting or criticizing specific process designs or operating practices of that facility. It should be stressed that each K-T plant is unique and that numerous design options exist for pollutant reduction within the process depending upon customer requirements.

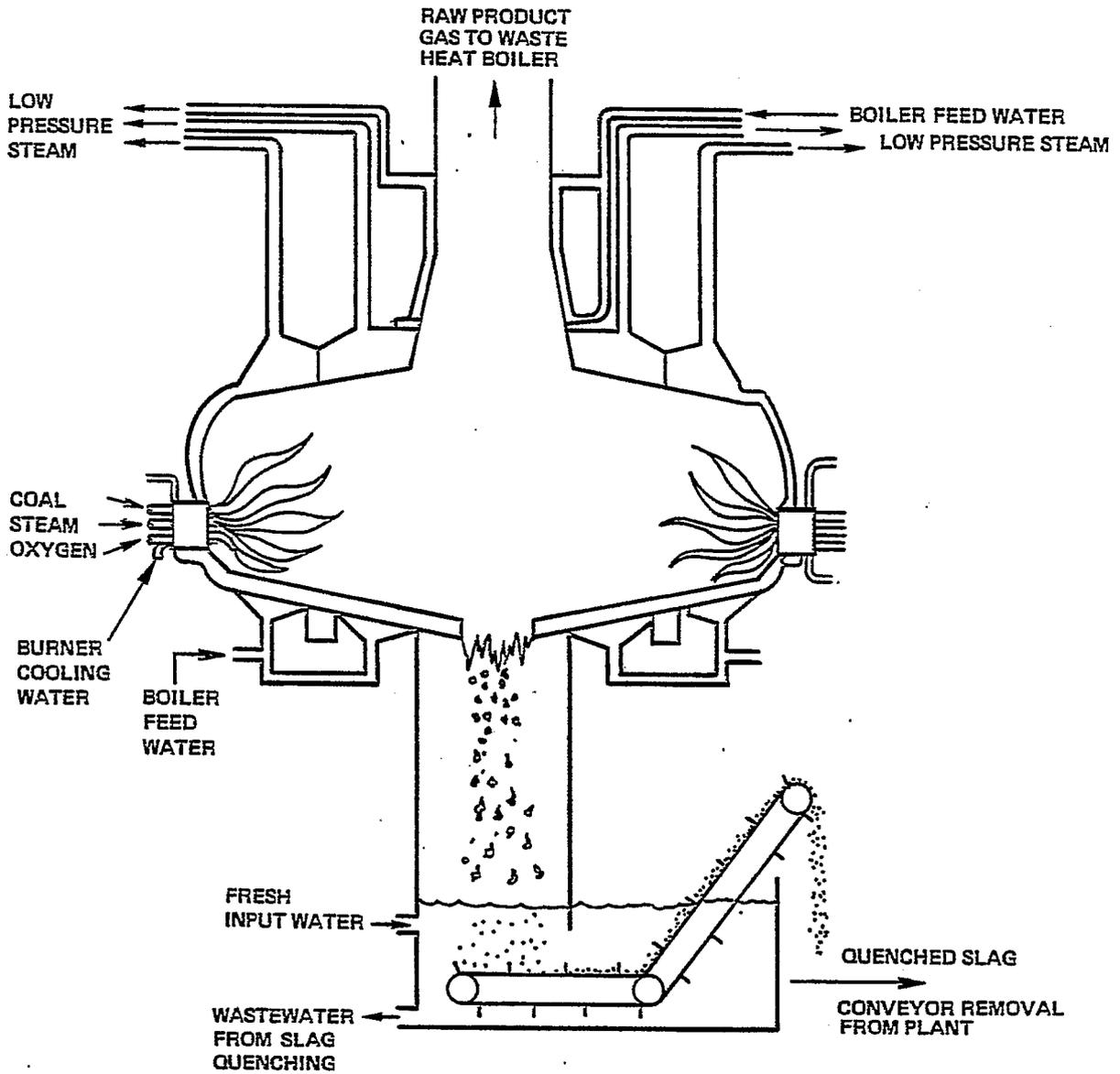


Figure 1. Koppers-Totzek Gasifier

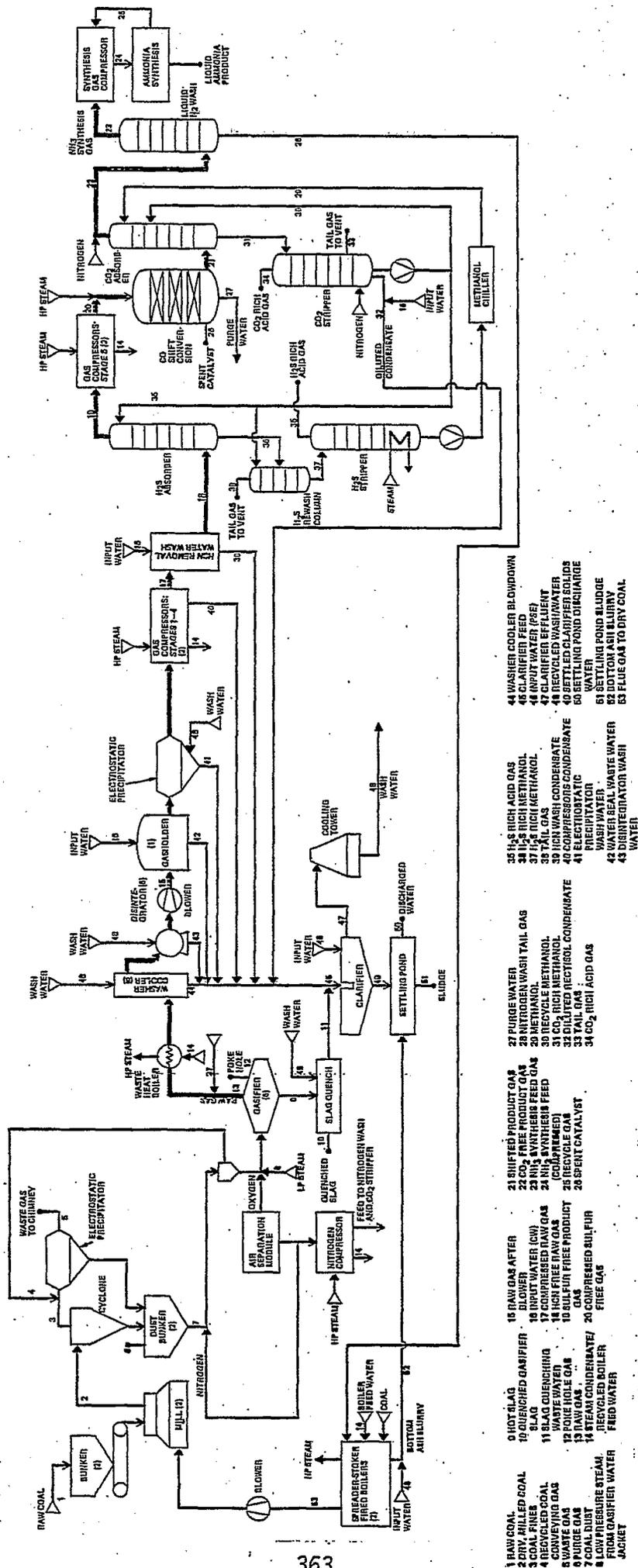


Figure 2. Diagram of Number 4 Ammonia Plant at Modderfontein

APPROACH

The nine streams included in this STE along with their stream numbers which correspond to Figure 2, are as follows:

- Solids
 - Coal Dust Feed/7
- Gas Streams
 - Raw Product Gas/15
 - Tail Gas from H₂S Absorber/38
 - Tail Gas from CO₂ Absorber/33
- Aqueous Streams
 - Input Water (Purified Sewage Effluent)/46
 - Input Water (Cooling Water)/16
 - Settling Pond Effluent/50
 - Compressor Condensate Wastewater/40
 - Diluted Rectisol Condensate Wastewater/32

The basic approach was to perform a comprehensive organic and inorganic characterization of these nine streams per the EPA procedures for Level 1 and Level 2 environmental assessments and for Priority Pollutants (1, 2, 3). The Level 1 methods provide a broad semi-quantitative survey from which constituents found to be present at levels of potential concern are selected for further quantitative examination, Level 2. The Priority Pollutant screening consists of analyses for a specific list of 129 pollutants of concern to the EPA.

The sampling and analysis responsibilities for the K-T facility test were divided between TRW and GKT. GKT performed all of the sampling and most of the on-site analyses during a three week period in November 1979. TRW arranged to have the remaining time-critical analyses performed by a local South African laboratory (McLachlan & Lazar Pty LTD) and to have portions of the coal feed and aqueous process stream samples shipped back to TRW for analysis.

Level 1 Analysis

Most of the Level 1 analyses that are time critical were performed by GKT (i.e., all gas analyses and most wastewater quality tests). The only wastewater quality tests remaining were nitrates and BOD, which were then handled by McLachlan & Lazar in Johannesburg. Replicate analysis of a

few of the species measured by GKT were also performed by the local lab for quality assurance. The methods used by GKT and the commercial laboratory were for the most part comparable to U.S. methods and were acceptable for source evaluations. The analysis of organic materials and trace metals was performed by TRW on preserved aliquots of the aqueous stream samples that were shipped back to the U.S. The methods used for the Level 1 analyses were taken from the EPA-IERL/RTP procedures manual (1).

Level 2 Analysis

Level 2 analyses of the aqueous Modderfontein samples consisted of atomic absorption techniques (AAS) for Fe and Mn, and a high performance liquid chromatography (HPLC) technique for polynuclear organic material (POM) compounds. These two metals and the POM compounds were selected on the basis of comparing the Level 1 data to the EPA's discharge multimedia environmental goal values (4), thus determining the potentially hazardous species present which warranted further investigation, and by examining which Level 2 data requirements had not already been met by either the wastewater quality or priority pollutant analyses.

The AAS techniques were standard methods (5). The HPLC technique for POMs utilized a reverse phase, quarternary solvent system for separation of three-ring and larger POM compounds. Both UV and fluorescence detectors were used in tandem in order to yield corroborative data for the identification and quantitation of the compounds present. Further qualitative data for POM identification was obtained by collecting the HPLC fractions and analyzing them by GC/MS.

Priority Pollutant Screening Analysis

The analyses for organic priority pollutants were done in three phases. Volatile, acid extractable non-volatile and base-neutral extractable non-volatile organics were tested in accordance with the EPA procedures manual (3). The samples were analyzed by computerized gas chromatography-mass spectrometry (GC/MS) using an INCOS data system. A computer program was used to reduce the data. The results were manually examined and if necessary, modified. The thirteen priority pollutant metals (i.e., Ag, As, Be, Cd, Cr, Cu, Hg, Pb, Mn, Sb, Se, Tl, and Zn) were analyzed by a combination of flame and flameless atomic absorption techniques in accordance with the EPA protocol (3).

Source Analysis Model

All of the data obtained from this STE were used in the EPA's Source Analysis Model/IA, which compares the measured concentrations of the constituents analyzed to the EPA's Discharge Multimedia Environmental Goals (6). This model calculates discharge severities based on the constituent concentrations alone (total discharge severity) and on the concentrations combined with the stream flow rate (weighted discharge severity). This approach is being used uniformly by all of the EPA's contractors in the coal conversion area and thus provides a consistent basis for evaluating STE data.

RESULTS

Coal Feed Stream

The results of the proximate and ultimate analysis on the coal feed, shown in Table 1, show that the sample may be characterized as Bituminous, High Volatile B coal. When compared to most U.S. coals it is found to be very high in ash content and low in sulfur. A trace element survey, more precise determinations of the major minerals present and other measurements were also performed. This data will be included in the Source Test and Evaluation Report currently in preparation for the EPA.

Gas Streams

All gas analyses were performed by GKT and the data obtained are shown in Table 2. The raw gas results reflect the average composition from all five gasifiers (the stream was sampled at a common line leading to the gas holder) after the gas has been water-washed for particulate removal. A description of the major reactions that take place in the raw gas washing stages is as follows:

- NH_3 , HCN , SO_2 , and to a small degree H_2S and CO_2 , are dissolved in the wash water.
- H_2S is eventually converted to $\text{S}_2\text{O}_3^{=}$, $\text{SO}_4^{=}$, and insoluble metal sulfides due to the pH, temperature, and flyash content of the water.
- HCN reacts with the sulfur compounds to form SCN^- and with the iron content of the flyash to form insoluble complexes.
- Additional oxidation reactions occur which are catalyzed by the flyash involving NH_3 , $\text{SO}_3^{=}$, $\text{S}_2\text{O}_3^{=}$, CN^- , and SCN^- .

TABLE 1
 PROXIMATE AND ULTIMATE RESULTS
 FROM COAL ANALYSIS

Proximate Analysis		Ultimate Analysis	
	<u>As Received</u>		<u>As Received</u>
% Moisture	1.49	% Moisture	1.49
% Ash	19.60	% Carbon	64.41
% Volatile	27.52	% Hydrogen	3.72
% Fixed Carbon	51.39	% Nitrogen	1.12
	<u>100.00</u>	% Chlorine	0.01
Btu/lb.	10853	% Sulfur	0.99
% Sulfur	0.99	% Ash	19.60
		% Oxygen (diff)	8.66
			<u>100.00</u>

Table 2. GAS ANALYSIS DATA

Parameter/Units	Raw Gas	Tail Gas from H ₂ S Rewash Column	Tail Gas from CO ₂ Stripper
Flowrate, Nm ³ /hr	103,600	13,700	48,800
H ₂ O g/Nm ³	54	5	5
H ₂ Vol.% (dry)	28.2	<0.1	<0.1
CO "	59.1	1.9	0.3
CO ₂ "	10.9	52.6	84.3
N ₂ /Ar*	1.8	45.5	15.4
CH ₄ "	<0.1	<0.1	<0.1
H ₂ S mg/Nm ³ (dry)	6,300	†	<1
COS "	740	†	<3
CS ₂ "	450	†	<10
SO ₂ "	14	<3	<3
NH ₃ "	57	39	3
HCN "	76	62	8
NO _x "	28	<1	<1
Mercaptans "	<1	<1	<1

* By difference

† Not determined

The main components in the water-washed gas are then H₂O, CO, CO₂, H₂, and N₂. Data on hydrocarbons contained in the raw gas stream were not obtained due to problems with on-site analytical instrumentation, but low concentrations would be expected due to the high temperature of the K-T gasification reaction.

The two tail gas streams from the Rectisol module consist primarily of CO₂, the nitrogen used for methanol stripping, small amounts of CO and H₂O and traces of NH₃ and HCN. During the test period, plant operating data indicated that temperature control in the Rectisol unit was not working properly with the result that sulfur species levels in the H₂S stripper tail gas were outside design specifications and were not typical of normal Rectisol unit operation. Therefore sulfur species data on this tail gas stream are not included in Table 2. A design value of less than 2 ppm total sulfur is quoted by GKT.

Use of the SAM/IA model, which assesses the potential health and ecological effects of discharge streams based on chemical constituents, yielded the calculated Total Discharge Severity (TDS) and Weighted Discharge Severity (WDS) values shown in Table 3. In the tail gas stream from the H₂S absorber, CO, HCN, and NH₃ are present at levels of potential concern; and in the tail gas from the CO₂ absorber, CO and NH₃ are of concern.

Table 3. SUMMARY OF SAM/IA TDS AND WDS RESULTS FOR GAS STREAMS

TDS and WDS Values	Tail Gas from H ₂ S Rewash	Tail Gas from CO ₂ Stripper
Total Discharge Severity (TDS)		
Health-Based	5.6 E + 02	7.6 E + 01
Ecology-Based	2.9 E + 02	3.4 E + 01
Weighted Discharge Severity (WDS)		
Health-Based	2.1 E + 03	1.0 E + 03
Ecology-Based	1.1 E + 03	4.6 E + 02

Aqueous Streams

The results of the Level 1 standard wastewater analyses performed jointly by GKT, TRW and McLachlan & Lazar are summarized in Table 4. The

Table 4. WASTEWATER QUALITY TEST DATA

Parameter/Units	Input Water (PSE)	Input Water (CW)	Settling Pond Effluent	Process Waters	
				Compressor Condensate	Rectisol Condensate
Flowrate, m ³ /hr	215	34	230	9.1	3.9
pH	6.8	8.5	8.7	8.1	8.6
TSS, mg/L	<1	8	<1	6	45
TDS, mg/L	1,580	1,460	1,560	220	1,520
Hardness, mg/L	450	620	540	53	620
Conductivity, μ mhos/cm	2,300	1,900	2,100	5,800	1,900
BOD, mg/L	5	4	4	550	800
COD, mg/L	16	24	4	600	1,600
TOC, mg/L	31	16	5	140	590
NH ₃ , mg/L	73	3	33	940	38
CN ⁻ , mg/L	0.2	1.2	0.2	8.9	2.8
SCN ⁻ , mg/L	2.1	2.1	1.8	14	120
H ₂ S, mg/L	<1	<1	<1	49	2.8
S ₂ O ₃ ⁼ , mg/L	<1	<1	<1	6.3	17
SO ₃ ⁼ , mg/L	<1	<1	<1	<1	<1
SO ₄ ⁼ , mg/L	580	850	730	53	500

settling pond effluent, the only aqueous stream discharged by the plant, appears from the data to be quite similar to the input waters. This would seem to indicate that any aqueous pollutants contributed by the gasification process are essentially removed in the settling pond.

The results of the Level 1 survey for organics, shown in Table 5,

Table 5. LEVEL 1 ORGANIC SURVEY DATA

Stream/Flowrate	Volatiles (mg/L)	Non-Volatiles (mg/L)	Total Organics (mg/L)
Input Water (PSE)/215 m ³ /hr	0.04	0.68	0.72
Input Water (CW)/34 m ³ /hr	<0.01	0.88	0.88
Settling Pond Effluent/230 m ³ /hr	0.05	0.06	0.10
Process Streams			
Compressor Condensate/9.1 m ³ /hr	0.01	3.83	3.84
Rectisol Condensate/3.9 m ³ /hr	0.49	33.4	33.9

indicate that the total organic loading was low and that the material present was primarily nonvolatile (BP >100°C). Examination of the non-volatile material by infrared (IR) spectroscopy indicated that the classes of compounds present in all of the samples are primarily saturated hydrocarbons along with some esters. There was also some IR evidence of low levels of aromatic hydrocarbons present in the compressor condensate and Rectisol unit samples. Examination of the nonvolatile samples by solids probe low resolution mass spectroscopy (LRMS) yielded additional information regarding the classes of compounds present. The intensity of the mass spectra peaks were used to assign relative concentration factors (100 = major, 10 = minor, 1 = trace) to the compound classes identified. The LRMS results are summarized in Table 6. The mass spectra data confirm the IR data indicating the presence of aliphatic hydrocarbons, esters, and traces of aromatics. Traces of phenols, cresols, and alcohols also appear in many of the samples. Significant levels of elemental sulfur (S₈) are also seen because of its appreciable solubility in the solvent used for these extractions (methylene chloride).

Table 6. ORGANIC COMPOUND CLASS DATA

Stream	Compound Class	Contribution to Total Organics
Input Water (PSE)	Esters (phthalates) Nitro Aromatic Hydrocarbons Primary Alcohols	Major Minor Minor
Input Water (CW)	Esters (phthalates)	Major
Settling Pond Effluent	Primary Alcohols Secondary Alcohols Aliphatic Hydrocarbons Esters (phthalates) Unsaturated Alkyl Halides Ketones	Major Major Minor Minor Trace Trace
Process Streams		
Compressor Condensate	Sulfur (Sg) Ethers Esters (phthalates) Phenols Chlorinated Phenols Chlorinated Cresols Polynuclear Organic Materials (POMs) Carboxylic Acids	Major Major Minor Trace Trace Trace Trace Trace
Rectisol Condensate	Aliphatic Hydrocarbons Sulfur (Sg) Polynuclear Organic Materials (POMs) Phenols Esters (phthalates)	Major Minor Trace Trace Trace

The Level 1 inorganic survey of the aqueous samples consisted of a spark source mass spectroscopy (SSMS) analysis. The data indicated that, based upon elemental composition, the settling pond effluent is quite similar to the input waters. Similarity between these streams based upon standard wastewater parameters was previously noted. The only trace elements that show an increase from input water levels to settling pond effluent levels are cesium, strontium, barium, gallium, and molybdenum. This is in general agreement with the trace element analysis of the coal. Other elements (i.e., aluminum, iron, and manganese) actually show a significant decrease in the settling pond effluent compared to the input water.

As is mentioned in the analytical approach, the Level 1 data were compared to the EPA's Discharge Multimedia Environmental Goals (DMEGs) using the SAM/IA model in order to determine which species were present at levels of potential concern and were thus candidates for further investigation. Those species determined to be of interest were then compared to the priority pollutant list. It was found that most of the Level 2 data requirements would be satisfied by the priority pollutant analyses and that the only additional determinations needed were the quantitation of Fe and Mn in most of the samples and quantitation of polynuclear organic material (POM) compounds in the Rectisol condensate samples. It is thus appropriate to discuss the Level 2 and priority pollutant results together as a coordinated analytical effort.

The organic priority pollutant data are summarized in Table 7. The results show that very few of the 116 organic priority pollutant compounds were found. Those that were present were mostly at very low concentrations. The level of concern specified by the EPA's Effluent Guidelines Division is 10 µg/L.

The results of the HPLC analysis for POMs performed on the methylene chloride extracts from the two Rectisol unit samples indicated that each extract contained essentially the same POMs at very similar levels. Eleven distinct POM compounds were detected. Comparison of retention time data as well as relative response ratio for the two detectors with similar data for available standards enabled the positive identification and quantitation of five compounds, Table 8. Those compounds which overlap

Table 7. ORGANIC PRIORITY POLLUTANT DATA

Sampling Day	Stream Description/Stream Number	Priority Pollutant Compounds Found					
		Base/Neutral Fraction		Acid Fraction		Volatiles	
		Compound	µg/L	Compound	µg/L	Compound	µg/L
Nov. 12	Input Water--Purified Sewage Effluent	Nitrobenzene 1,2,4-Trichlorobenzene Isophorone Bis (2-Ethylhexyl)phthalate Di-n-octylphthalate	T T T T T	None Detected		None Detected	
Nov. 19	Input Water--Cooling Water	Butylbenzylphthalate	T	None Detected		Chloroform	T
Nov. 12	Settling Pond Effluent	None Detected		None Detected		None Detected	
Nov. 19	Settling Pond Effluent	Butylbenzylphthalate	T	None Detected		Chloroform	T
Nov. 12	Combined Condensates from #1--4 Compressors	Naphthalene	T	4-Chloro-m-Cresol	2.3	None Detected	
Nov. 19	Combined Condensates from #1--4 Compressors	Naphthalene Diethylphthalate Di-n-butylphthalate Butylbenzylphthalate	T T 6.0 T	Phenol Pentachlorophenol	T T	Chloromethane Bromomethane Chloroform	7.8 49 T
Nov. 12	Condensate from Rectisol Unit	Naphthalene Fluorene Anthracene plus phenanthrene Fluoranthene Pyrene Butylbenzylphthalate	T T 6.3 25 T	None Detected		Chloroform	T
Nov. 19	Condensate from Rectisol Unit	Acenaphthalene Dimethylphthalate Fluorene Diethylphthalate Anthracene plus phenanthrene Fluoranthene Pyrene Chrysene	T T 1.0 T 4.6 19 97 34	Phenol 2,4-Dimethylphenol	T T	Chloroform	T

T = Trace (<1µg/L)

Table 8. LEVEL 2 POM DATA

Compounds Identified	11/12/79 Rectisol Condensate	11/19/79 Rectisol Condensate
Fluoranthene	24 µg/L	17 µg/L
Pyrene	32 µg/L	25 µg/L
1,2-Benzofluorene	15 µg/L	15 µg/L
1,2-Benzanthracene	23 µg/L	16 µg/L
Benzo(k)fluoranthene	2 µg/L	2 µg/L

with the priority pollutant screening (i.e., fluoranthene and pyrene) are more accurately quantitated by the HPLC technique. The priority pollutant screening also identified a four-ringed compound as chrysene which in the HPLC analysis was determined to be 1,2-benzanthracene (also four-ringed).

HPLC fractions were collected and analyzed by gas chromatography/mass spectrometry (GC/MS) to obtain molecular weight data on the remaining unknown compounds. The five unidentified POMs are believed to be present at levels less than 30 µg/L based on the HPLC peak areas. They had molecular weights of 230 (1), 242 (2), and 252 (2).

The health-based DMEGs for the identified POM compounds range from 670 µg/L to 24,000 µg/L, while ecology-based DMEGs are 100 µg/L for all five of these POMs. Comparison of data and DMEGs shows that the levels measured would not be considered to be of concern.

It should be noted that the very toxic POM benzo(a)pyrene was one of the standards used in this analysis. None of the HPLC peaks matched the retention time and response ratios for B(a)P. Thus the unidentified compounds with MW 252 are clearly some other POM with the identical molecular weight.

The priority pollutant metals screening involves the analysis of 13 elements each of which has its own level of concern. These elements and the corresponding levels of concern which have been defined by the EPA are: Ag - 5 ppb, Tl - 50 ppb, Sb - 100 ppb, As - 25 ppb, Se - 10 ppb, Zn - 1,000 ppb, Pb - 25 ppb, Cd - 5 ppb, Ni - 500 ppb, Be - 50 ppb, Cu - 20 ppb, Cr - 25 ppb, and Hg - 1 ppb. The results obtained from atomic

adsorption and emission spectroscopy analyses for these thirteen elements plus the two elements (Fe and Mn) quantitated for Level 2 requirements are presented in Table 9. The data show that the process waters (compressor condensate and Rectisol unit samples) frequently exceed the levels of concern particularly for Se, Zn, Cu and Hg. However, as was noticed in the Level 1 SSMS inorganic survey, the only aqueous discharged stream (settling pond effluent) is relatively clean compared to both the process streams and the input waters (purified sewage effluent and cooling water). Overall reduction in trace element levels across the plant were observed for Sb, As, Zn, Pb, Ni and Ca.

All of the data obtained on the aqueous streams were evaluated using the SAM/IA model to assess the potential health and ecological effects of the streams. Of particular interest is the discharged stream, the settling pond effluent. The TDS and WDS values obtained for this discharge as compared to the input streams supplied as process water to the plant, are summarized in Table 10. The fact that the health-based values for the aqueous input and discharge streams reflect a potential concern is due mainly to Mn and Fe and to a lesser extent phosphorus. The ecology-based values are entirely due to phosphorus. The ecology DMEG value for phosphorus and its various anions is extremely low ($0.5 \mu\text{g/L}$) and thus easily becomes the most significant value obtained in the SAM/IA calculations. However ecology-based severity values >1 were also obtained for Cd, Cu, Mn, Ni, Pb, S, Zn, and phthalate esters in the input water streams and Cd, Mn, Ni, and S in the settling pond discharge stream. The reduction in both TDS and WDS values for the effluent versus the input water appears to be due to a decrease in the concentrations of the phthalate esters, phosphorus, Cu, Pb, and Zn. These and other constituents as well appear to be transferred to the settling pond sludge.

Table 9. INORGANIC-PRIORITY POLLUTANT AND LEVEL 2 DATA

Element	Concentration, ppb				
	Input Water (PSE)	Input Water (CW)	Settling Pond Effluent	Process Waters	
				Compressor Condensate	Rectisol Condensate
Antimony	10	<3	<3	<3	<3
Arsenic	33	<5	9	<5	11
Beryllium	<0.5	<0.5	<0.5	<0.5	<0.5
Cadmium	1.3	<0.5	<0.5	<0.5	<0.5
Chromium	<5	7	6	6	7
Copper	78	43	6	31	90
Lead	50	28	<5	19	13
Mercury	0.5	<0.2	<0.2	250	23
Nickel	180	<10	<10	<10	190
Selenium	<2	<2	3	3,500	26
Silver	<1	<1	<1	<1	<1
Thallium	<5	<5	<5	<5	<5
Zinc	660	3,500	<100	270	2,600
Iron	<100	700	140	1,200	4,000
Manganese	1,300	<50	720	<25	50

Table 10. SAM/IA RESULTS FOR AQUEOUS STREAMS

Stream.	Total Discharge Severity (TDS)		Weighted Discharge Severity (WDS)	
	Health-Based	Ecology-Based	Health-Based	Ecology-Based
Discharge Water--Settling Pond Effluent	6.1 E + 00	1.9 E + 02	3.9 E + 02	1.2 E + 04
Input Water--Purified Treated Sewage	9.8 E + 00	1.6 E + 04	5.9 E + 02	9.6 E + 05
Input Water--Cooling Water	6.7 E + 00	4.2 E + 03	6.4 E + 01	4.0 E + 04

CONCLUSIONS

The limited source test program conducted at the Modderfontein facility has provided some of the key data needed for the environmental assessment of Koppers-Totzek based synthetic fuels plant which may be built in the United States. The data obtained do not indicate that any special problems should be encountered in controlling the process effluents to environmentally acceptable levels for plants built in the U.S. For example, the wastewater treatment at Modderfontein, consisting of a clarifier and settling pond, was adequate to produce a final discharge that had lower pollutant levels than the fresh input waters supplied to the plant.

Relatively steady state conditions were realized during the test period, thus most of the samples taken were generally representative of typical plant operation. This in turn indicates that the data can reliably be used as intended. Nearly full design capacity was obtained throughout the test period. All collection of samples and associated operating data occurred at production rates of between 102,000 and 104,000 normal cubic meters per hour (Nm^3/h) of dry raw gas and the gasification plant operated in a very stable manner with no process upsets.

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AN ENVIRONMENTALLY BASED EVALUATION OF
THE MULTIMEDIA DISCHARGES FROM THE KOSOVO LURGI
COAL GASIFICATION SYSTEM

By

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ABSTRACT

The U.S. Environmental Protection Agency and the government of Yugoslavia have jointly sponsored a cooperative environmental data acquisition program. This program has focused upon a commercial-scale medium-Btu Lurgi gasification facility which is currently operating in the Kosovo region of Yugoslavia. The objective of this program was to characterize the uncontrolled discharge streams associated with the Kosovo facility in order to gain insight into control technology needs for future U.S. Lurgi plants. The Kosovo study was undertaken because the Lurgi process has a significant potential for future use in the United States.

In the Kosovo test program, the most environmentally significant components in the plant's key feed, product, and discharge streams were identified and quantified. Also, selected in-plant process streams were sampled and analyzed to gain insight into how specific pollutants distributed themselves among the plant's gaseous, aqueous, and solid discharge streams. The EPA's Source Analysis Model/1A was used to identify and prioritize the pollutants found in the plant's discharge streams.

The results of the Kosovo test program indicate that there are many gaseous, aqueous, and solid discharge streams from a Lurgi gasification facility which have the potential to significantly impact the environment. The key pollutants identified in the plant's gaseous discharge streams included reduced sulfur and nitrogen species (H_2S , mercaptans, HCN, and ammonia), hydrocarbons (benzene), and CO. Key pollutants in the Phenosolvan wastewater included phenols, cyanides, sulfides, and total organics. Effective controls for the waste streams containing these pollutants will be essential to minimize the environmental problems associated with Lurgi gasification technology.

In general, trace elements were not found to be a significant problem at Kosovo. The dry gasifier ash met the RCRA Extraction Procedure test criteria for nonhazardous wastes. Trace organics, particularly polynuclear aromatic compounds which are likely to be present in streams containing tar aerosols, should be given attention in the development of controls for U.S. Lurgi facilities.

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An international program sponsored by the Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency, is being conducted in the Kosovo region of Yugoslavia to characterize potential environmental problems associated with Lurgi gasification technology. The study, conducted over a three year period, was a cooperative endeavor between scientists from Yugoslavia and EPA/Radian. The program was undertaken because the Lurgi gasification process has significant potential for use in the United States.

The purpose of the Kosovo study was to characterize the uncontrolled discharges from a commercial Lurgi facility. This was done to gain insight into the environmental control needs for future U.S. Lurgi gasification plants. The test program was conducted in four phases whose objectives were:

<u>Phase</u>	<u>Objective</u>
I	Identify and quantify major and minor pollutants in the plant's discharge streams.
II	Identify and quantify trace pollutants in the plant's discharge streams.
III	Characterize ambient air pollutants in the plant's vicinity.
IV	Measure fugitive emission rates in the plant.

The program schedule is shown in Figure 1. Negotiations for this cooperative program were initiated in 1974. Testing, which was initiated in 1977, has been carried out in six individual campaigns over a three year period. Phase I results were reported previously (Ref. 1 through 3). Documentation of the results from Phases II and III will become available in 1981. Testing for fugitive emissions (Phase IV) was completed in August, 1980, and the results are currently being evaluated.

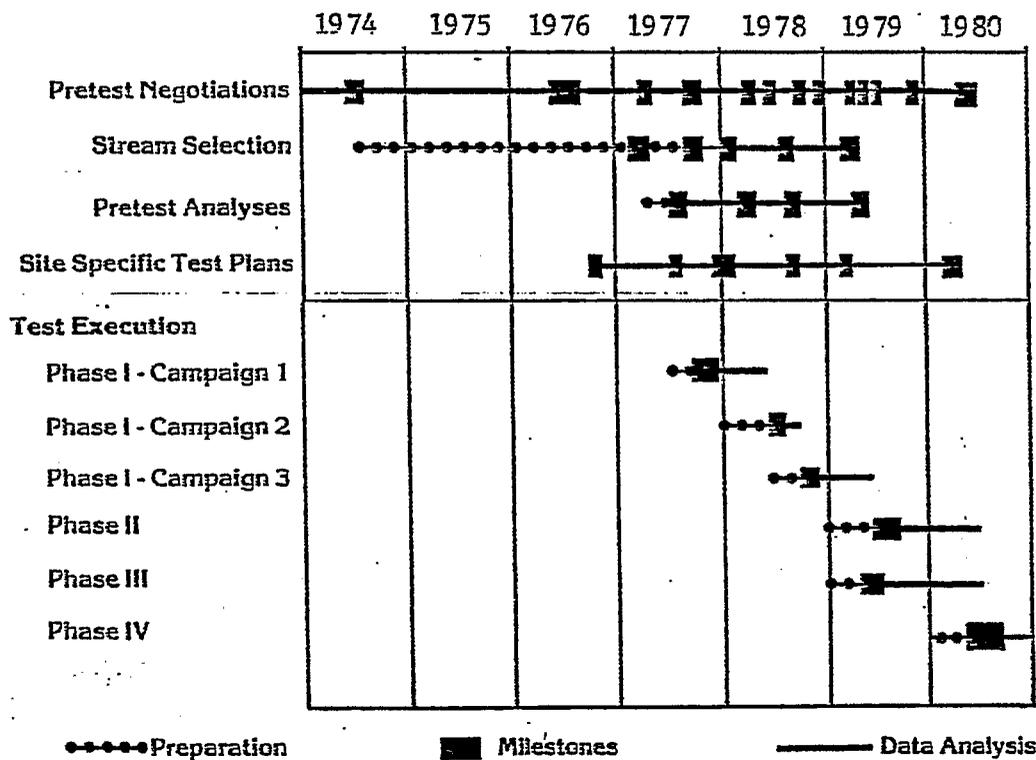


Figure 1. Kosovo test program schedule.

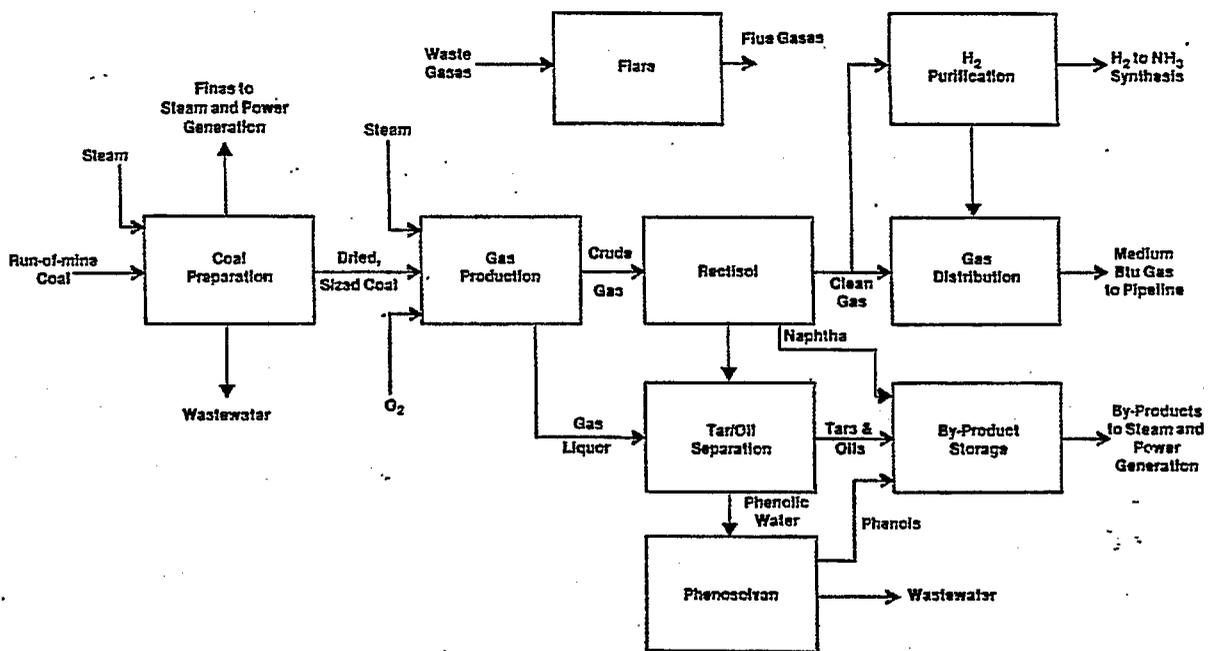


Figure 2. Simplified flow diagram of the Kosovo coal gasification plant.

This paper presents an overview of the Phase I and II test results. These results address the major, minor, and trace pollutants found in the plant's key process and discharge streams. An assessment of the severity of the plant's gaseous, aqueous, and solid discharges is included. This assessment is based upon the use of the EPA-IERL's Source Analysis Model/1A (SAM/1A). This model prioritizes pollutants based on their potential for causing adverse health effects.

Plant Description

Detailed descriptions of the Kosovo coal gasification plant were provided in previous publications (Ref. 1 through 3). A brief plant description is included here to facilitate understanding of the results.

The Kosovo Lurgi gasification facility is an integral part of a large mine-mouth industrial complex. A simplified flow diagram is shown in Figure 2. The gasification plant consumes dried lignite and produces two primary products: a medium-Btu fuel gas having a net heating value of approximately 14 MJ/m^3 @ 25°C (360 Btu/scf), and hydrogen which is used as an ammonia synthesis feedstock. Several hydrocarbon by-products including light tar, medium oil, naphtha, and crude phenol are also produced.

Run-of-mine coal which contains around 50 weight percent moisture is dried by the Fleissner process (high temperature steam soak) to around 25 weight percent moisture and sized to select particles between 6 and 60 mm in diameter. Typical feed coal properties are presented in the results section. After sizing, the dried coal is fed to the Lurgi gasifiers where it reacts with oxygen and steam at 2.5 MPa (25 atm) pressure. The crude product gas is cooled and then cleaned to remove acid gases prior to its transportation by pipeline to the utilization site. In the cooling step, tars, oils, naphtha, and phenolic water are condensed and removed from the gas. In the acid gas removal step, H_2S and CO_2 are removed by sorption into cold methanol. The rich methanol is regenerated by depressurization and heating. The H_2S -rich waste gas released by the regeneration step is sent to a flare while the CO_2 -rich waste gas is vented directly to the atmosphere. Tar and oil are separated from the phenolic water by decantation after which the water soluble organics (crude phenols) are removed from the wastewater by extraction with diisopropyl ether. Four liquid by-products: naphtha, medium oil, light tar, and crude phenol are collected in storage tanks and used as fuels. Ammonia, removed from the phenolic water by steam stripping, is vented to the atmosphere.

Figure 3 shows the design flow rates of the plant's major inlet and outlet streams. These flow rates are based on design conditions with five of six Lurgi gasifiers in operation. As indicated in Figure 3, the plant is designed to produce 25 Mg ($65,000 \text{ m}^3$ @ 25°C) of product gas for every 80 Mg of dried coal consumed.

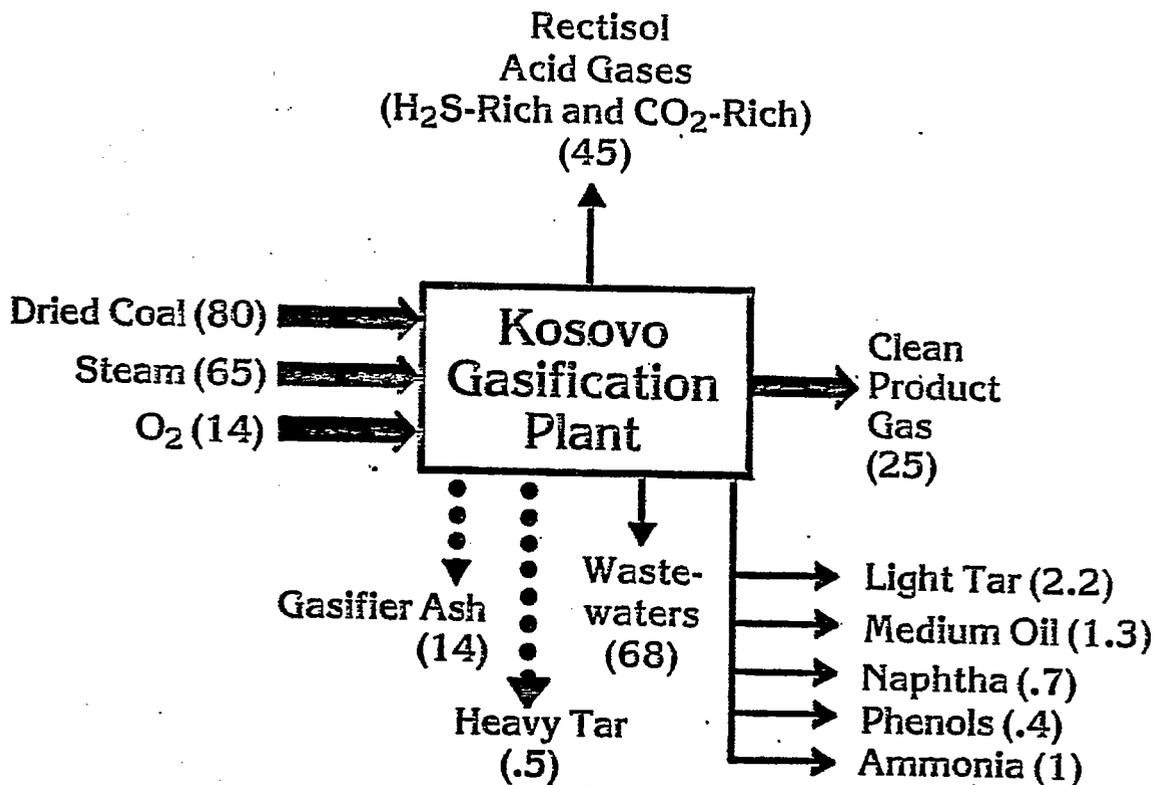
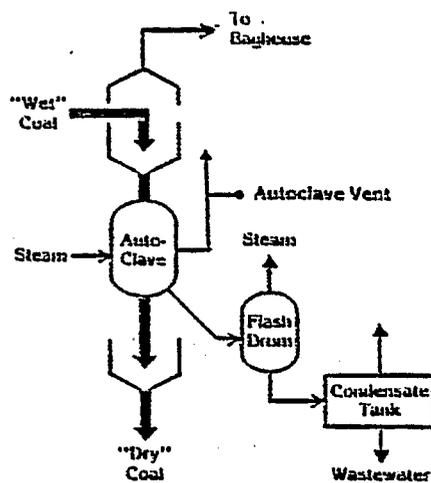


Figure 3. Major stream flow rates in the Kosovo gasification plant (megagrams/hr).



—•— indicates sampling point

Figure 4. Kosovo coal drying section.

The Kosovo plant is smaller than proposed first generation U.S. Lurgi gasification plants, but it contains many of the process units which are likely to be employed in those plants. For this reason, the plant is considered to be representative of the Lurgi facilities likely to be built in the U.S. in the near future.

While many of the process units employed at Kosovo are representative of those proposed for use in future U.S. Lurgi facilities, the environmental control practices followed at the Kosovo plant are not. Thus, while the discharges that enter the environment at Kosovo are not representative of those that would be encountered in similar U.S. facilities, the types of control problems facing U.S. Lurgi plant operators will be similar to those found at Kosovo. A study of the waste and process streams at the Kosovo plant should aid U.S. plant designers in developing the process modifications and control schemes necessary to achieve U.S. standards of environmental protection.

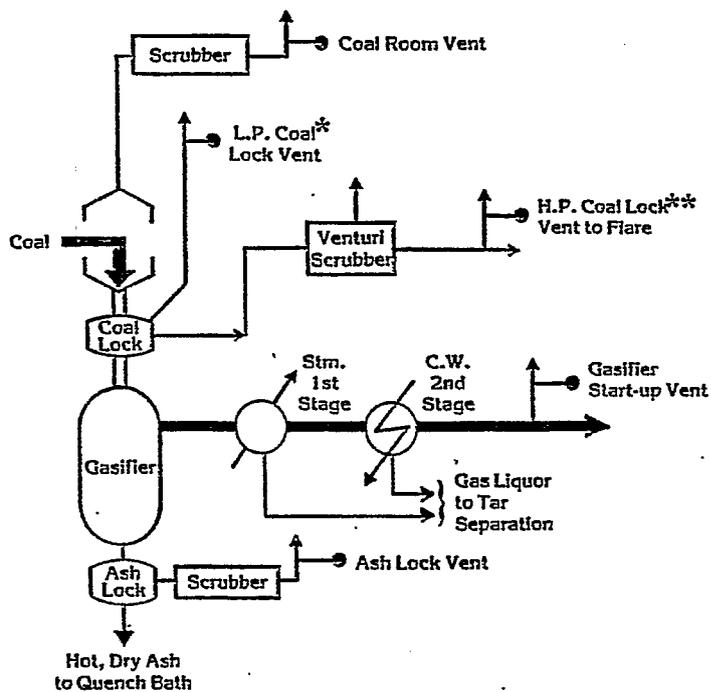
Test Rationale

The Kosovo gasification plant contains approximately 70 streams which have a significant potential for adversely impacting the environment. However, since the cost of characterizing such a large number of streams was considered prohibitive, during Phase I, approximately 50 streams were surveyed. In this survey, the major pollutants present in the process and uncontrolled discharge streams were identified. Based on these results, a limited number (20 to 30) of streams were selected for detailed study in Phase II.

Process and discharge streams were selected for study for one or more of the following reasons:

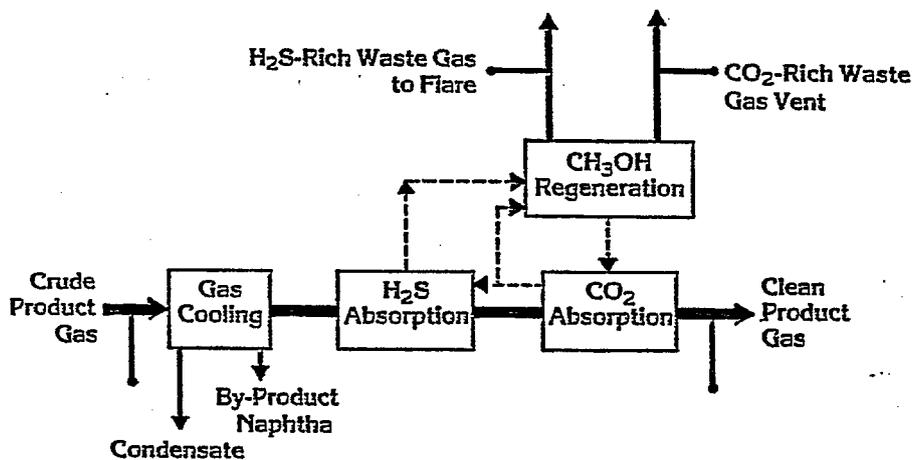
- high discharge rate,
- significant pollutant concentration,
- needed for trace pollutant fate determination, and/or
- provided useful process information.

Figures 4 through 10 show simplified flow schemes of the primary process units of the Kosovo plant. Streams selected for Phase II testing are identified in these figures.



*L.P. - Low Pressure
 **H.P. - High Pressure
 —●— indicates sampling point

Figure 5. Kosovo Gas Production section.



—●— indicates sampling point

Figure 6. Kosovo Rectisol section.

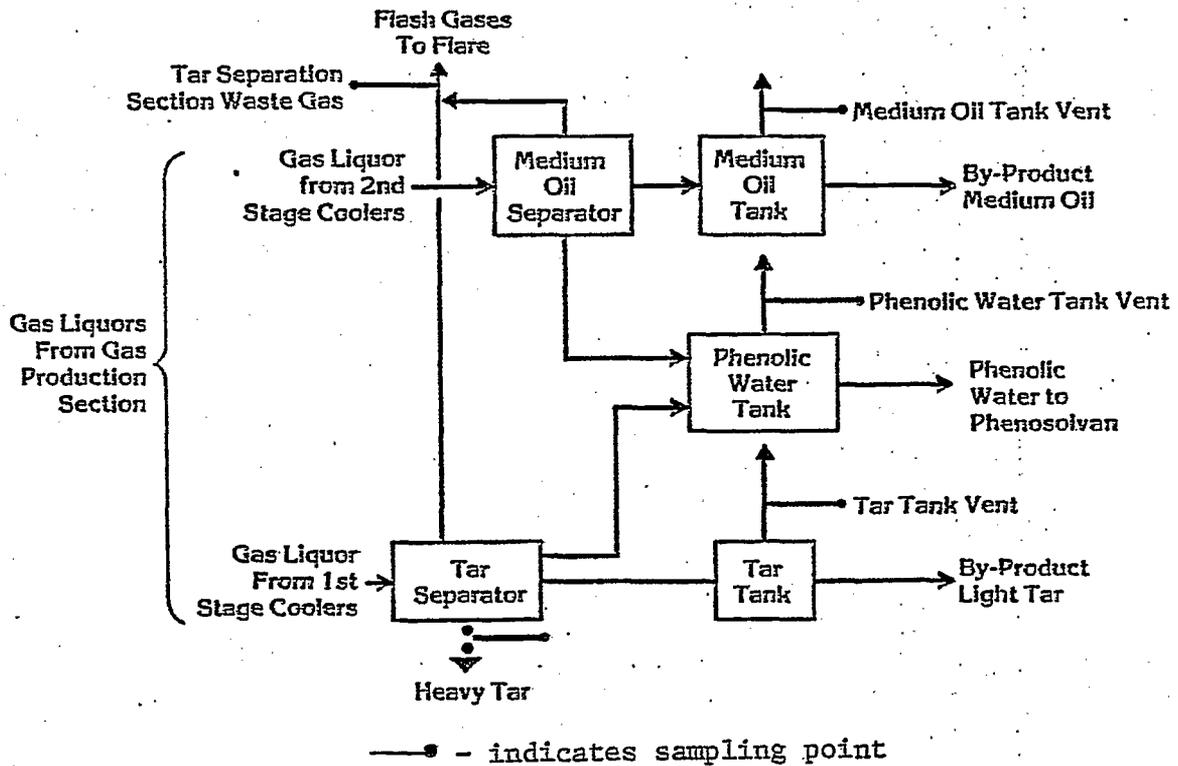


Figure 7. Kosovo Tar Separation section.

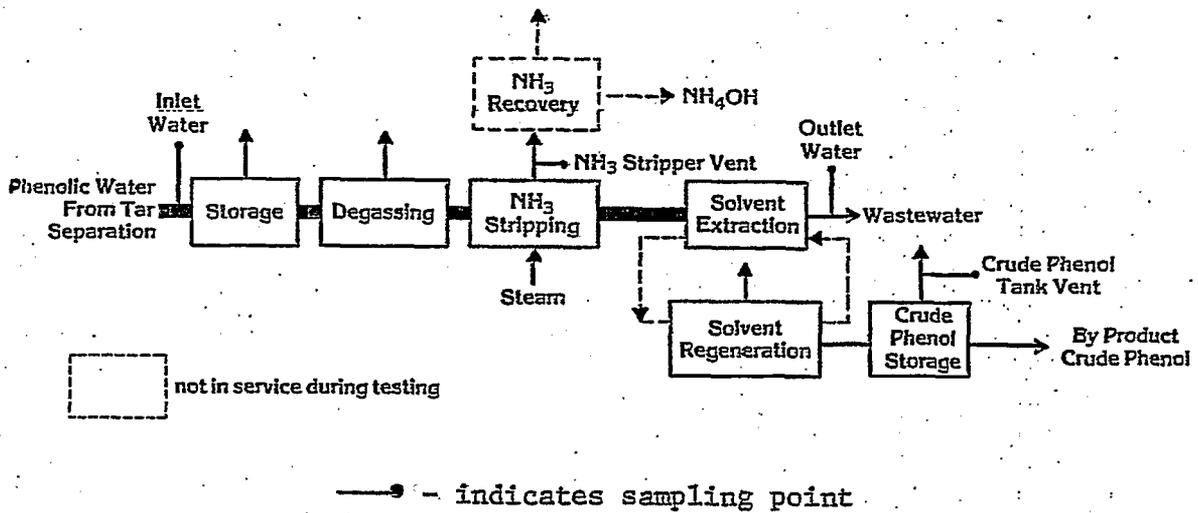
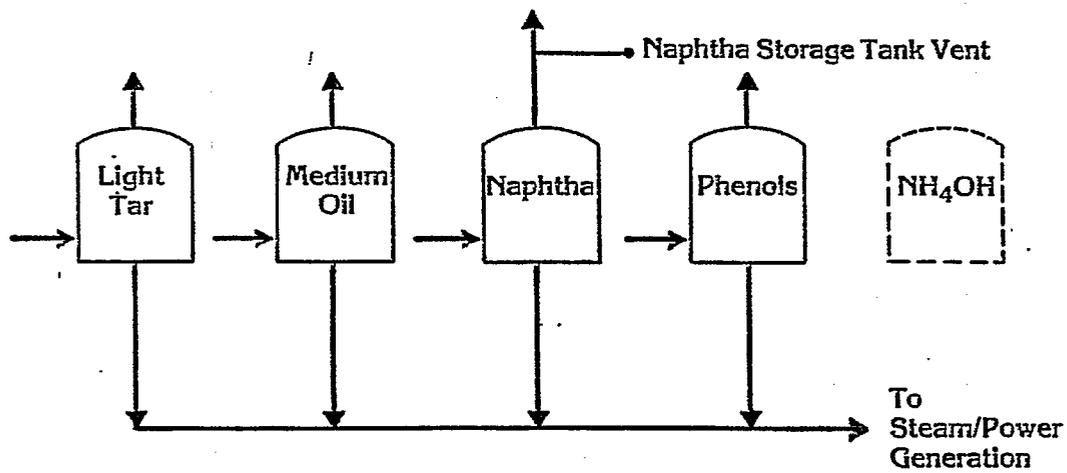


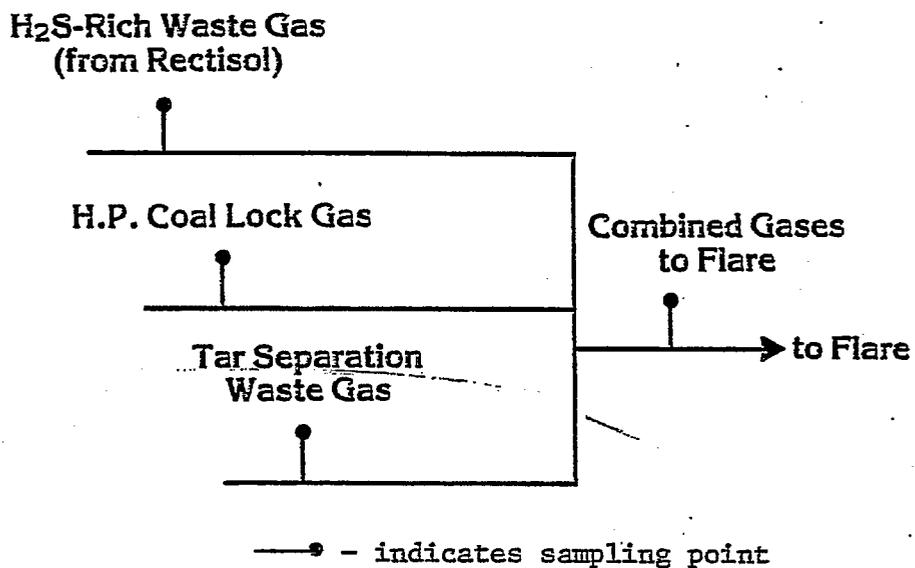
Figure 8. Kosovo Phenosolvan section.



 not in service during testing

—●— indicates sampling point

Figure 9. Kosovo By-Product Storage section.



—●— indicates sampling point

Figure 10. Kosovo Flare Feed system.

Stream Parameters: The Phase I and Phase II characterization efforts addressed the following parameters:

Gaseous Streams

- Flow rate
- Particulate concentration
- Gas composition
- Condensible organics
- Trace elements

Aqueous Streams

- Water quality parameters
- Trace elements
- Organic constituents

Solids

- Proximate analyses
- Ultimate analyses
- Trace elements
- Leachate analyses

Liquid By-Products

- Bulk composition
- Trace elements

Sampling and Analytical Methods: With the exception of the condensible organics analysis, all gas stream characterization work was performed on-site. The methods used for gaseous sampling and analysis are listed in Table 1. Liquid and solid analyses were performed where applicable, with either EPA or ASTM standard methods. These methods are identified and discussed elsewhere (Ref. 3). New methods, developed specifically to characterize sulfur- and nitrogen-containing organic compounds in liquid by-products will be reported separately.

Data Evaluation - Source Analysis Model 1/A

The Source Analysis Model 1/A (SAM/1A) is a procedure developed by EPA-IERL for evaluating discharge stream data. Its principle strength is that it makes possible the reduction of pollutant discharge data to a common numerical base so that discharges can be ranked or prioritized.

TABLE 1. SAMPLING AND ANALYTICAL METHODS

Parameter	Collection Method	Analytical Method
<u>CONDENSIBLE HYDROCARBONS:</u>		
Condensible Hydrocarbons	Gas stream cooled to 0°C and resulting condensate trapped in impingers. The remaining condensible hydrocarbons trapped on XAD-2 resin.	Organic material extracted from condensate and resin with CH ₂ Cl ₂ . Extract analyzed with gas chromatography/mass spectrometry.
Benzene, Toluene, and Xylene	Vapors trapped from gas stream by activated carbon.	Vapors solvent extracted from carbon and analyzed by GC with flame ionization detector.
<u>GASEOUS SPECIES BY GC:</u>		
Fixed Gases (CO, H ₂ , CO ₂ , N ₂ , O ₂ , CH ₄)	Sample was heated, filtered and dried then compressed into silanized glass bombs for analyses.	Gas chromatograph with thermal conductivity detector.
Hydrocarbons C ₁ - C ₆ , C ₆ ⁺ Benzene, Toluene, and Xylene	Sample was heated, filtered and dried then compressed into silanized glass bombs for analyses.	Gas chromatograph with flame ionization detector.
Sulfur Species (H ₂ S, COS, CS ₂ , SO ₂ , Mercaptans)	Sample was heated, filtered and dried then compressed into silanized glass bombs for analyses.	Gas chromatograph with flame photometric detector.

(Continued)

TABLE 1 (Continued). SAMPLING AND ANALYTICAL METHODS

Parameter	Collection Method	Analytical Method
<u>PARTICULATE:</u>		
Suspended Particulate	EPA Method 5, gas filtered at 250°F out of stack.	Gravimetric.
	EPA Method 17, gas filtered at duct temperature in stack.	Gravimetric.
Suspended Particulate Plus Condensibles	Condensation and collection in a series of water filled impingers.	Filtration, extraction with CH ₂ Cl ₂ , Gravimetric.
<u>TRACE ELEMENTS:</u>		
Non-Volatile Elements (Be, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sr, Tl, V, Zn)	Two impingers with 10% HNO ₃ followed by two impingers with 10% NaOH.	Dissolution, AA with Graphite Furnace.
Volatile Elements (Hg, As, Sb, Se)	Two impingers with 10% HNO ₃ followed by two impingers with 10% NaOH.	Dissolution, AA with Hydride Generation.
Iron and Nickel Carbonyls	Two fritted impingers with 3% HCl.	AA with Graphite Furnace.
<u>OTHER GASES:</u>		
Ammonia	Two fritted impingers with 0.1 N H ₂ SO ₄ .	Distillation into boric acid and back titration with sulfuric acid.

(Continued)

TABLE 1* (Continued). SAMPLING AND ANALYTICAL METHODS

Parameter	Collection Method	Analytical Method
Hydrogen Sulfide	Two fritted impingers with 0.1 N cadmium acetate.	Iodine addition and back titration with thiosulfate.
Hydrogen Cyanide	Two fritted impingers with 0.1 N cadmium acetate followed by two fritted impingers with 0.1 N NaOH.	Distillation and titration with silver nitrate.
Phenols	Two fritted impingers with 0.1 N NaOH.	Spectrophotometric determination by reaction with 4-aminoantipyrine.

The SAM/IA model is based upon the use of discharge multimedia environmental goals (DMEG's) to compute Discharge Severity (DS) values (Ref. 4). DMEG's are concentration levels below which the discharged component is of low concern for its potential effects on either human health or the ecology. Thus, it is a "target value" for components in discharge streams. DMEG's have been defined for many substances representing 26 classes of organic compounds (Ref. 5). Target levels have been defined in terms of their effect on both human health and ecology for discharges to the three environmental media: air, water, and soil. DMEG (Air/Health) values for 16 components whose concentrations were measured in this study, are shown graphically in Figure 11. A reciprocal of DMEG is plotted since DS is the product of concentration and 1/DMEG as defined below:

$$DS = \frac{\text{Measured Concentration of a Pollutant}}{\text{DMEG of that Pollutant}}$$

Since the DMEG allows the severity of different compounds to be related to a common numerical base ("multiples of the target value"), a stream's total discharge severity (TDS) can be determined by summing the DS values for all components in that stream:

$$TDS = \sum DS.$$

The TDS value provides a basis for comparing uncontrolled discharge streams, and, therefore, provides a basis for identifying the most severe (highest TDS) streams.

Discharge severity is a concentration - based value that does not take into account the quantity of mass emitted. Used alone it cannot define the environmental effects of a discharge because such effects are related to both quantity and severity. With the SAM/IA Model, the environmental significance of a pollutant in a given discharge stream is defined by its Weighted Discharge Severity (WDS):

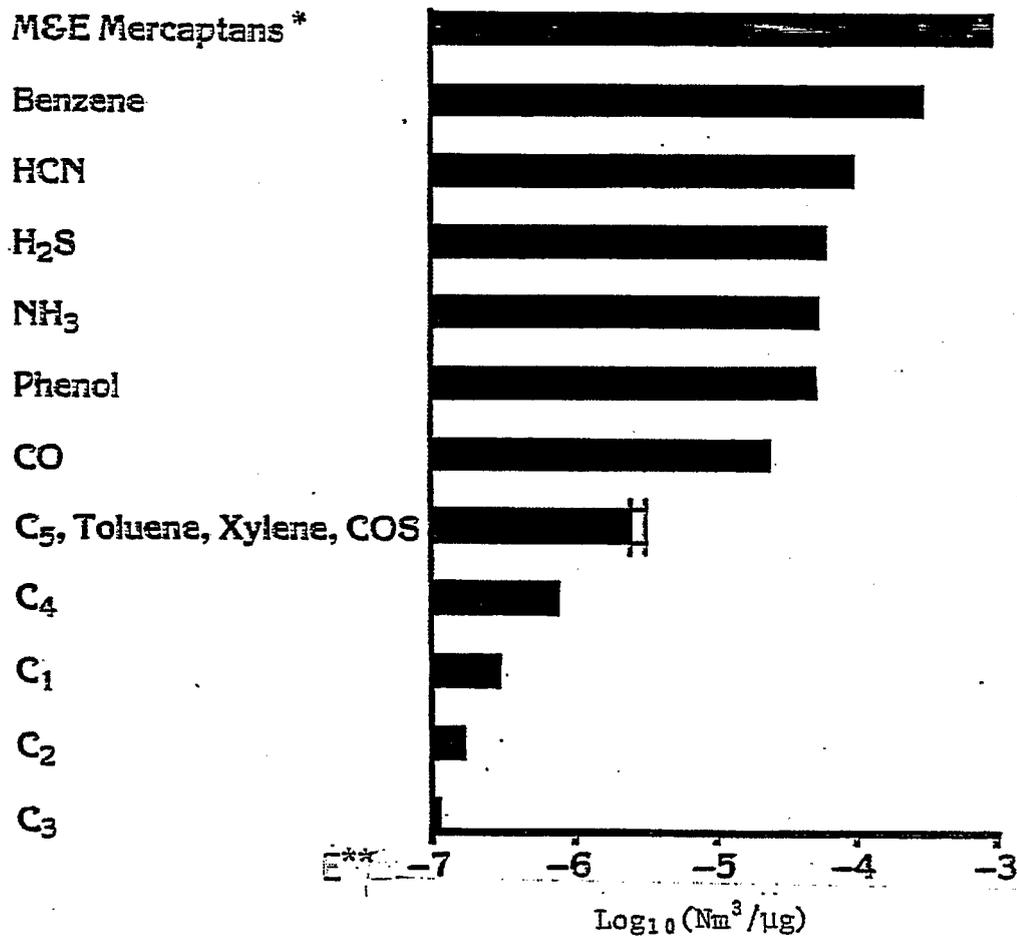
$$WDS = F \cdot DS$$

where F = Stream Flow Rate;

and further, the environmental significance of that discharge stream is defined by its Total Weighted Discharge Severity (TWDS):

$$TWDS = F \cdot \sum DS = F \cdot TDS$$

By comparing discharge streams within a given medium, such as gaseous, aqueous, or solid, the stream with the highest TWDS value may be selected as the most environmentally significant.



*Methyl and Ethyl Mercaptans

E** = Exponential (E-5 = 10⁻⁵)

Figure 11. Key Kosovo gaseous pollutants in order of severity (1/DMEG).

Results and Discussion

The results obtained during the Kosovo study consist of stream composition and flow rate data. The data presented and discussed in this section were selected from Phases I and II as "best values" based on engineering and analytical judgment. The results discussed here are for the streams selected for detailed examination in the Phase II test program.

Gaseous Streams: Test data for gaseous streams are presented in Tables 2 and 3. In Table 2, the concentration data are given in molar concentration units (vol % or ppmv) while in Table 3, these data are expressed in mass concentration units ($\mu\text{g}/\text{m}^3$). Oxygen and nitrogen analyses were included in the fixed gas analyses for quality control. Samples showing abnormal levels of O_2 and N_2 (indicating an air leakage into the sample) were resampled.

The data in Table 3 were used to calculate the mass discharge rate from each stream for each major pollutant. Table 4 summarizes the streams having the highest concentration and those having the highest mass flow for each type of pollutant measured. As this table shows, a single stream, such as the ammonia stripper vent, can be the source of several pollutants at comparatively high concentrations. The table also indicates that the H_2S -rich waste gas and CO_2 -rich waste gas streams are of concern because of the high flow rates of these streams. In addition, the by-product tank vents (naphtha storage tank, medium oil tank, phenolic water tank) are significant because of high pollutant concentrations.

Figure 12 shows a graphic representation of the mass flow rate of the major gaseous pollutants. As shown, C_1 to C_6+ hydrocarbons and sulfur species pollutants are produced in the largest quantities. Most of the sulfur species are sent to the flare, whereas most of the ammonia and phenols are discharged directly to the atmosphere. The C_1 to C_6+ hydrocarbons are well distributed among most of the flare feed and uncontrolled discharge streams.

Discharge severity values accent pollutants of greatest concern in terms of their potential to cause adverse health or environmental effects. Figure 13 illustrates the relationship between DS values and pollutant mass concentration data for the major pollutants in the coal lock vent discharge. Note that BTX (benzene, toluene, and xylene) and mercaptans, which are at relatively low concentrations (Figure 13A), emerge as pollutants of high concern when the severity of the discharge is investigated (Figure 13B).

TABLE 2. KOSOVO GASEOUS STREAM COMPOSITION DATA

PLANT SECTION: SAMPLE POINT:	GAS PRODUCTION			RECTIFIOL			
	3.2 Low Pressure Coal Lock Vent	3.3 Gasifier Start-up Vent	3.6 High Pressure Coal Lock (Flare Feed Stream)	7.1 H ₂ S-rich * Waste Gas (Flare Feed Stream)	7.2 CO ₂ -rich Waste Gas Vent	7.3 Crude Gas (Process Stream)	7.4 Product Gas (Process Stream)
Dry Gas Flow Rate (m ³ /gasifier-hr @ 25°C)	21	-	230	3600	3600	18,800*	13,100*
Temperature (°C)	56	-	54	12	19	22	-
Moisture Content (%)	44	70	11	3.9	5.1	2.5	4.1
Molecular Wt. of Dry Gas	23.5	33.1	24.9	43.0	42.2	21.9	10.3
Composition (Dry Basis)							
<u>Fixed Gases (Vol %)</u>							
H ₂	37	0.09	32	0.11	Tr	38.1	60
O ₂	0.27	4.5	0.24	Tr	Tr	0.36	0.44
N ₂	0.18	42	0.14	Tr	Tr	0.64	0.38
CH ₄	8.6	1.6	10.5	4.3	1.2	11.5	16
CO	14.6	14	12	1.1	Tr	15	22
CO ₂	36.5	34	42	88	94	32	0.02
<u>Sulfur Species (ppmv)</u>							
H ₂ S	13,000	6300	3500	45,400	39	6000	NF
COS	110	110	120	420	62	97	0.17
CH ₃ SH	420	490	460	2100	8.5	590	1.1
C ₂ H ₅ SH	220	240	210	780	4.4	200	1.0
<u>Hydrocarbons (Vol %)</u>							
C ₂ H ₆	0.22	0.15	0.42	0.82	1.6	0.47	0.15
C ₂ H ₄	Tr	0.05	Tr	Tr	Tr	0.04	Tr
C ₃ 's	0.14	0.08	0.25	0.63	0.28	0.19	Tr
C ₄ 's	0.05	0.03	0.11	0.32	Tr	0.074	Tr
C ₅ 's	Tr	0.007	0.01	0.04	Tr	0.044	Tr
C ₆ +	0.12	0.09	0.08	0.21	NF	0.064	0.03
<u>Aromatic Species (ppmv)</u>							
Benzene	760	90	550	110	1.0	750	-
Toluene	220	10	100	8	Tr	230	-
Xylene & Ethylbenzene	75	Tr	38	NF	Tr	100	-
Phenols	5.7	630	2.5	Tr	NF	Tr	Tr
Higher Aromatics	-	-	-	-	-	-	-
<u>Nitrogen Species (ppmv)</u>							
NH ₃	2400	11,000	NF	2200	4.6	3.3	Tr
HCN	600	2,900	170	200	13	320	-

Tr - Traces = 0.01 vol. % for fixed gases, 1 ppmv for all others.
 NF - Not Found = less than a trace.
 * = Design Value.
 - = No Data Available.

(Continued)

TABLE 2 (Continued). KOSOVO GASEOUS STREAM COMPOSITION DATA

PLANT SECTION:	TAR SEPARATION				PHENOSOLVAN NH ₃ Stripper Vent	BY- PRODUCT STORAGE 15.3 Naphtha Storage Tank Vent	FLARE SYSTEM 20.1 Combined Gas to Flare
	13.1 Tar Tank Vent	13.3 Medium Oil Tank Vent	13.6 Tar Separation Waste Gas(Flare Feed Stream)	13.7 Phenolic Water Tank Vent			
Dry Gas Flow Rate (m ³ /gasifier-hr @ 25°C)	0.55	1.7	28*	5.5	260	4.5	1330
Temperature (°C)	52	42	40	76	91	32	21
Moisture Content (%)	14	8.4	7.7	42	76	5	2.5
Molecular Wt. of Dry Gas	29.1	32.5	39.0	34.4	32.7	33.3	41.7
Composition (Dry Basis)							
<u>Fixed Gases (Vol %)</u>							
H ₂	Tr	Tr	11	Tr	NF	NF	Tr
O ₂	19	0.45	Tr	13	-	2.6	0.10
N ₂	77.5	1.1	Tr	39	-	84	0.21
CH ₄	0.16	7.6	3.5	0.2	Tr	NF	6.2
CO	Tr	5.9	1.1	NF	NF	NF	1.9
CO ₂	0.86	56	77.5	35	55	0.85	88
<u>Sulfur Species (ppmv)</u>							
H ₂ S	6900	26,000	9000	12,600	19,500	NF	10,600
COS	110	96	120	41	NF	NF	250
CH ₃ SH	390	5200	2500	2100	290	2600	2500
C ₂ H ₅ SH	240	2100	1600	7200	100	9700	190
<u>Hydrocarbons (Vol %)</u>							
C ₂ H ₆	Tr	0.34	0.33	} 0.02	} Tr	} Tr	0.77
C ₂ H ₄	-	Tr	Tr				Tr
C ₃ 's	0.01	0.30	0.41	0.02	Tr	0.07	0.38
C ₄ 's	Tr	0.25	0.41	0.02	Tr	0.08	0.04
C ₅ 's	Tr	0.09	0.09	0.006	Tr	5.3	0.06
C ₆ +	0.37	2.4	1.3	1.8	NF	-	-
<u>Aromatic Species (ppmv)</u>							
Benzene	2000	7650	9600	11,000	Tr	37,600	640
Toluene	960	1400	1200	2300	-	1900	215
Xylene & Ethylbenzene	220	140	150	280	Tr	60	33
Phenols	57	110	4.2	Tr	6200	Tr	Tr
Higher Aromatics	2.2	-	4.9	3.1	-	-	-
<u>Nitrogen Species (ppmv)</u>							
NH ₃	2600	19	19,300	12,000	418,000	NF	NF
HCN	130	57	64	38	4800	1100	100

Tr - Trace = 0.01 vol. % for fixed gases, 1 ppmv for all others.

NF - Not Found = less than a trace.

* = Design Value.

- = No Data Available.

TABLE 3. COMPONENT CONCENTRATIONS IN KOSOVO GASEOUS STREAMS

PLANT SECTION:	RECFYISOL					
	GAS PRODUCTION			Product Gas		
SAMPLE POINT:	3.2 Low Pressure Coal Lock Vent	3.6 High Pressure Coal Lock Vent (Flare Feed Stream)	7.1 H ₂ S-Rich Waste Gas (Flare Feed Stream)	7.2 CO ₂ -Rich Waste Gas Gas Vent	7.3 Grude Product Gas	7.4 Clean Product Gas
Component ($\mu\text{g}/\text{m}^3$ @ 25°C)	Lock Vent	Coal Lock Vent (Flare Feed Stream)	Waste Gas (Flare Feed Stream)	Gas Vent	Product Gas	Product Gas
<u>Fixed Gases</u>						
H ₂	3.05E07	2.64E07	9.06E04	Tr	3.14E07	4.94E07
O ₂	3.53E06	3.14E06	Tr	Tr	4.70E06	5.75E06
N ₂	2.06E06	1.60E06	Tr	Tr	7.32E06	4.35E06
CH ₄	5.64E07	6.88E07	2.82E07	7.84E06	7.54E07	1.05E08
CO	1.67E08	1.37E08	1.26E07	Tr	1.71E08	2.52E08
CO ₂	6.56E08	7.55E08	1.58E09	1.69E09	5.81E08	3.60E05
<u>Sulfur Species</u>						
H ₂ S	1.81E07	4.87E06	6.32E07	5.43E04	8.35E06	NF
COS	2.70E05	2.95E05	1.03E06	1.52E05	2.38E05	4.17E02
CH ₃ SH	8.25E05	9.04E05	4.13E06	1.67E04	1.16E06	2.16E03
C ₂ H ₅ SH	5.57E05	5.33E05	1.98E06	1.12E04	5.08E05	2.54E03
<u>Hydrocarbons</u>						
C ₂ H ₆	2.70E06	5.16E06	1.01E07	1.97E07	5.77E06	1.84E06
C ₃ H ₈	Tr	Tr	Tr	Tr	4.58E05	Tr
C ₄ H ₁₀	2.52E06	4.50E06	1.14E07	5.04E06	3.42E06	Tr
C ₅ H ₁₂	1.19E06	2.61E06	7.60E06	Tr	1.76E06	Tr
C ₆ H ₁₄	Tr	2.95E05	1.18E06	Tr	1.30E06	Tr
C ₇ H ₁₆	4.22E06	2.82E06	7.39E06	NF	2.25E06	1.06E06
C ₈ H ₁₈	2.43E06	1.76E06	3.51E05	3.19E03	2.39E06	Tr
Toluene	8.30E05	3.76E05	3.00E04	Tr	8.66E05	Tr
Xylene & Ethylbenzene	3.25E05	1.65E05	NF	Tr	4.34E05	Tr
Phenols	2.19E04	9.61E03	Tr	NF	Tr	Tr
<u>Nitrogen Species</u>						
NH ₃	1.67E06	NF	1.53E06	3.20E03	2.30E03	Tr
HCN	6.62E05	1.80E05	2.21E05	1.44E04	3.53E05	Tr
Dry Gas Flow Rate (m ³ /gasifier-hr @ 25°C)	21	230	3,600	3,600	18,800*	13,100*

NF = Not Found
Tr = Trace
* = Design Value

(Continued)

TABLE 3 (Continued). COMPONENT CONCENTRATIONS IN KOSOVO GASEOUS STREAMS

PLANT SECTION:	TAR SEPARATION		PHENOSOLVAN		BY-PRODUCT STORAGE		FLARE SYSTEM	
	13.1	13.2	13.6	13.7	14.5	15.3	20.1	
SAMPLE POINT:	Tar Tank Vent	Medium Oil Tank Vent	Tar Separation Waste Gas (Flare Feed Stream)	Phenolic Water Tank Vent	Ammonia Stripper Vent	Naphtha Storage Tank Vent	Combined Gas to Flare	
Component ($\mu\text{B}/\text{m}^3$ @ 25°C)								
<u>Fixed Gases</u>								
H ₂	Tr	Tr	9.06E06	Tr	NF	NF	Tr	
O ₂	2.48E08	5.88E06	Tr	1.70E08	-	3.40E07	1.31E06	
N ₂	8.87E08	1.26E07	Tr	4.46E08	-	9.61E08	2.40E06	
CH ₄	1.04E06	4.98E07	2.29E07	1.31E06	Tr	NF	4.06E07	
CO	Tr	6.75E07	1.26E07	NF	NF	NF	2.17E07	
CO ₂	1.55E07	1.01E09	1.40E09	6.29E08	9.89E08	1.53E07	1.58E09	
<u>Sulfur Species</u>								
H ₂ S	9.61E06	3.62E07	1.25E07	1.75E07	2.72E07	NF	1.48E07	
CS ₂	2.70E05	2.36E05	2.94E05	1.01E05	NF	NF	6.14E05	
CH ₃ SH	7.66E05	1.02E07	4.91E06	4.13E06	5.70E05	5.11E06	4.91E06	
C ₂ H ₅ SH	6.09E05	5.33E06	4.06E06	1.83E07	2.54E05	2.46E07	4.82E05	
<u>Hydrocarbons</u>								
C ₂ H ₆	Tr	4.18E06	4.05E06	2.46E05	Tr	Tr	9.46E06	
C ₂ H ₄	-	Tr	Tr	-	-	-	Tr	
C ₃ H ₈	1.80E05	5.40E06	7.39E06	3.60E05	Tr	1.80E05	1.17E07	
C ₄ H ₁₀	Tr	5.94E06	9.74E06	4.75E05	Tr	1.66E06	9.03E06	
C ₅ H ₁₂	Tr	2.65E06	2.65E06	1.77E05	Tr	2.36E06	1.18E06	
C ₆ H ₆	1.30E07	8.45E07	4.58E07	6.34E07	NF	1.87E08	2.11E06	
Benzene	6.38E06	2.44E07	3.06E07	3.51E07	-	1.20E08	2.04E06	
Toluene	3.61E06	5.27E06	4.52E06	8.66E06	-	7.15E06	8.09E05	
Xylene & Ethylbenzene	9.54E04	6.06E05	6.51E05	1.21E06	Tr	2.60E05	1.43E05	
Phenols	2.19E05	4.24E05	1.62E04	Tr	2.38E07	Tr	Tr	
<u>Nitrogen Species</u>								
NH ₃	1.81E06	1.32E04	1.34E07	8.35E06	2.91E08	NF	NF	
HCN	1.44E05	6.28E04	7.05E04	4.20E04	5.30E06	1.21E06	1.10E05	
Dry Gas Flow Rate ($\text{m}^3/\text{gasifier-hr}$ @ 25°C)	0.55	1.7	20*	5.5	260	4.5	1,330	

NF = Not Found
 Tr = Trace
 * = Design Value

TABLE 4. MAJOR KOSOVO DISCHARGE STREAMS BASED ON POLLUTANT CONCENTRATION AND MASS FLOW RATE

Pollutant	HIGHEST CONCENTRATION			GREATEST MASS FLOW RATE		
	Direct		Total Plant*	Direct		Total Plant*
	Atmospheric Discharges	Total Plant*		Atmospheric Discharges	Total Plant*	
CO	LP Coal Lock Vent	LP Coal Lock Vent	LP Coal Lock Vent	LP Coal Lock Vent	H ₂ S-Rich Waste Gas	H ₂ S-Rich Waste Gas
C ₁ - C ₆	Naphtha Storage Tank Vent	Naphtha Storage Tank Vent	Naphtha Storage Tank Vent	CO ₂ -Rich Waste Gas Vent	H ₂ S-Rich Waste Gas	H ₂ S-Rich Waste Gas
BTX†	Naphtha Storage Tank Vent	Naphtha Storage Tank Vent	Naphtha Storage Tank Vent	Phenolic Water Tank Vent	Tar Separation Waste Gas	Tar Separation Waste Gas
Total Sulfur Species	Medium Oil Tank Vent Naphtha Storage Tank Vent Phenolic Water Tank Vent	H ₂ S-Rich Waste Gas	H ₂ S-Rich Waste Gas	Ammonia Stripper Vent	H ₂ S-Rich Waste Gas	H ₂ S-Rich Waste Gas
H ₂ S	Medium Oil Tank Vent	H ₂ S-Rich Waste Gas	H ₂ S-Rich Waste Gas	Ammonia Stripper Vent	H ₂ S-Rich Waste Gas	H ₂ S-Rich Waste Gas
COS	LP Coal Lock Vent	H ₂ S-Rich Waste Gas	H ₂ S-Rich Waste Gas	CO ₂ -Rich Waste Gas	H ₂ S-Rich Waste Gas	H ₂ S-Rich Waste Gas
Mercaptans	Naphtha Storage Tank Vent	Naphtha Storage Tank Vent	Naphtha Storage Tank Vent	Ammonia Stripper Vent	H ₂ S-Rich Waste Gas	H ₂ S-Rich Waste Gas
Phenols	Ammonia Stripper Vent	Ammonia Stripper Vent	Ammonia Stripper Vent	Ammonia Stripper Vent	Ammonia Stripper Vent	Ammonia Stripper Vent
NH ₃	Ammonia Stripper Vent	Ammonia Stripper Vent	Ammonia Stripper Vent	Ammonia Stripper Vent	Ammonia Stripper Vent	Ammonia Stripper Vent
HCN	Ammonia Stripper Vent	Ammonia Stripper Vent	Ammonia Stripper Vent	Ammonia Stripper Vent	Ammonia Stripper Vent	Ammonia Stripper Vent

*Includes both direct discharge and flare feed streams.
†Benzene, Toluene, and Xylenes.

Figure 12A.

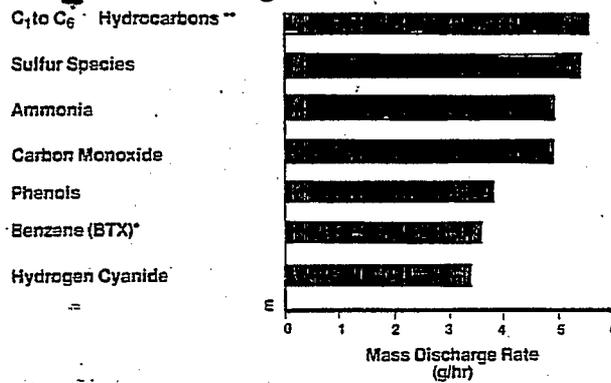


Figure 12B.

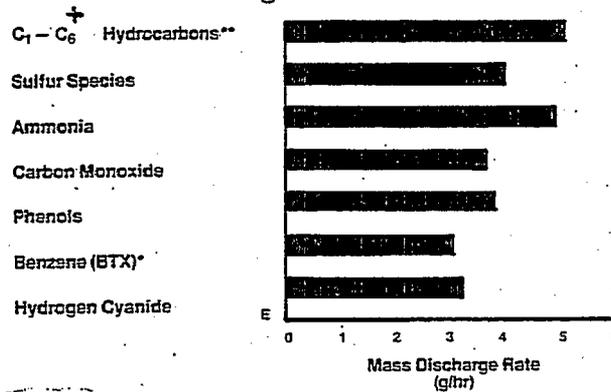
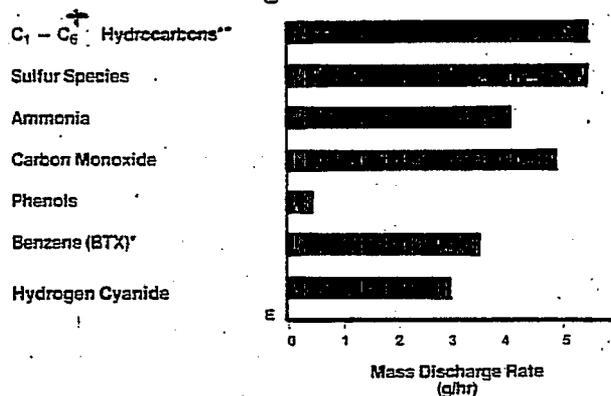


Figure 12C.



*BTX = Benzene, Toluene, Xylenes

**Excluding Benzene

A. Plant-Wide Discharge and Flare Feed Streams

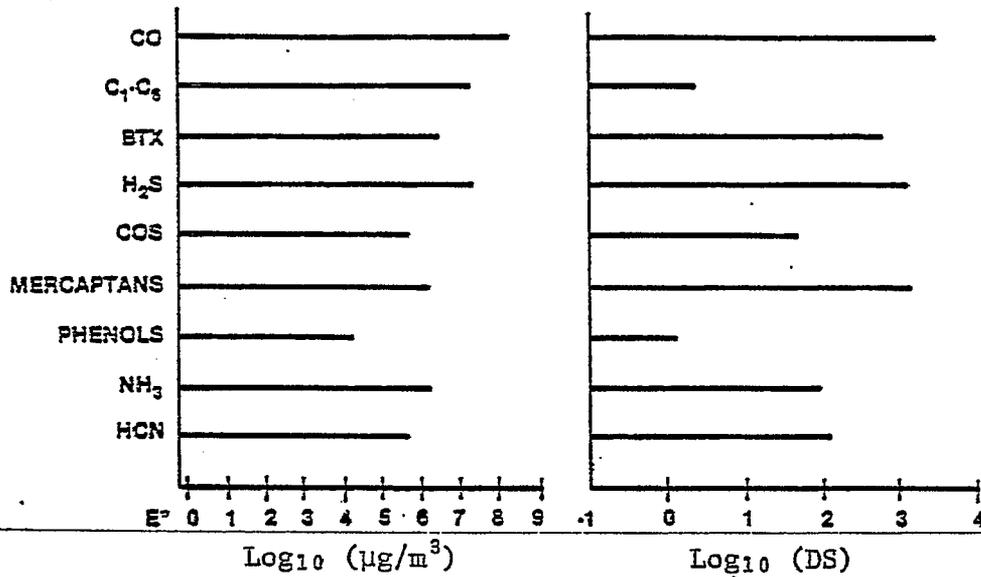
B. Discharge Streams Only

C. Flare Feed Streams Only

Figure 12. Total mass flow rate in Kosovo Gaseous Streams.

Figure 13A.

Figure 13B.



Mass concentration of pollutants
in LP coal lock vent

Discharge Severity of pollutants
in LP coal lock vent

*Exponential (E05 = 10⁵)

Figure 13. Comparison of mass concentrations with calculated discharge severities in the low pressure coal lock vent discharge stream.

Discharge severity values for the individual pollutants and total stream discharge severity values for the plant's key gaseous streams are listed in Table 5. Figure 14 shows a comparison of these total stream discharge severities for the seven uncontrolled discharge streams examined during Phase II. From this comparison it is evident that the discharge from the naphtha storage tank vent is several hundred times more severe (DS on the order of 70,000) than the discharge from the CO₂-rich waste gas vent (DS on the order of 200). However, when the flow rates of the respective streams are taken into consideration, the two streams have comparable TWDS values as is illustrated in Figure 15. The relationship of flow rate and TDS to TWDS is illustrated well in Figure 15 for the seven uncontrolled streams. Since the bar graphs are plotted on a log scale, the sum of the logs of the flow component and the TDS component equals the log of the TWDS. From this plot, streams can be prioritized according to flow rate, DS, or TWDS:

- Largest Stream (highest flow rate) - CO₂-rich waste gas vent.
- Most Severe Stream (highest TDS) - Naphtha storage tank vent.
- Most Environmentally Significant Stream (highest TWDS) - Ammonia stripper vent.

Figure 15 illustrates why the very large stream with a low TDS value (CO₂-rich waste gas) and the very small stream with a high TDS value (tar tank) are both environmentally significant (TWDS values are comparable).

Pollutant WDS values from the seven uncontrolled discharge streams are shown in Figure 16. This prioritization indicates that, of the pollutants discharged from the Kosovo plant, ammonia and sulfur species (H₂S and mercaptans) are the most environmentally significant (highest WDS values).

Particulates in Gaseous Streams: Particulate loadings were measured in six gaseous discharge streams. Except for the coal room vent (a dry stream), all measurements were made by the wet impinger method. In this method, particulates are collected as three fractions:

- filterable solids,
- dissolved solids, and
- tars and oils (condensable organics).

TABLE 5. DISCHARGE SEVERITY DATA FOR KOSOVO GASEOUS DISCHARGE STREAMS

PLANT SECTION: SAMPLE POINT: Component Discharge Severities	GAS PRODUCTION		RECTISOL		TAR SEPARATION		
	3.2 Low Pressure Coal Lock Vent	3.3 Gasifier Start Up Vent (Flare Feed Stream)	3.6 High Pressure Coal Lock (Flare Feed Stream)	7.1 H ₂ S-rich Waste Gas (Flare Feed Stream)	7.2 CO ₂ -rich Waste Gas Vent	13.1 Tar Tank Vent	13.3 Medium Oil Tank Vent
<u>Fixed Gases</u>							
CH ₄	1.70E01	3.20E-00	2.10E01	8.53E00	2.44E00	1.72E-01	1.50E01
CO	4.20E03	4.00E03	3.43E03	3.14E02	2.90E00	2.90E00	1.70E03
CO ₂	7.30E01	6.80E01	8.40E01	1.76E02	1.88E02	1.71E00	1.12E02
<u>Sulfur Species</u>							
H ₂ S	1.20E03	5.84E02	3.24E02	4.21E03	3.61E00	6.40E02	2.41E03
COS	6.13E-01	6.13E-01	6.70E-01	2.34E00	3.34E-01	6.13E-01	5.40E-01
CH ₃ SH	8.30E02	9.62E02	9.03E02	4.12E03	1.70E01	7.70E02	1.02E04
C ₂ H ₅ SH	5.60E02	6.10E02	5.33E02	2.00E03	1.11E01	6.10E02	5.33E03
<u>Hydrocarbons</u>							
C ₂ H ₆	4.42E-01	3.02E-01	8.50E-01	1.70E00	3.22E00	2.01E-04	6.84E-01
C ₃ H ₈	2.01E-04	-	2.01E-04	2.01E-04	2.01E-04	2.01E-04	2.01E-04
C ₄ H ₁₀	2.80E-01	1.60E-01	5.00E-01	1.30E00	5.60E-01	2.00E-02	6.00E-01
C ₄ H ₈	8.50E-01	5.10E-01	1.90E-00	5.42E00	1.70E-03	1.70E-03	4.24E00
C ₅ H ₁₂	8.41E-03	5.90E-01	8.41E-01	3.40E00	8.41E-03	8.41E-03	7.60E00
C ₆ H ₁₄	1.20E01	9.10E00	8.04E00	2.11E01	-	3.72E01	2.41E02
<u>Aromatic Species</u>							
Benzene	8.10E02	9.60E01	5.90E02	1.20E02	1.10E00	2.12E03	8.13E03
Toluene	2.20E00	7.60E-01	9.90E-01	7.90E-02	9.94E-03	9.51E00	1.40E01
Xylene and Ethylbenzene (as xylene)	7.40E-01	-	3.74E-01	-	1.40E-02	2.20E-01	1.40E00
Phenols (as Phenol)	1.20E00	1.30E02	5.10E-01	-	-	1.16E01	2.22E01
<u>Nitrogen Species</u>							
NH ₃	9.30E01	4.30E02	-	8.50E01	1.77E-01	1.00E02	7.32E-01
HCN	6.02E01	2.91E02	1.70E01	2.00E01	1.30E00	1.30E01	5.71E00
Total Stream Discharge Severity	7.88E03	7.19E03	5.92E03	1.11E04	2.32E02	4.31E03	2.82E04
Dry Gas Flow Rate (m ³ /gasifier-hr@25°C)	21.0	-	230	3600	3600	0.55	1.7
Total Weighted Discharge Severity (m ³ /gasifier-hr@25°C)	1.65E05	-	1.36E06	3.99E07	8.37E05	2.20E03	4.79E04

(Continued)

TABLE 5 (Continued). DISCHARGE SEVERITY DATA FOR GASEOUS DISCHARGE STREAMS AT KOSOVO

PLANT SECTION: SAMPLE POINT: Component Discharge Severities	TAR SEPARATION		PHENOLSOLVAN		BY-PRODUCT STORAGE		FLARE SYSTEM	
	13.6 Tar Separation Waste Gas (Flare Feed Stream)	13.7 Phenolic Water Tank Vent	14.5 Ammonia Stripper Vent	15.3 Naphtha Storage Tank Vent	20.1 Combined Gas to Flare			
<u>Fixed Gases</u>								
CH ₄	7.00E00	4.00E-01	2.00E-02	-	-	1.23E01		
CO	3.14E 02	7.00E01	1.10E02	1.70E00	-	5.43E02		
CO ₂	1.56E 02	-	-	-	-	1.76E02		
<u>Sulfur Species</u>								
H ₂ S	8.40E02	1.20E03	2.00E03	-	NF	9.84E02		
COS	6.70E-01	2.30E-01	-	-	-	1.40E00		
CH ₃ SH	4.10E03	4.12E03	6.30E02	5.10E03	-	4.91E03		
C ₂ H ₅ SH	4.91E03	1.82E04	2.80E02	2.50E04	-	4.82E02		
<u>Hydrocarbons</u>								
C ₂ H ₆	6.64E-01	4.02E-02	9.5E-03	2.01E-04	-	1.50E00		
C ₂ H ₄	2.01E-04	-	-	-	-	2.01E-04		
C ₃ H ₈	8.20E-01	4.00E-02	2.00E-02	2.00E-02	-	1.32E00		
C ₃ H ₆	7.00E00	3.40E-01	1.70E-03	1.20E00	-	5.42E00		
C ₄ H ₁₀	7.60E00	5.10E-01	8.41E-03	6.73E00	-	3.40E00		
C ₆ H ₆	1.30E02	1.81E02	1.00E-02	5.33E02	-	1.00E01		
<u>Aromatic Species</u>								
Benzene	1.02E04	1.20E04	-	4.00E04	-	6.80E02		
Toluene	1.20E01	2.30E01	-	1.90E01	-	2.12E00		
Xylene & Ethylbenzene (as xylene)	1.50E00	2.80E00	2.30E-06	5.91E-01	-	3.30E-01		
Phenols (as Phenol)	8.50E-01	2.04E-05	1.40E03	5.30E-05	-	5.30E-05		
<u>Nitrogen Species</u>								
NH ₃	7.44E02	4.63E02	1.61E04	1.10E02	-	1.00E01		
HCN	6.40E00	3.81E00	5.31E02	-	-	-		
Total Stream Discharge Severity	2.06E04	3.67E04	2.07E04	7.08E04	-	1.22E04		
Dry Gas Flow Rate (m ³ /gasifier-hr @ 25°C)	28	5.5	260	4.5	-	1330		
Total Weighted Discharge Severity (m ³ /gasifier-hr @ 25°C)	7.66E05	2.02E06	5.39E06	3.19E05	-	1.62E07		

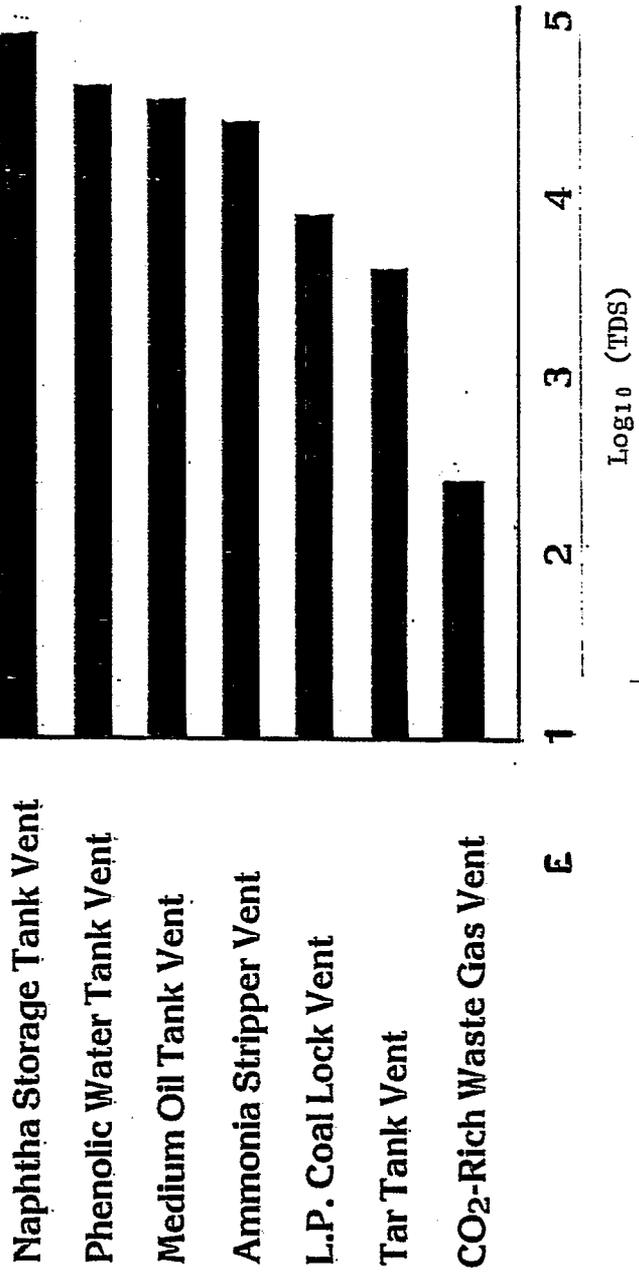


Figure 14. Key Kosovo gaseous discharge streams in order of decreasing TDS.

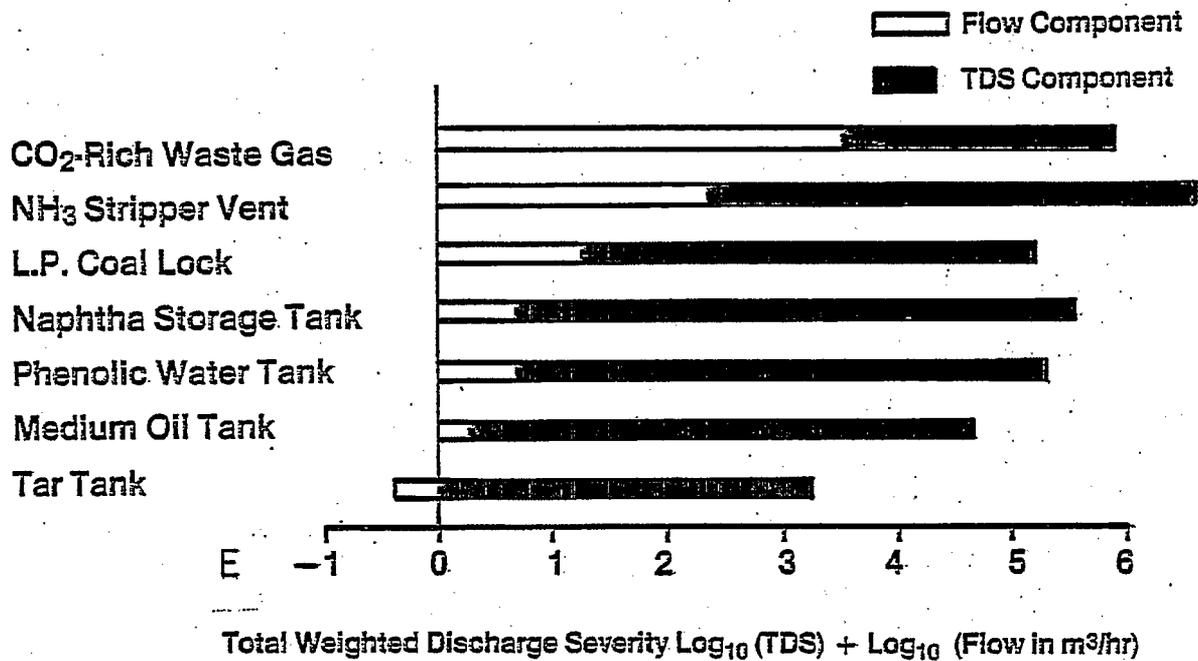
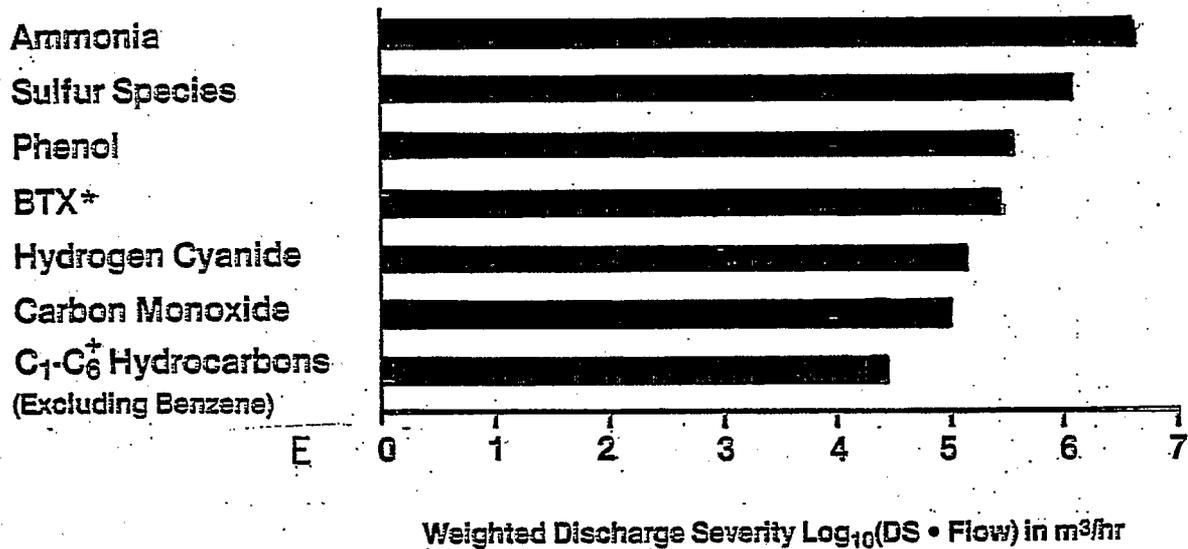


Figure 15. TWDS for key Kosovo gaseous discharge streams.



*Benzene, Toluene, and Xylenes

Figure 16. Most significant gaseous pollutants (plant-wide) in uncontrolled discharge streams.

The particulate data are shown in Table 6. This discussion will focus on the results from the impinger collections and particularly on those collected from the LP coal lock vent. This stream is emphasized because of the potential environmental significance of the particulates that it transports.

As indicated below, a major portion of the particulate catch from most gaseous streams consisted of condensed organics (tars and oils):

<u>Stream</u>	<u>Tars and Oils (Wt % in Particulates)</u>
LP coal lock vent	90
Gasifier start-up vent	95
HP coal lock vent	69
Tar separation waste gases	72
Combined gas to flare	76

Analytical results are not yet available from these collections; however, by-product analysis data can be used to make judgments about the significance of these particulates. For example, the LP coal lock vent discharge contained $8.1E06 \mu\text{g}/\text{m}^3$ of particulates of which $7.3E06 \mu\text{g}/\text{m}^3$ were tars and oils. In order to provide an estimate of the PNA content of the particulates in this stream, it was assumed that the PNA concentrations in the condensed organic fraction of the particulates (tars and oils) were the same as the PNA concentrations in the by-product tars and oils. Table 7 shows the concentrations of several of the most severe PNA's contained in the light tar and the medium oil. Using the following data:

<u>LP Coal Lock Vent</u>	<u>Concentration $\mu\text{g}/\text{m}^3$</u>	<u>Mass Flow g/hr</u>
Total Particulate	8.1E06	1.7E08
Tars and Oils in Particulate	7.3E06	1.5E08
Benzo(a)pyrene based on BaP in tar	1.5E03	3.2E04
Benzo(a)pyrene based on BaP in medium oil	0.5E03	1.0E04

the calculated concentration level of benzo(a)pyrene in the LP coal lock vent discharge is in the range of 500 to $1,500 \mu\text{g}/\text{m}^3$. This level of PNA's will increase the TWDS of the LP coal lock vent significantly. The effects of PNA's upon the TWDS values of key streams (using the average PNA content of light tar and medium oil) are shown in Figure 17. Note that the increase in TDS (and TWDS) by the inclusion of the PNA data elevates the LP coal lock vent to the same order of magnitude as the ammonia stripper vent and identifies it as the second most environmentally significant of the uncontrolled discharge streams at Kosovo (excluding flare feed streams - H_2S -rich waste gas, and HP coal lock vent).

TABLE 6. PARTICULATE CONCENTRATION DATA FOR KOSOVO GASEOUS STREAMS

STREAM TYPE:	DISCHARGE STREAMS			FLARE FEED STREAMS		
	2.2	3.2	3.3	3.6	13.6	20.1
SAMPLE POINT:		Low	Gasifier	High		
	Coal	Pressure	Start-up	Pressure	Tar	Combined
	Room Vent	Coal	Vent	Coal	Separation	Gases
		Lock Vent		Lock Vent	Waste Gas	to Flare
Dry Gas Flow Rate (m ³ /gasifier-hr @ 25°C)	7200	21	*	230	28	1330
Total Particulate. (mg/m ³ @ 25°C)	98	8100	9450	960	920	410
Condensed Organics (Tars and Oils)	**	7300	8980	660	660	310
Dissolved Solids	**	650	400	240	230	54
Filtered Solids	**	220	61	61	29	47

* - Variable Flow Rate.

** - Dry Stream; Analysis Not Applicable.

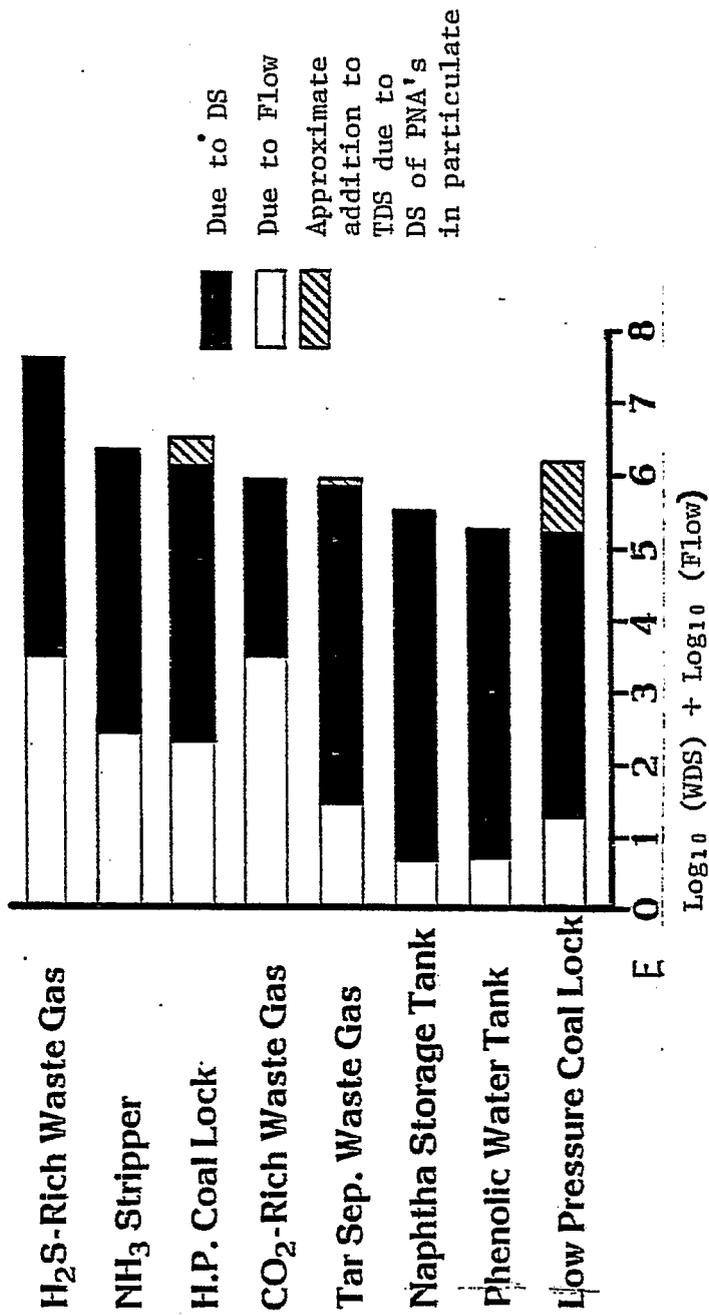


Figure 17. Total weighted discharge severity for key Kosovo gaseous streams.

TABLE 7. PNA'S IN KOSOVO LIGHT TAR AND MEDIUM OIL (µg/g)

Compound	Light Tar	Medium Oil
7,12-Dimethylbenz(a)anthracene	1,100	62
Benz(a)anthracene	490	160
Benzo(b)fluorene	310	120
Benzo(a)pyrene	210	68
Dibenzo(a)anthracene	23	7
3-methylcholanthrene	26	NF
252 Group	950*	280*

*Benzo(a)pyrene concentration = 24 Percent

Aqueous Streams: The two major aqueous waste streams in the Kosovo Gasification Plant are:

- Gasification section (quenched ash) wastewater, which is a combination of:
 - ash quench water,
 - coal bunker vent gas scrubber blowdown, and
 - ash lock vent gas scrubber blowdown; and
- Phenosolvan wastewater.

Water quality parameters and concentration data for anions and polynuclear aromatics (PNA's) are presented in Table 8.

Gasification section wastewaters contain a variety of pollutants including components leached from the ash or scrubbed from the coal bunker or ash lock vents and components which enter the system along with the ash quench and scrubber makeup water streams. The gasification wastewater has a high pH (due to the alkaline nature of the Kosovo ash) and significant concentrations of dissolved and suspended solids. Other components present (e.g., phenols, NH₃) indicate that at least a portion of the makeup water used in these systems was derived from process condensate. The presence of phenols and NH₃ in the ash lock vent gases tends to confirm this hypothesis since it would not be expected that phenols would be present in any of the other process streams entering the Kosovo ash lock system. The sulfur species detected in these wastewaters were present primarily in the form of sulfate.

TABLE 8. KOSOVO AQUEOUS STREAM DATA

PLANT SECTION: SAMPLE POINT:	GAS PRODUCTION		PHENOSOLVAN	
	12.3 Quenched Ash Wastewater	14.0 Phenolic Water	14.11 Phenosolvan Wastewater	
Design Flow Rate (m ³ /gasifier-hr)	3.0	>13	13	
pH	0.1 - 12.1	9.2	9.6	
Temperature (°C)	-	60	33	
<u>Solids Analysis (mg/L)</u>				
Total Solids	10,900	2,320	1,350	
Suspended Solids	8,760	150	1,160	
Dissolved Solids	2,100	1,170	190	
<u>Water Quality Parameters</u>				
COD (as mg O ₂ /L)	1,460	18,900	7,910	
Permanganate (mg/L)	8,060	14.2	4,040	
BOD ₅ (as mg O ₂ /L)	90	9,030	2,350	
<u>Aqueous Composition Data (mg/L)</u>				
TOC	-	4,970	1,470	
Total Phenols	-	2,120	230	
Volatile Phenols	0.17	-	130	
Free Ammonia	Tr	3,510	Tr	
Fixed Ammonia	1.9	250	205	
Cyanide	0.01	<1	0.019	
Nitrites	0.40	-	Tr	
Nitrates	4.8	<1	11.4	
Pyridines	-	142	-	
Chlorides	28	-	60	
Fluorides	0.91	-	Tr	
Total Sulfur	-	-	84	
Sulfites	Tr	-	-	
Sulfates	495	-	110	
Sulfides	Tr	-	-	
Thiocyanates	0.026	<75	<75	
Thiosulfates	Tr	-	Tr	
<u>PNA Analysis (mg/L)</u>				
Benz(a)anthracene	-	0.92	NF	
7,12-dimethylbenz(a)anthracene	-	0.23	NF	
Benzo(a)fluoroanthrene	-	0.68	NF	
Benzo(a)pyrene	-	0.19	NF	
3-methylcholanthrene	-	<0.004	NF	
Dibenz(a,h)anthracene	-	0.02	NF	
252 Group (as BaP)	-	1.26	0.19	

Tr = Trace
 NF = Not Found
 - = Not Analyzed

The Phenosolvan wastewater stream data presented in Table 8 indicates that a significant reduction in the organic pollutant loading is achieved in the Phenosolvan section. As expected, the phenol level was reduced significantly (by approximately 90 percent) by treatment in this section. It should also be noted that the concentrations of several significant PNA's were reduced to undetectable levels. The fate of the PNA's was not confirmed since no sample of the by-product phenol was obtained. Presumably this by-product stream was the vehicle by which the PNA's present in the inlet water left the unit.

Although a significant portion of the phenolic material was removed from the inlet water by the Phenosolvan unit, a significant amount of organic matter remained in the discharge. This assertion is supported by the following data from Table 8:

- o TOC in outlet water - 1,470 mg/L.
- o Phenols in outlet water - 230 mg/L.
- o Volatile phenols in outlet water - 130 mg/L.

The level of volatile phenols in the outlet water significantly exceeds the DMEG for aqueous discharges (DS Total Phenol = $2.6E04$). Since the composition of the unextracted TOC has not yet been determined, no realistic assessment has been made of the characteristics of the bulk of this material. However, in laboratory tests, a relatively large fraction of the inlet TOC (30 percent) remains in the wastewater after extraction in the laboratory with diethyl ether and methylene chloride at pH values of 1 and 12 (Ref. 6).

Solid Streams: Solid phase analytical results are summarized in Table 9. The data shown for the dried coal are based upon an average of approximately 40 different spot samples taken over a several month period. The ash values shown are averages of approximately 20 different samples taken over the same period.

On the average, very high carbon conversion levels were achieved (approximately 99 percent) in the Kosovo Lurgi gasifiers. This is expected for a highly reactive coal such as the lignite being processed at Kosovo. The ash from the gasifiers (after quenching) has a positive heating value, but would not be classified as ignitable and, therefore, would not require special handling in accordance with applicable RCRA criteria for ignitable wastes.

Heavy tar is another solid waste stream produced in the Kosovo gasification facility. Because of the high heating value of this stream as well as the likely presence of highly toxic organic materials, such as phenols and PNA's, this stream would probably be consumed in an on-site steam/power boiler or incinerator in the U.S. At Kosovo, this stream is landfilled.

TABLE 9. KOSOVO SOLID STREAM DATA

PLANT SECTION:	GAS PRODUCTION			TAR SEPARATION
	2.0	12.1	12.2	13.8
SAMPLE POINT:	Dried	Dry	Wet	
	Coal	Gasifier	Gasifier	Heavy Tar
		Ash	Ash	
<u>Ultimate Analysis (wt. %)</u>				
Moisture	20	2.1	not analyzed	(moisture free analysis)
Ash	14	94		6.6
Carbon	45	1.7		56.0
Sulfur	0.89	0.15		0.33
Hydrogen	3.5	0.25		7.6
Nitrogen	1.1	0.03		0.87
Oxygen	16	2.3		28.6
Chlorine	0.01	0.04		-
<u>Proximate Analysis (wt. %)</u>				
Moisture	24	2.1	34	not analyzed
Ash	14	94	59	
Volatile	36	6.5	6.0	
Fixed Carbon	27	-	1.3	
CO ₂	2.3	-	5.7	
Total Sulfur	1.2	0.15	0.09	
Free Sulfur	0.35	-	0.02	
Hydrogen	3.4	-	0.38	
Nitrogen/Oxygen	17	-	4.2	
Chlorine	0.01	-	-	
<u>Heating Values (kcal/kg)</u>				
Proximate HHV	3900	27.8	-	-
Proximate LHV	3700	-	-	-
Ultimate HHV	4100	-	-	6340
Specific Gravity	0.538	-	-	-

- = No Data Available

Product and By-Product Streams: The compositions of the products and by-products will affect their final uses and their resulting environmental impacts. Data for the crude and clean product gases are presented in Tables 2 and 3. Comparing the compositions of these streams indicates that the Rectisol unit has removed almost all of the acid gases (CO₂, H₂S, and NH₃) from the product gas.

Chemical analysis data for Kosovo by-products are shown in Table 10. Table 11 presents a comparison of some ultimate analysis data for the feed coal, heavy tar, and liquid by-products. Table 11 indicates that the sulfur contents of the liquid by-products become progressively higher in the "lighter" fractions. In contrast, the trend in the nitrogen values is reversed. These data indicate that heavy hydrocarbon by-products similar to those generated at Kosovo, could be used to satisfy some of the on-site fuel needs (e.g., for steam generation) of a U.S. Lurgi plant without an FGD unit if SO₂ emissions standards consistent with those for large fossil fuel fired steam generators were applicable.

Trace Elements: The trace element concentrations in a number of the plant's key feed, product, by-product, and waste streams were determined to establish whether any of these streams contained elements at concentration levels of concern. In addition, trace element leachabilities were evaluated for the gasifier ash to determine whether this material would be classified as an RCRA hazardous waste. Trace element concentration data are summarized in Tables 12 through 14. These data include both SSMS results, which provide a semiquantitative estimate of trace element concentrations on a broad screening basis, and AA results, which provide more accurate estimates of the concentrations of 15 selected elements. The elements selected for AA analysis were those which were indicated to be present at levels of potential concern by the SSMS results or through previous experience with gasification process waste streams.

The levels of trace elements in the discharge from the LP Coal Lock Vent shown in Table 13 are of particular interest. The concentration of arsenic (1,700 µg/m³) is 850 times its DMEG. Other elements in the LP Coal Lock Vent whose concentration exceeds their DMEG values are chromium (DS = 2.7E02), nickel (DS = 7.8E00), cadmium (DS = 2.7E00), beryllium (DS = 2.0E00), and mercury (DS = 1.1E00). With the possible exception of arsenic, these elements are probably being transported in the coal dust which is contained in the discharge. A significant level of mercury was found in the Phenolic water (Table 13). This value (0.14 mg/L) is 14 times its DMEG for aqueous discharge.

The completion of trace element balances were outside the scope of the Phase II effort. However, rough calculations of trace element distributions were performed to provide some insight into the behavior of trace elements in a Lurgi gasification system. These results are included in Table 13. Most of the recovered trace elements which entered the gasifier with the

TABLE 10. CHEMICAL AND PHYSICAL DATA FOR KOSOVO BY-PRODUCTS

By-Product:	Light Tar	Medium Oil	Naphtha
Specific Gravity (g/cm ³)	1.06	0.97	0.85
Higher Heating Value (kcal/kg)	8910	9500	9940
Lower Heating Value (kcal/kg)	8280	9400	8925
Ultimate Analysis (wt %)			
Carbon	82	82	86
Hydrogen	8.4	8.9	9.9
Nitrogen	1.3	1.00	0.18
Sulfur	0.49	0.83	2.2
Ash	0.22	0.03	---
Chlorine	---	---	---
Oxygen (difference)	7.8	8.2	2.2
Moisture Content (wt %)	1.1	0.8	---
PNA Analysis (mg/kg)			
Benz(a)anthracene	490	160	NF
7,12-dimethylbenz(a)anthracene	1100	62	NF
Benzo(b)fluoroanthrene	310	120	NF
Benzo(a)pyrene	210	68	NF
3-methylcholanthrene	26	NF	NF
Dibenz(a,h)anthracene	23	6.6	NF
252 Group (as BaP)	950	280	NF

NF = not found

- = no data available

TABLE 11. COMPARISON OF ULTIMATE ANALYSIS DATA FOR
SELECTED KOSOVO SOLIDS AND BY-PRODUCTS

Component	Dried Coal	Heavy Tar*	Light Tar	Medium Oil	Naphtha
C	45	56	82	82	86
H	3.5	7.6	8.4	8.9	9.9
N	1.1	0.87	1.3	1.0	0.2
S	0.89	0.33	0.49	0.83	2.2
Ash	14	6.6	0.22	0.03	-
O	16	29	7.8	8.2	2.1
Moisture	20	-	1.1	0.8	-
HHV**	16.3	26.5	37.3	40.0	41.6
SO ₂ ***	1090	250	260	420	1060

* Moisture Free Analysis

** Higher Heating Value expressed as KJ/g.

*** Expressed as ng/J assuming 100% conversion of S to SO₂.

NOTE-SO₂ Emission Limitations for Large Fossil Fuel Fired Steam
Generators (40 CFR 60D):

Coal and Solid Fuels - 520 ng/J (1.2 lb/10⁶ Btu)

Liquid Fuels - 340 ng/J (0.8 lb/10⁶ Btu)

TABLE 12. A SURVEY OF TRACE ELEMENTS IN KOSOVO STREAMS ANALYZED BY SSMS

SAMPLE POINT:	2.0	12.1	12.2	15.2	14.11
Trace Element	Dried Coal (mg/kg)	Dry Gasifier Ash (mg/kg)	Wet Gasifier Ash (mg/kg)	Medium Oil (mg/L)	Phenolsolvan Wastewater (mg/L)
Ag	NF	NF	NF	NF	NF
Al	>1000	>1000	—	0.09	0.1
As	2	62	—	0.4	0.02
B	21	190	630	0.07	0.1
Ba	110	>1000	1670	0.09	0.05
Be	NF	4	NF	NF	NF
Bi	NF	NF	NF	0.01	NF
Br	2	17	—	NF	0.009
Ca	>1000	>1000	—	5	6
Cd	0.4	NF	1.2	0.01	NF
Ce	3	29	—	0.003	NF
Cl	32	45	—	0.008	0.08
Co	0.4	4	15	0.004	0.003
Cr	11	2	240	0.02	0.005
Cs	0.1	3	—	NF	NF
Cu	8	27	76	0.5	0.03
Dy	NF	2	—	NF	NF
Er	NF	0.5	—	NF	NF
Eu	<0.3	1	—	NF	NF
F	2	=710	—	=0.03	=0.02
Fe	>1000	>1000	—	2	0.5
Ga	2	17	37	NF	NF
Gd	NF	2	—	NF	NF
Ge	0.1	0.5	—	NF	0.03
Ho	NF	0.6	—	NF	NF
I	0.5	2	—	NF	0.02
K	>1000	>1000	—	0.3	1
La	2	21	NF	NF	NF
Li	1	28	—	0.001	0.003
Ln	NF	NF	—	<0.004	NF
Mg	>1000	>1000	—	>10	2
Mn	230	>1000	2700	0.02	0.01
Mo	6	6	30	0.005	NF
Na	>1000	>1000	—	0.1	4
Nb	3	10	—	NF	NF
Nd	0.8	10	—	NF	NF
Ni	23	180	180	0.03	0.08
Np	NF	10	—	NF	NF
P	780	>1000	—	0.1	0.08
Pb	2	9	27	0.09	0.07
Pr	0.9	5	—	NF	NF
Rb	5	35	—	NF	NF
S	>1000	420	—	0.6	>10
Sb	NF	2	NF	NF	NF
Sc	1	12	20	<0.001	<0.005
Se	0.6	< 1	—	0.02	0.03
Si	>1000	>1000	—	2	1
Sm	1	9	—	NF	NF
Sr	0.5	0.8	NF	0.008	0.009
Sr	91	320	4100	0.008	0.02
Tb	NF	0.4	—	NF	NF
Te	0.4	< 1	—	NF	NF
Th	< 2	9	—	<0.02	<0.04
Tl	660	>1000	2300	0.09	0.02
U	< 2	2	—	0.07	<0.03
V	8	67	140	0.01	0.003
Y	2	17	39	0.003	<0.03
Zn	1	33	56	0.3	0.7
Zr	6	33	180	<0.003	0.02

NF = not found
 — = no data available

TABLE 13. TRACE ELEMENTS IN KEY KOSOVO STREAMS
ANALYZED BY ATOMIC ABSORPTION SPECTROMETRY

Trace Element	SOLIDS					
	2.0 Dried Coal		12.1 Dry Gasifier Ash		13.8 Heavy Tar	
	Concentration (mg/Kg)	Mass Flow (g/hr)	Concentration (mg/Kg)	Mass Flow (g/hr)	Concentration (mg/Kg)	Mass Flow (g/hr)
As	59	940	75	200	16	1.6
Be	1.0	16	2.5	6.8	0.29	0.029*
Cd	4.0	64	69	190	3.7	0.37
Ce	3.4	54	17	46	1.5	0.15
Cr	87	1400	180	490	30	3.0
Cu	43	690	40	110	6.0	0.60
Hg	0.74	12	0.30	0.82	0.64	0.064
Mo	6.4	100	8.9	24	0.85	0.085
Ni	150	2400	320	860	21	2.1
Pb	8.2	130	52	140	64	6.4
Sb	NF	NF	NF	NF	3.9	0.39
Se	20	320	24	65	2.6	0.26
Sr	190	3000	370	1000	41	4.1
Tl	NF	NF	NF	NF	NF	NF
V	14	220	100	270	5.7	0.57
Zn	140	2200	2.1	5.7	98	9.8

NF = below detection limits

(Continued)

TABLE 13 (Continued). TRACE ELEMENTS IN KEY KOSOVO STREAMS
ANALYZED BY ATOMIC ABSORPTION SPECTROMETRY

SAMPLE POINT:	LIQUID BY-PRODUCT						WATER	
	15.1		15.2		15.3		14.0	
	Light Tar Concentration (mg/kg)	Mass Flow (R/hr)	Medium Oil Concentration (mg/kg)	Mass Flow (R/hr)	Naphtha Concentration (mg/kg)	Mass Flow (R/hr)	Phenolvan Concentration (mg/L)	Inlet Water Mass Flow (R/hr)
As	1.7E+01	6.8E 00	2.0E 00	5.0E-01	5.5E-01	8.5E 02	1.0E-01	1.3E 00
Be	9.0E-02	3.6E-02	NF	NF	1.8E-03	2.7E-04	NF	NF
Cd	6.6E-01	2.64E-01	7.7E-02	1.9E-02	8.0E-04	1.2E-04	1.4E-03	1.8E-02
Co	NF	NF	2.0E-01	4.5E-02	5.0E-03	7.7E-04	NF	NF
Cr	3.0E 00	1.2E 00	4.0E 00	1.0E 00	1.0E 01	1.5E 02	2.3E-02	3.0E-01
Cu	1.6E+01	6.4E 00	1.1E 00	2.8E-01	1.5E-01	2.4E-02	1.1E-02	1.4E-01
Hg	NF	NF	2.0E-01	5.2E-02	1.3E-01	2.0E-02	1.4E-01	8.2E 00
Mo	NF	NF	1.9E-01	4.8E-02	9.0E-03	1.4E-03	NF	NF
Ni	9.0E-00	3.6E 00	NF	NF	1.4E-01	2.1E-02	1.3E-02	1.7E-01
Pb	6.8E 00	2.7E 00	1.4E 00	3.5E-01	6.4E-02	9.8E-03	1.4E-02	1.8E-01
Sb	NF	NF	NF	NF	1.2E-02	1.9E-03	NF	NF
Se	1.6E 00	6.4E-01	1.9E 00	4.8E-01	7.3E-01	1.1E-01	5.0E-02	6.5E-01
Sr	2.0E+01	8.0E 00	8.6E 00	2.2E 00	NF	NF	1.0E-01	1.3E 00
Tl	NF	NF	NF	NF	NF	NF	NF	NF
V	NF	NF	NF	NF	NF	NF	NF	NF
Zn	2.8E+01	1.1E+01	1.5E+01	3.8E 00	1.4E-01	2.1E-02	2.8E-01	3.6E 00

NF = Not Found (below detection limits)

(Continued)

TABLE 13 (Continued). TRACE ELEMENTS IN KEY KOSOVO STREAMS
ANALYZED BY ATOMIC ABSORPTION SPECTROMETRY

Trace Element	GASES				Percentage of Amount Found in Dried Coal Accounted For in the Streams Listed in this Table
	3.2 Low Pressure Coal Lock Vent		20.1		
	Concentration (mg/L)	Mass Flow (g/hr)	Concentration (mg/L)	Mass Flow (g/hr)	
As	1.7E-03	3.6E-02	1.9E-06	2.5E-03	22
Be	4.0E-06	8.4E-05	NF	NF	43
Cd	2.7E-05	5.7E-04	2.4E-07	3.2E-04	298
Ce	4.9E-06	1.0E-04	1.7E-07	2.3E-04	85
Cr	2.7E-04	5.7E-03	NF	NF	35
Cu	1.8E-04	3.8E-03	5.8E-06	7.7E-03	17
Hg	5.3E-05	1.1E-03	NF	NF	23
Mo	4.5E-05	9.5E-04	NF	NF	24
Ni	1.2E-04	2.5E-03	7.5E-06	1.0E-02	36
Pb	7.2E-05	1.5E-03	1.0E-06	1.3E-03	115
Sb	NF	NF	NF	NF	-
Se	NQ	NQ	7.2E-06	9.6E-03	21
Sr	6.1E-04	1.3E-02	4.4E-06	5.9E-03	34
Tl	NF	NF	NF	NF	-
V	9.0E-06	1.9E-04	NF	NF	123
Zn	1.6E-03	3.4E-02	3.1E-05	4.1E-02	1.5

NF = below detection limits
NQ = present but not quantifiable

TABLE 14. TRACE ELEMENTS IN KOSOVO ASH LEACHATES ANALYZED BY SSMS

Trace Element	RCRA LEACHATE (Acid)		ASTM LEACHATE (Neutral)	
	Composition (mg/L)	D.S. Value	Composition (mg/L)	D.S. Value
Al	0.01	1.30E-04	2	2.50E-02
As	<0.004	<1.60E02	0.01	4.00E-02
B	0.09	1.91E-03	0.1	2.12E-03
Ba	3	6.00E-01	0.05	1.00E-02
Be	NF	-	NF	-
Bi	NF	-	NF	-
Br	<0.008	0.0	0.4	0.0
Cd	NF	-	NF	-
Ce	NF	-	NF	-
Cl	0.05	3.84E-05	0.7	5.40E-04
Co	<0.001	<1.33E-03	<0.007	<9.33E-03
Cr	0.3	1.20E 00	0.5	2.00E 00
Cs	0.004	3.33E-06	NF	-
Cu	0.01	2.00E-03	0.03	6.00E-03
Dy	NF	-	NF	-
Er	NF	-	NF	-
Eu	NF	-	NF	-
F	0.8	2.10E-02	7	1.84E-01
Fe	10	6.70E 00	0.1	6.70E-02
Ga	NF	-	0.02	2.70E-04
Gd	NF	-	NF	-
Ge	<0.001	<1.20E-04	0.01	1.20E-03
Ho	NF	-	NF	-
I	NF	-	0.005	0.0
La	NF	-	NF	-
Li	0.03	9.10E-02	0.07	2.12E-01
Mg	2	2.22E-02	NF	-
Mn	0.001	4.00E-03	0.02	8.70E-02
Mo	0.1	1.33E-03	0.05	6.70E-04
Na	>2	>2.50E-03	NF	-
Nb	NF	-	0.006	1.81E-05
Ni	0.04	1.73E-01	0.02	8.70E-02
Np	NF	-	NF	-
P	0.02	1.33E-02	0.2	1.33E-02
Pb	0.008	3.20E-02	0.07	2.80E-01
Pr	NF	-	NF	-
Rb	0.04	2.22E-05	0.09	5.00E-05
S	>6	0.0	NF	-
Sb	<0.002	<2.70E-04	NF	-
Sc	<0.001	<1.30E-06	<0.003	<3.74E-06
Se	0.01	2.00E-01	0.007	1.40E-01
Si	8	5.33E-02	7	4.70E02
Sm	NF	-	NF	-
Sr	<0.001	0.0	NF	-
Sr	4	8.70E-02	0.3	6.52E-03
Tb	NF	-	NF	-
Te	NF	-	NF	-
Th	<0.008	<1.30E-03	<0.04	<6.34E-03
Ti	0.01	1.11E-04	0.02	2.22E-04
U	<0.007	<1.20E-04	<0.03	<5.00E-04
V	0.07	2.80E-02	0.004	1.60E-03
Y	0.008	5.33E-04	NF	-
Zn	0.05	2.00E-03	0.08	3.20E-03
Zr	<0.006	<8.00E-05	NF	-

NF = Not Found

feed coal were found in the gasifier ash. The recovery values shown are based upon the use of plant design flow data for the feed, by-product, and waste streams considered. The only trace elements found in any significant concentrations in streams other than the dry gasifier ash are antimony and lead (in the heavy tar), and copper (in the by-product naphtha). Very poor calculated recoveries were obtained for most of the trace elements (on the order of 20 to 40 percent). Zinc recoveries were particularly poor, with less than 5 percent of the coal input zinc accounted for. These poor recovery values are probably the result of several factors including: actual stream flow measurements were not obtained for many of the streams, time phased sampling was not attempted, and a statistically significant data base was not obtained.

The largest solid waste stream generated in a Lurgi gasification plant is quenched gasifier ash. In order to determine the leaching characteristics of this material and to predict its classification under RCRA guidelines, a series of leaching studies were conducted. The results of these tests, which are reported in Table 14, indicate that no trace elements were present in the ash leachate in sufficient concentrations which would cause this material to be classified as hazardous.

A Comparison of Discharge Streams Plant Wide: TWDS values for all major discharge streams - aqueous, gaseous, and solid - are shown in Figure 18. Attention is called to the flow rate units: liters per gasifier hour - aqueous streams; cubic meters per gasifier hour - gaseous streams; and kilograms per gasifier hour - solid streams. These are the units of the DMEGS used. Figure 18 shows the streams prioritized in each discharge medium according to their TWDS values.

Mass Balances for Key Species: Figure 19 summarizes the results of mass balance calculations for carbon, sulfur, and nitrogen species in the Kosovo plant. The amount of carbon found in key Kosovo solid, liquid, and gaseous streams, expressed as a percentage of the carbon entering the gasifier in the dried coal indicates that the majority of the carbon entering the system with the dried coal leaves in gaseous streams. It is significant that there is almost as much carbon (mainly as CO₂) in the H₂S-rich waste gas flare feed stream (88 vol. % CO₂) as there is in the CO₂-rich waste gas stream (94 vol. % CO₂). Small quantities of the inlet carbon ends up in the gasifier ash (0.7%), aqueous wastewaters (0.3%), and the remaining gaseous discharge streams (excluding the CO₂-rich waste gas stream).

Most of the sulfur leaves the plant in the H₂S-rich waste gas stream. Of the remaining sulfur, the majority appears in the by-products - naphtha (1.5%), medium oil (1.1%), and light tar (1.1%) - and the ammonia stripper vent (3.7%). A small percentage is discharged in the ash (1.3%), heavy tar (0.2%), and aqueous wastewaters (0.9%). The relatively poor accountability of the sulfur balance is probably due to variations in the input coal sulfur content, variations in flow rate measurements, and the lack of time-phased sampling.

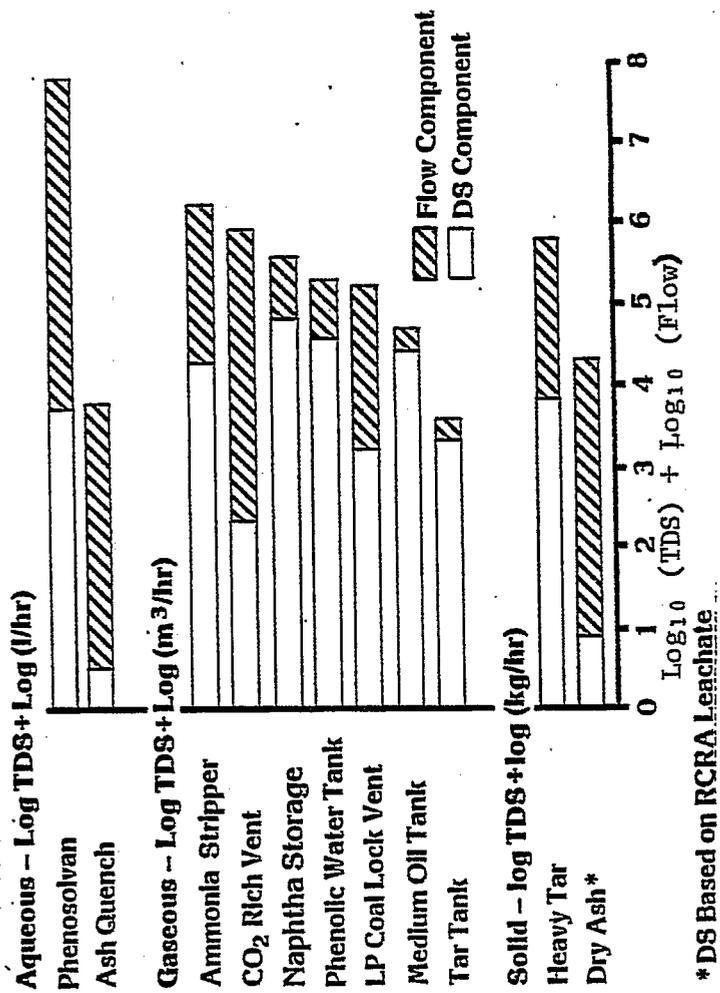


Figure 18. Total weighted discharge severity of uncontrolled Kosovo discharge streams.

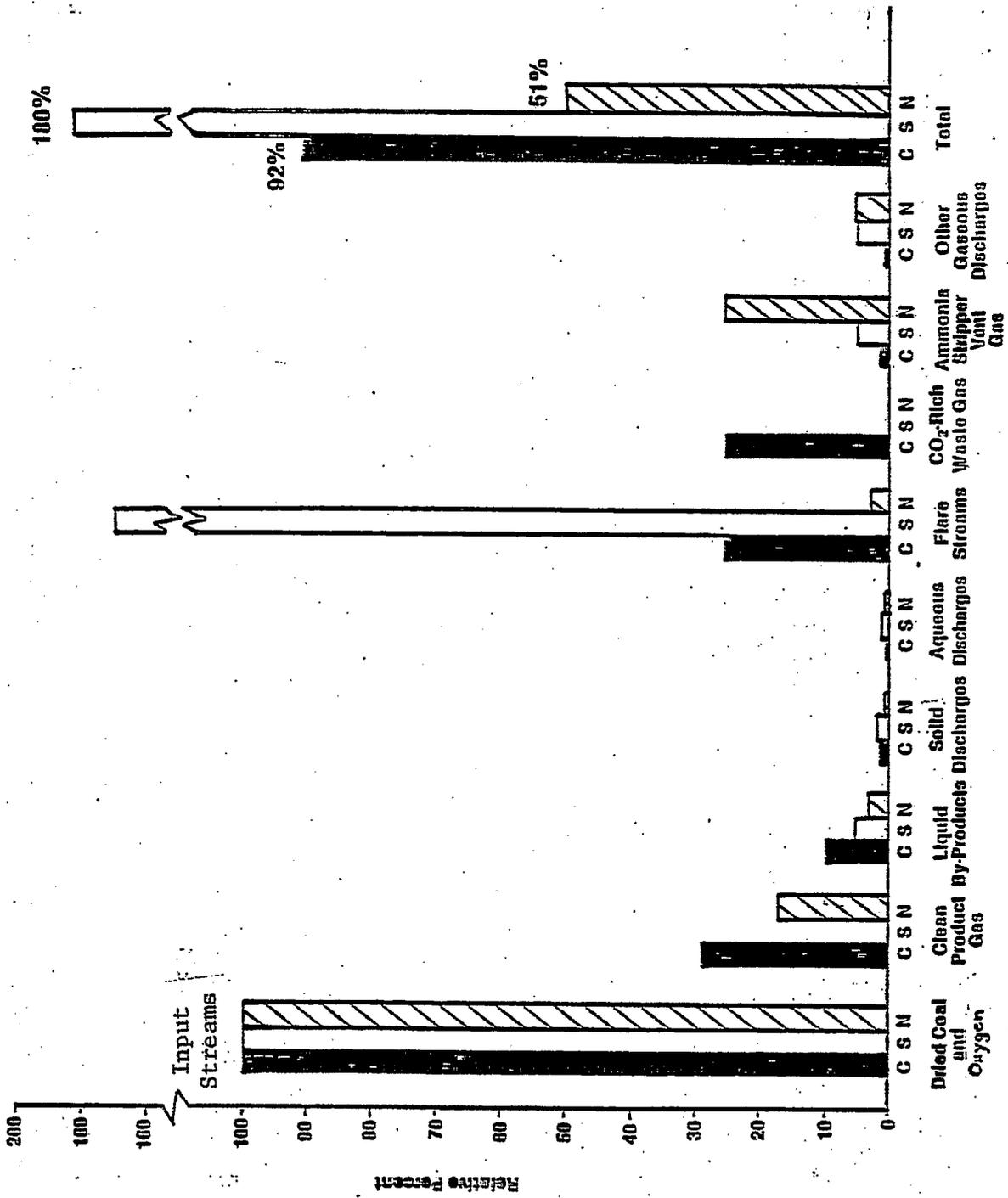


Figure 19. Summary of Carbon, Sulfur, and Nitrogen Mass Balance Results for the Kosovo Plant

Nitrogen entering in the dried coal and oxygen feed streams is converted primarily to ammonia, hydrogen cyanide, a number of organic nitrogen compounds, and N_2 . Most of this nitrogen appears in gaseous discharge streams. A large percentage is discharged in the ammonia stripper vent (which contains 41.8 vol. % NH_3 on a dry basis).

Summary and Conclusions: The Kosovo Phase II data has corroborated substantially the indications from the Phase I test results and has also added significant new information about the aqueous and solid discharges from the Kosovo plant. It has also provided significant information about trace pollutants, both organic and inorganic. The following are some of the more salient findings:

- All process units studied have a significant potential for polluting the environment.
- The highest priority streams in each medium are:
 - H_2S -rich waste gas,
 - Phenosolvan wastewater, and
 - heavy tar.
- The CO_2 -rich waste gas may contain significant levels of nonmethane hydrocarbons and mercaptans.
- PNA's make a significant contribution to the discharge severity (DS) of tar-bearing streams (e.g., LP Coal Lock vent and heavy tar).

The severity of the coal lock vent discharge is increased significantly by the contribution of PNA's in the tar aerosols.

- Benzo(a)pyrene and 7,12-Dimethylbenz(a)anthracene are the two most significant (highest D.S. values) pollutants in Kosovo tar.
- Trace elements appear to be less significant than trace organics as pollutants in organic containing streams.
- Ash leaching problems appear to be of low concern. Concentrations of all trace elements were at least an order of magnitude lower in the RCRA leach test results than those levels specified in the EP toxicity test.
- After Phenosolvan treatment, the treated process condensate contained undetectable levels of PNA's, but high residual organic material concentrations and high solids concentrations.

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INEP - S. Kapor

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AMBIENT AIR DOWNWIND OF THE KOSOVO GASIFICATION COMPLEX:
A COMPENDIUM

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ABSTRACT

In an attempt to obtain environmental impact data for a commercial scale coal gasification facility the Environmental Sciences Research Laboratory-RTP (ESRL-RTP) Aerosol Research Branch, conducted a 16-d continuous ambient air study in the Region Kosovo, Yugoslavia. Five sampling sites were established around and ≈2 km outside the fence line of the Kosovo medium BTU Lurgi gasification complex.

Organics in total particulate matter; total and fine particle mass, inorganics, and elemental species; trace metal in size-fractionated particles; and vapor phase organics were determined. Physical and chemical analyses were carried out on particulate matter using gravimetric analysis, ion chromatography, and scanning electron microscopy. Elemental analysis was done using the inductively coupled argon plasma emission technique, proton-induced X-ray emission, and combustion analysis. Both particle catches and vapors trapped on Tenax resins were subjected to organic analysis using gas chromatography. The chromatographic fractions were identified and quantified using flame ionization detection, sulfur and nitrogen specific detectors, and mass spectrometry. A comprehensive quality assurance and quality control program was implemented to ensure the validity of the samples collected and analyzed.

A number of United States and Yugoslavian laboratories participated in the ambient air sampling and analysis phases of this study. This paper is a compendium of the major results and conclusions obtained by the participant laboratories.

INTRODUCTION

The Environmental Sciences Research Laboratory-RTP (ESRL-RTP) Aerosol Research Branch conducted an ambient air study near the commercial medium BTU Lurgi coal gasification plant located in the Kosovo Region of Yugoslavia. The objectives of the study were to characterize the ambient aerosols and volatile organic pollutants downwind of the Kosovo complex, to correlate specific pollutants to the gasification plants, and to evaluate the impact of the Lurgi gasification process on the air quality downwind of the Kosovo complex. This study represents Phase III of the Industrial Environmental Research Laboratory-RTP (IERL-RTP) multimedia assessment program at the Kosovo complex.

The Kosovo Industrial Complex (Kombinat Kosovo) consists of a coal processing facility, a coal gasification plant (six Lurgi gasifiers), a fertilizer plant, a steam plant, a 790 MW lignite burning power plant, and a gasification process by-product storage area. Major activities outside the complex are lignite coal mining, lignite ash disposal (piles), and farming. Forty-eight trains (27 diesel and 21 steam) pass along the southern edge of the Kosovo complex daily. Several improved analytical techniques and procedures were developed by Radian Corporation^{1,2,3} and by the Oak Ridge National Laboratory^{4,5,6} in anticipation of difficulty in differentiating the complex sources in the area.

SAMPLING STRATEGY

Five sampling sites were located around and ≈ 2 km outside the fence line of the Kosovo complex. Using the stack of the steam plant as a center reference point and Yugoslav wind direction data for the month of May (average winds from Northeast), the sampling stations were deployed in a manner indicative of prevailing upwind, downwind, and crosswind locations (see Figure 1).

Each sampling station was equipped to collect total suspended particulate (TSP) matter for organic analysis; total ($<15 \mu\text{m}$) and fine ($<2.0 \mu\text{m}$) particles for gravimetric, inorganic, and elemental analysis; size-fractionated particles for elemental analysis; and organic vapors. The sample collection equipment at each station consisted of:

1. one 24 h HiVol sampler ($1.1 \text{ m}^3/\text{min}$) using a 265 mm diameter Gelman Microquartz filter and a HiVol motor exhaust filtration system⁷;
2. one 24 h Tenax vapor trap system⁸ (4 l/min) which taps into the post-filter section of the HiVol sampling head;
3. one 6 h LoVol sampler (28 l/min) using two 47 mm diameter Gelman Microquartz filters, one total ($<15 \mu\text{m}$) and one fine ($<2.0 \mu\text{m}$), preceded by a Southern Research Institute - Cyclone II⁹;
4. one 6 h modified Battelle cascade impactor¹⁰ (1 l/min);
5. one 7 d time-phased aerosol sampler¹⁰ (≈ 2 l/min); and
6. one Sears 3 kW gasoline electric power generator positioned 40 m downwind of the sampling equipment.

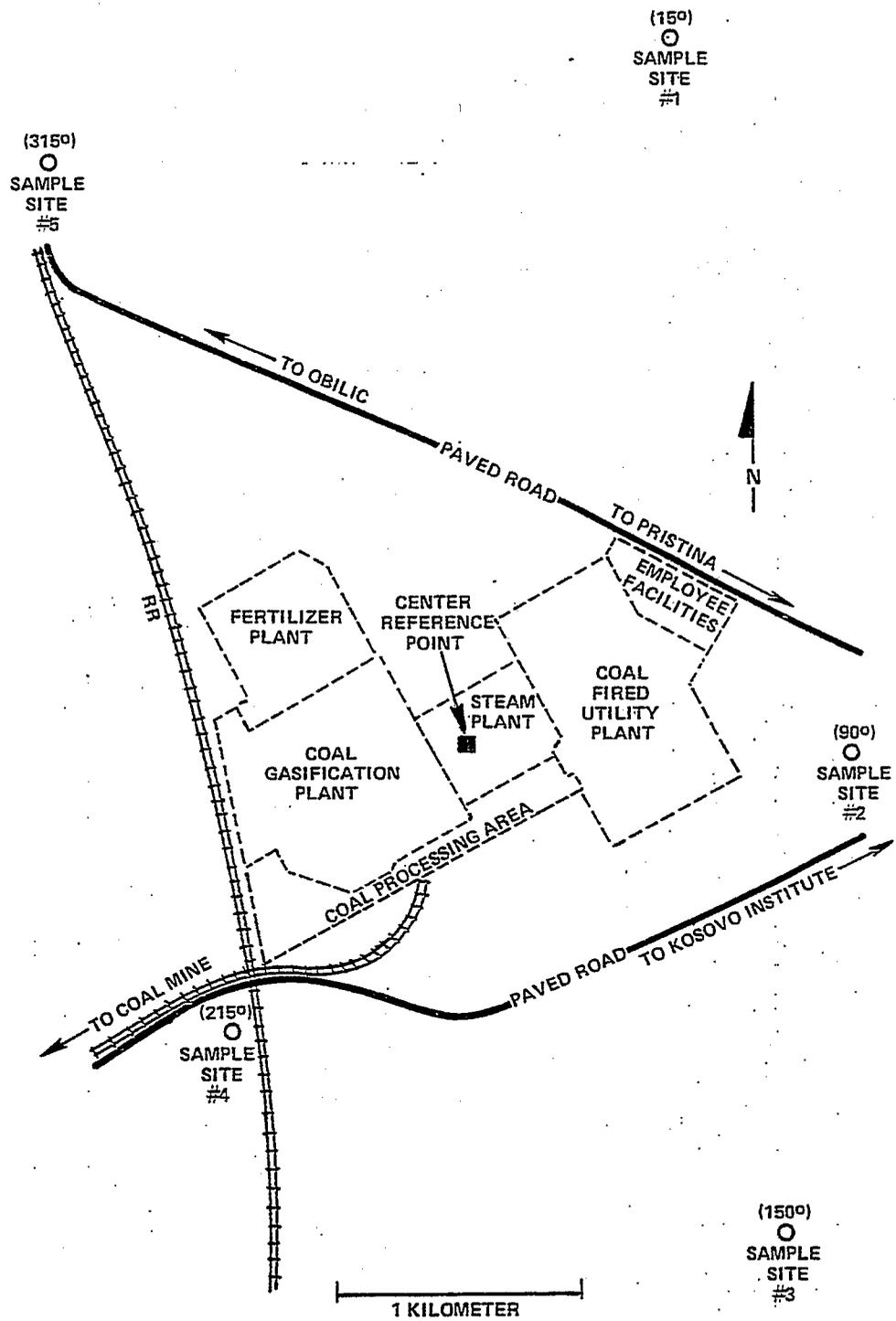


Figure 1. Schematic of the Kosovo complex with the five sampling sites indicated (Reference 1).

Site No. 3 was equipped with a Bendix Aerovane (6 blade) wind speed, wind direction, and time system. Site No. 5 was equipped with a Climatronics meteorological station and a Datal Data Logger II magnetic tape system which recorded wind speed, wind direction, solar flux, barometric pressure, temperature, and time. The meteorological data from Site No. 5 were used to calculate percent downwind values for each site location.¹

Mass measurements on LoVol filters were made on a Mettler Model ME 30/36 Electronic Microbalance. Quality assurance audits¹ covering sample collection media preparation, equipment calibration and operation, initial and final gravimetric measurements, sample storage and transport, and sample documentation were conducted daily by on-site personnel representing the prime contractor, Radian Corporation. All aspects of sample collection and handling, except quality assurance/quality control, were carried out by Yugoslav personnel under American supervision.

Sampling began at 0000 h on May 14 and ended at 2400 h on May 29, 1979. Approximately 3000 samples were collected during the study. The samples were distributed between several investigators for analysis (see Table 1).

ANALYSIS STRATEGY

The objectives of the analysis program were to analyze the aerosols and vapors collected in the vicinity of the Kosovo complex, and to compare the ambient air results with those obtained from the analysis of Kosovo gasification process emissions and by-product streams. To accomplish these objectives four integrated courses of analysis were followed: (1) physical characterization

Table 1. SAMPLES COLLECTED AND RESPECTIVE RECIPIENTS^a

ORGANIZATION	HIVOL FILTERS	ORGANIC VAPOR TRAPS	BATTELLE IMPACTOR DISC SETS	STREAKER SAMPLER SLIDES	LOVOL FILTERS	GRAB SAMPLE BOMBS
INEP ^b	42	83	157	6	316	3
RADIAN	23	42			326 ^c	
ORNL	22	42				
FSU			161	12		
EPA/GKPB						3
TOTALS	87	167	318	18	642	6

^aFROM REFERENCE 1.

^bINEP (INSTITUT ZA PRIMENU NUKLEARNE ENERGIJE, BELGRADE, YUGOSLAVIA).

^cTHE OREGON GRADUATE CENTER RECEIVED TWO SECTIONS FROM EACH LOVOL FILTER IN RADIAN'S POSSESSION.

of the aerosol; (2) carbon speciation of the aerosol; (3) inorganic analysis of the aerosol; and (4) organic analysis of the species in the vapor phase and adsorbed on the aerosol.

The percentage of time that each station was located downwind from the gasification plant was of interest for the purpose of correlating identified chemical species with their source(s). The reduction and analysis of the Climatronics meteorological data indicated that Site No. 4 was the predominant downwind location ($\approx 40\%$) and that Sites No. 1 and No. 5 were the predominant upwind locations ($\approx 1\%$). Site No. 3 ($\approx 20\%$) was an intermediate location. Samples from Sites 1, 3, and 4 received first priority for screening and analysis.

ANALYSIS RESULTS

Physical Analysis

Gravimetric data showed that the ambient aerosol loadings (both $<15 \mu\text{m}$ and $<2.0 \mu\text{m}$) were significantly greater downwind of the Kosovo complex than upwind (note Figure 2). The increase was greater for the coarse (total minus fine) aerosol fraction than for the fine fraction. The particulate matter collected downwind of the complex appeared to be mineral; only small amounts ($<1\%$) of typically spherical fly ash material were observed. The latter result indicates that the sampling stations were located in areas least affected by the plume of the Kosovo power plant.

Carbon Analysis

Carbon speciation analysis by Huntzicker, et al. (Oregon Graduate Center)¹¹ showed the coarse aerosol fractions from Site

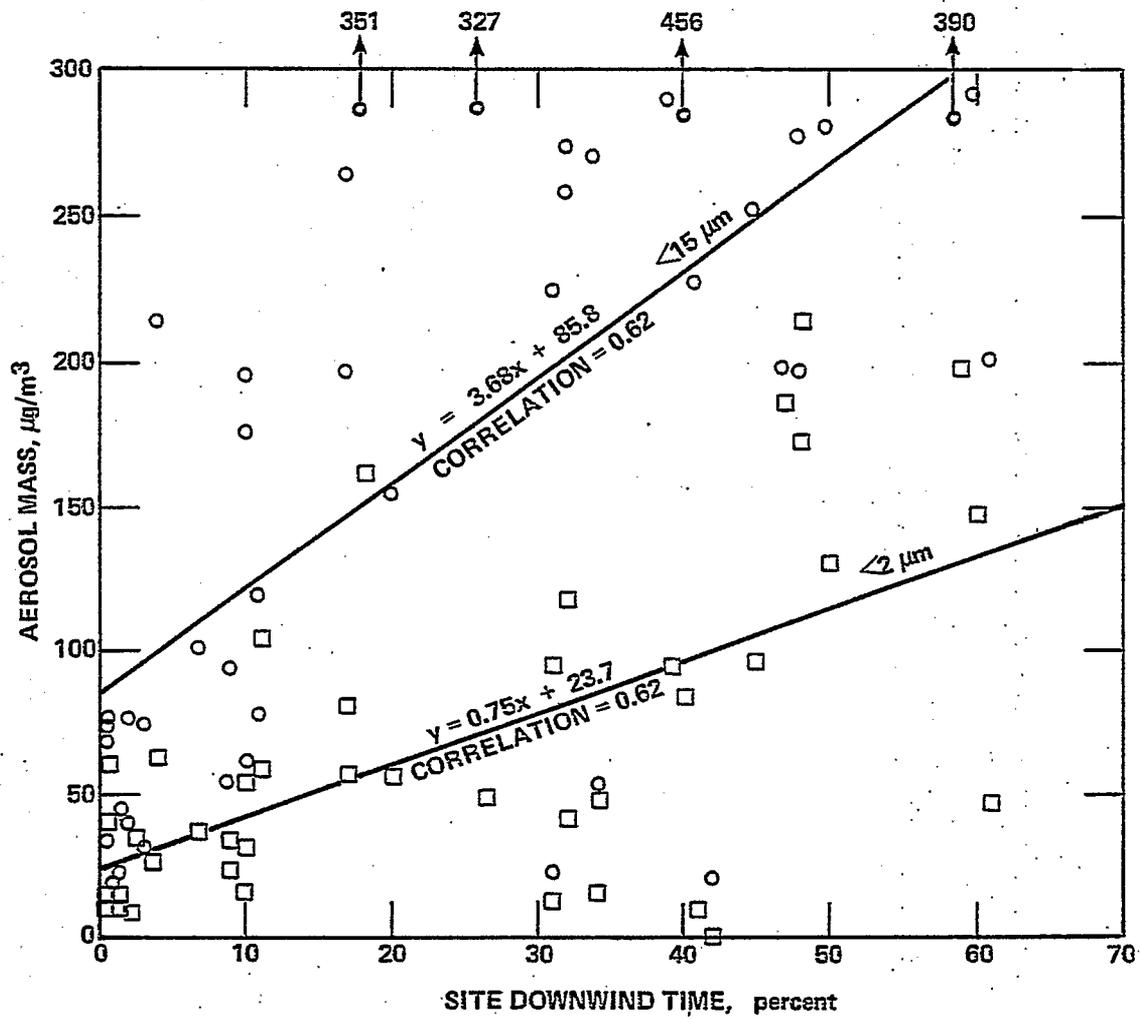


Figure 2. A Plot of the <15 μm and <2.0 μm particle fractions versus percent downwind. The lines are the linear-least-squares plot of the data (Reference 1).

No. 4 (downwind) to exhibit a very strong periodicity in elemental carbon concentration. This peaking always appeared at night. Weaker periodicities were observed for coarse organic carbon and total (<15 μm) carbonate carbon. Site No. 4 also exhibited a daytime peaking trend in organic carbon concentration in the fine aerosol fraction. An explanation for this pattern has not yet been developed. The elemental carbon and organic carbon in the fine fraction were weakly correlated ($r = 0.36$) at Site No. 4, suggesting a multiplicity of sources and poor mixing. At Site No. 5 (upwind), the organic and elemental carbon in the fine fraction were strongly correlated ($r = 0.77$). For all sites and sampling periods, when the percent of time downwind was <5%, the correlation coefficient was 0.63. The latter two results indicate well aged aerosol similar to aerosol sampled at urban U.S. sites. The high concentrations of carbonate carbon (up to $12 \mu\text{C}/\text{m}^3$) observed during many of the high mass loading periods suggest blowing coal dust. This is a reasonable assumption in that Kosovo lignite is rich in carbonate.¹² Total carbon analysis data obtained by Radian¹ showed that a higher percentage of carbon was collected downwind of the plant and that the additional carbon was >2.0 μm in diameter. Upwind, \approx 70-80% of the carbon was in the <2.0 μm fraction.

Inorganic Analysis

Preliminary data from Boueres, et al. (Florida State University)¹³ on the time phase streaker sampler at Site No. 4 showed regular daytime peaking of sulfur and iron as well as lead and zinc. These element pairs are not synchronous but may be related to the peaking seen by Huntzicker, a possibility now being investi-

gated. There are some indications of photochemical activity and sulfur transformation chemistry. However, this inference will remain speculative until more definitive data are obtained through a more detailed analysis of the impactor and streaker data bases.

Figure 3 shows the average background concentration of sulfur at all sites to be on the order of $2 \mu\text{g}/\text{m}^3$. With the exception of Site No. 5, all sites show maxima in $[\bar{S}]$ occurring at different times of the day between 1200 and 1800 h. Each maximum of $[\bar{S}]$ appears to be composed of a distinct peak superimposed on a smooth (bell shaped) maximum. From the wind direction and site position information, we hypothesize that the distinct peak may be associated with direct emission plus rapid heterogeneous transformation within the plume. The other two components (the background and the smooth maximum) may be associated with homogeneous nucleation, slow heterogeneous reaction, and resuspension of particles deposited in the soil.¹⁴

Preliminary assessment of the Kosovo samples thus far suggests that most of the observed trace metal aerosol components were derived from sources other than the coal gasification plant. Radian's^{1,15} inorganic analyses also show no correlations between concentration and percent downwind from the coal gasification facility for any soluble (Na^+ , NH_4^+ , NO_3^- , Cl^- , and $\text{SO}_4^{=}$) or elemental species except total carbon (discussed above). Iron, lead, and zinc data analyses are incomplete at this time.

Organic Analysis

The Tenax resin cartridges analyzed by Radian¹ showed organic species in the volatility range from benzene to pyrene. Benzene

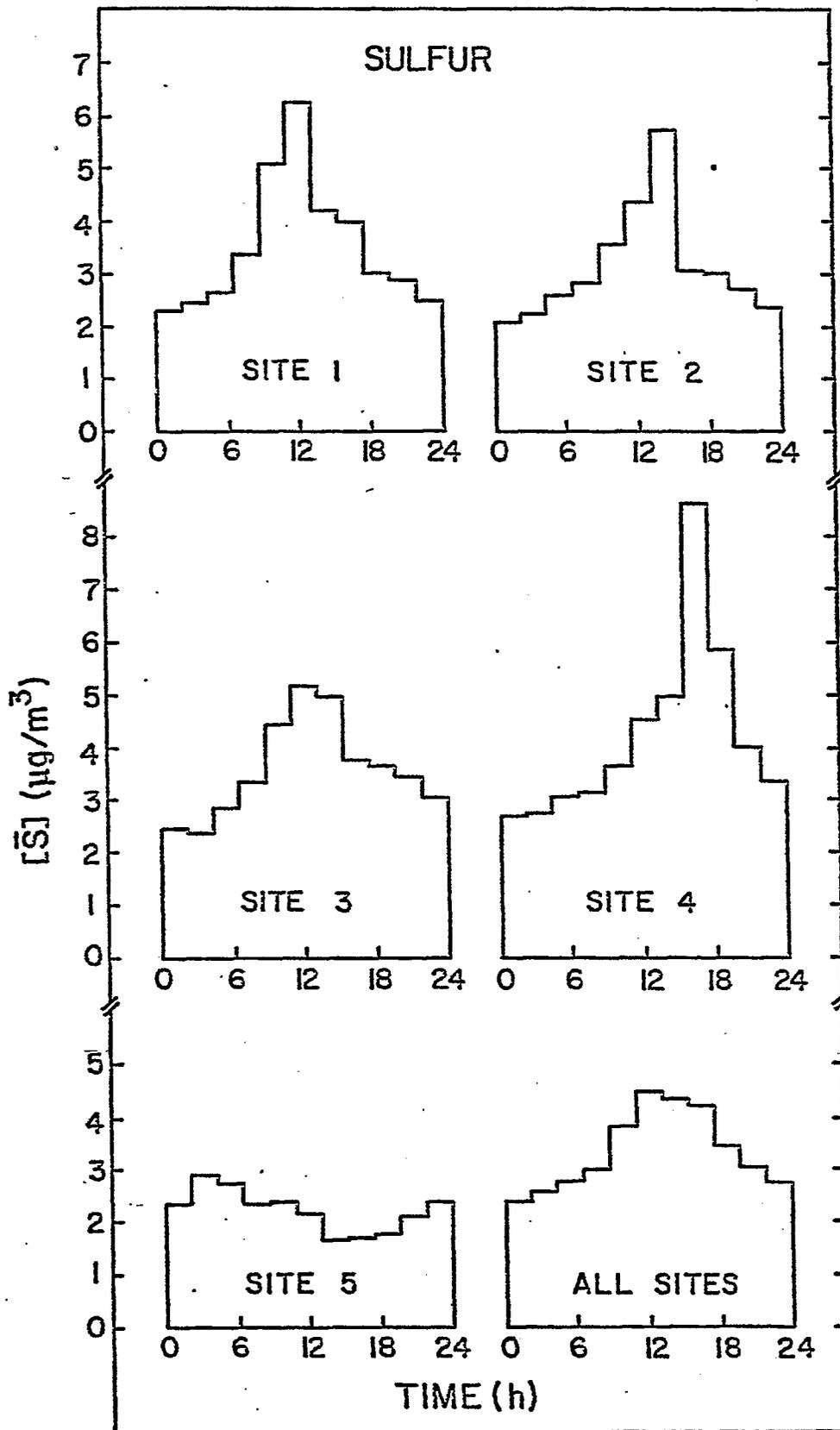


Figure 3. Histograms showing the average daily pattern of aerosol sulfur concentrations at all sites individually and their overall grand average. Plotted are the 2-h averages of $[S]$ for the 15.5 days of sampling (14-26 May 1979) (Reference 14).

and toluene (and possibly other volatile species) experienced breakthrough and were not quantifiable, but xylenes and all heavier compounds were quantitatively collected. There is a clear distinction (with some overlap) between the organic compounds adsorbed on the particulate matter caught on the HiVol filter and in the vapors sorbed on the Tenax resin. The vapors spanned benzene (MW 78) to pyrene (MW 202). The filter samples contained polynuclear aromatic hydrocarbons (PAH's) from naphthalene (MW 128) through the benzopyrene isomeric group (MW 252).

Mass spectrometric analysis of Tenax and filters samples succeeded in tentatively identifying more than 50 organic compounds and isomeric groups in the ambient air downwind of the Kosovo Industrial Complex. The list of identified compounds includes: alkylated benzenes through C₄ substitution, polyaromatic hydrocarbons (PAH's) and alkylated PAH's through benzopyrenes, linear and heterocyclic hydrocarbons, phenols, ketones, alkylated pyridines and quinolines, alkylated thiophenes, and dibenzofuran. Some of the volatile organic compounds detected in the ambient air were identical to some of the compounds found in certain emissions from the coal gasification plant (see Figures 4-7).

Quantification by mass spectrometry and flame ionization detection placed the maximum individual concentrations of naphthalene in the vapor phase and benzopyrene isomer group adsorbed on the particulate matter at 8 $\mu\text{g}/\text{m}^3$ and 0.08 $\mu\text{g}/\text{m}^3$, respectively, when extrapolated to 100% downwind. The basis for such an extrapolation is shown in Figure 8. Comparison of measured concentrations with Ambient-Multimedia Environmental Goal (A-MEG)¹⁶ values

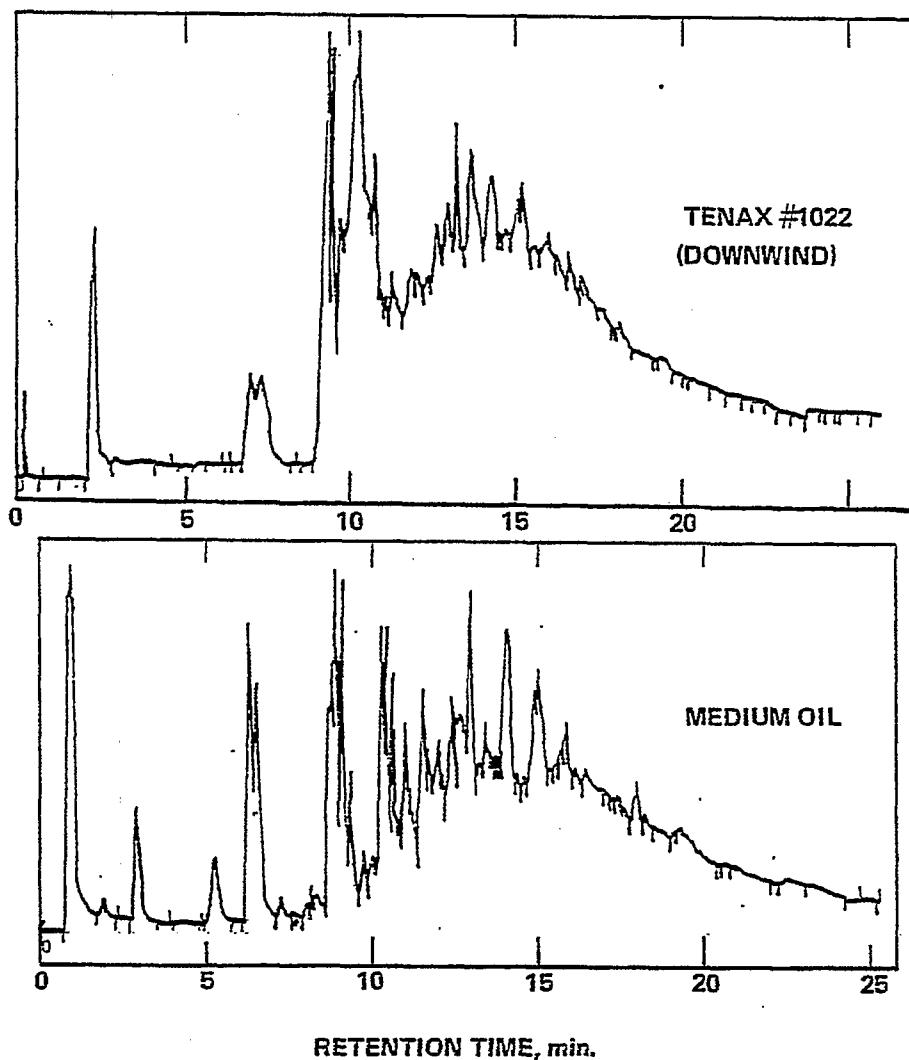


Figure 4. GC-HECD sulfur compound profiles for a downwind Tenax vapor trap extract (#1022, day 6, site #4) and for Kosovo medium oil (Reference 1).

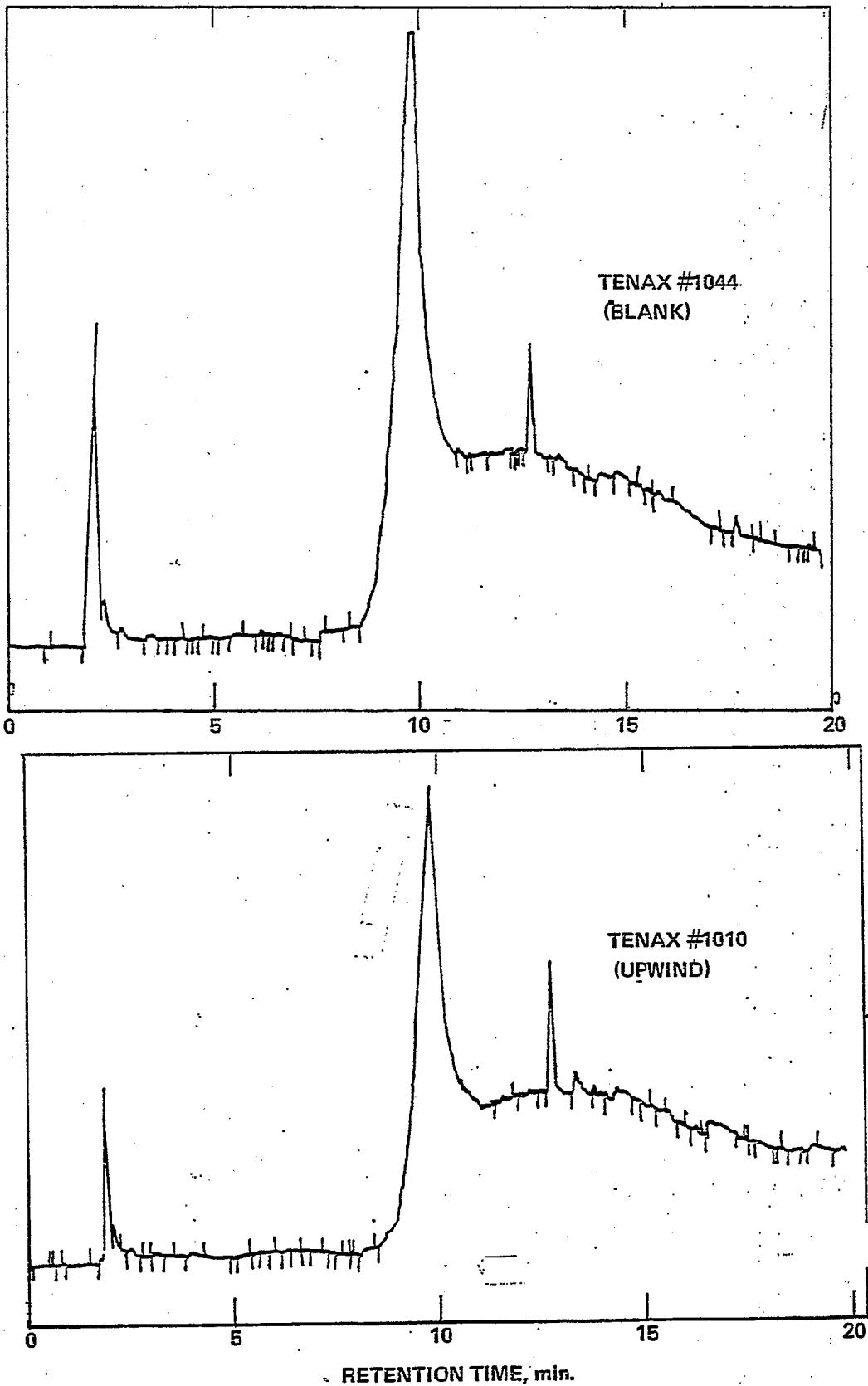


Figure 5. GC-HECD sulfur compound profiles for an upwind (#1010, day 6, site #1) and a blank (#1044) Tenax vapor trap extract (Reference 1).

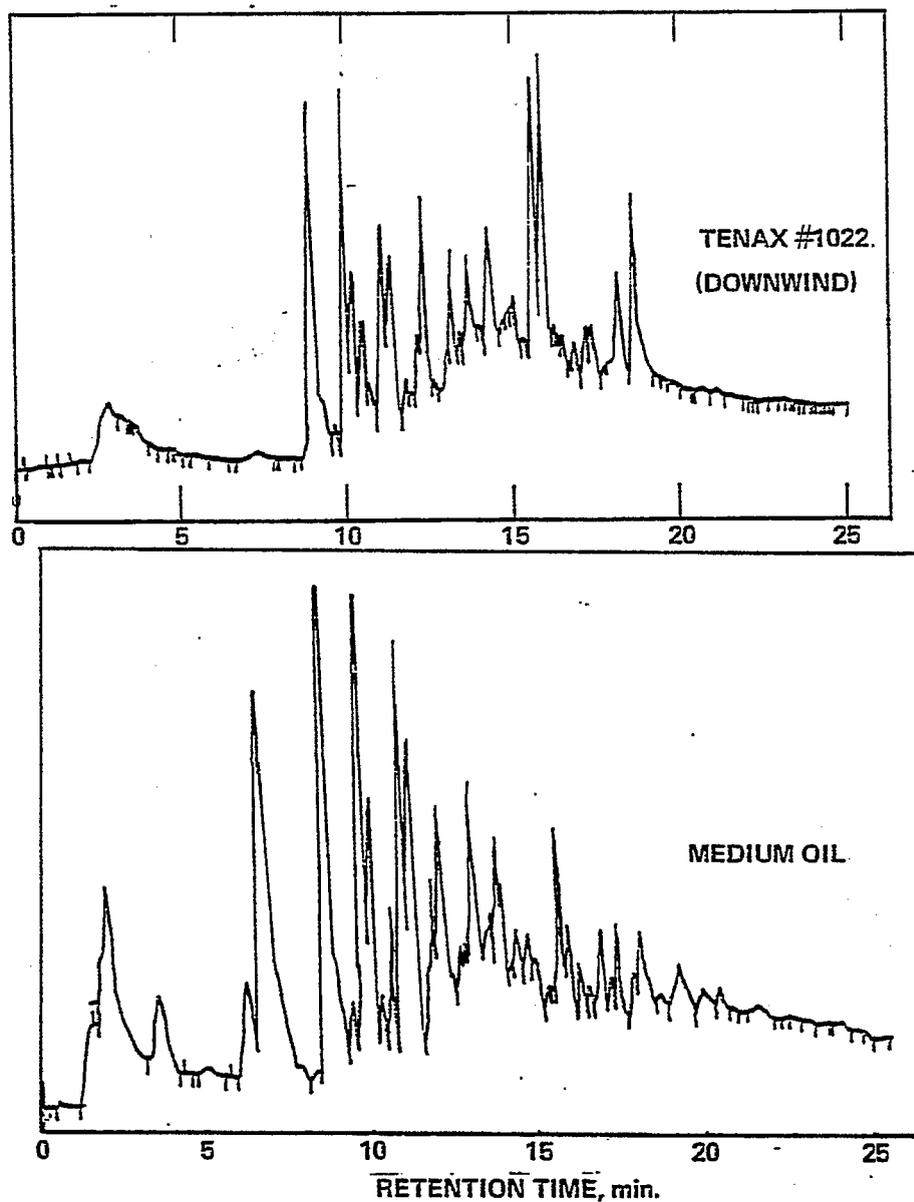


Figure 6. GC-HECD nitrogen compound profiles for a downwind Tenax vapor trap extract (#1022) and for Kosovo medium oil (Reference 1).

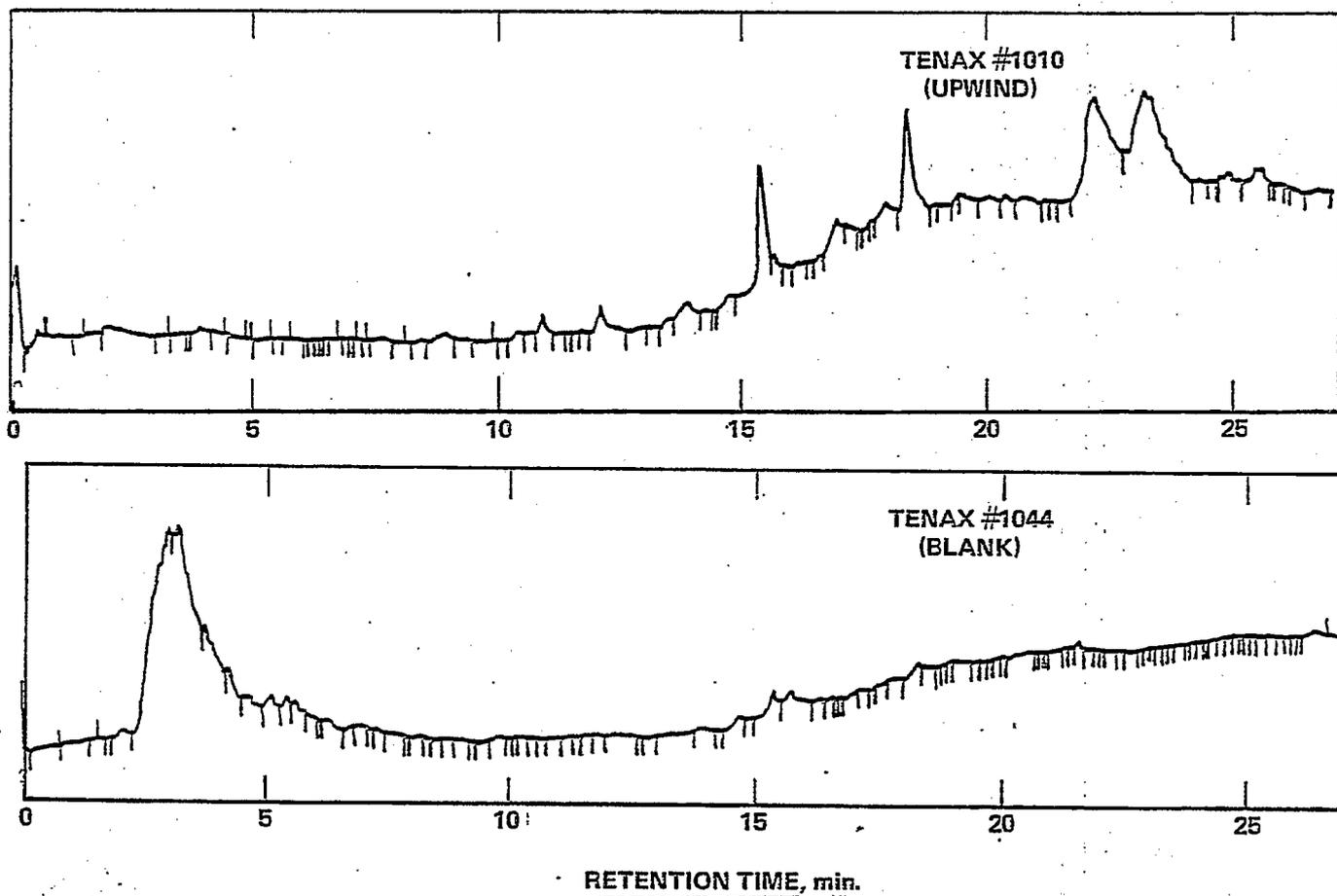


Figure 7. GC-HECD nitrogen compound profiles for an upwind (#1010) and a blank (#1044) Tenax vapor trap extract (Reference 1).

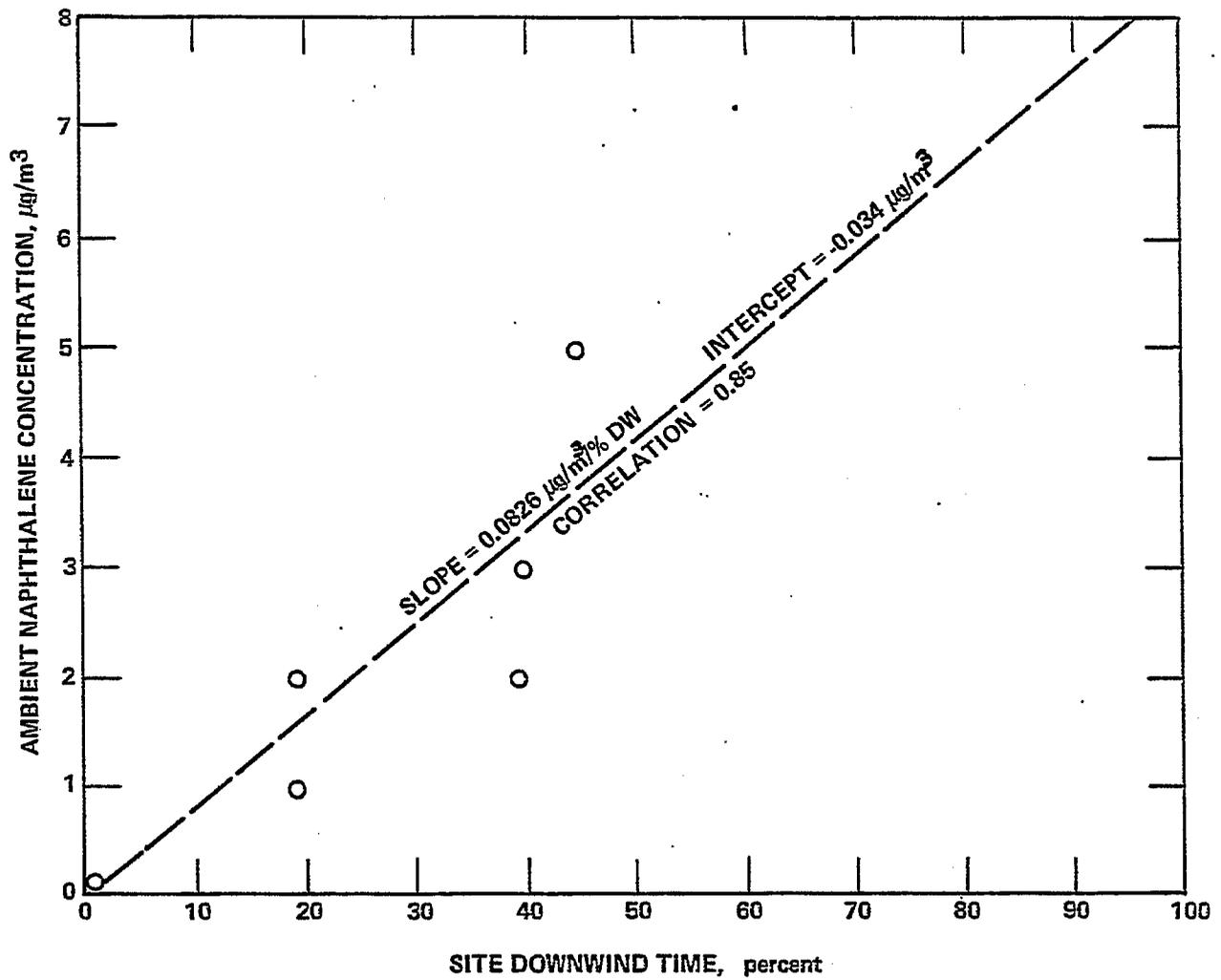


Figure 8. Correlation of organic loading in Kosovo ambient air with the percent of time the sampling site was downwind of the coal gasification plant (Reference 1).

indicates that certain species (e.g., benzopyrene isomer) may cause harmful health effects. A-MEG's are target value ambient air concentration levels below which the component is of low concern for its potential effects..

Griest, et al. (Oak Ridge National Laboratory)¹⁷ used analytical procedures different from those of Radian and observed 120 vapor phase organics in the ambient air surrounding the Kosovo Industrial Complex. The 28 major components are listed in Table 2. The majority of the vapor phase organics were C₁-C₃ alkyl-substituted benzenes. Also present were diaromatics (such as naphthalenes and biphenyl) and several oxygenated species (such as benzaldehyde, acetophenone, phenol, and the cresols). Concentrations of individual constituents ranged from 0.02 to 9.0 µg/m³, with toluene, phenol, benzaldehyde, and acetophenone being the major species in the vapor phase samples. Naphthalene, phenol, and the cresols were more concentrated in samples collected downwind of the gasifiers. Blanks were virtually featureless. (It should be noted here that the Tenax cartridges (200) used in this study were prepared by the Oak Ridge National Laboratory in October 1978.)

Approximately 100 aerosol phase constituents were observed in the gas chromatographic analysis of the unfractionated filter extracts. Filter blanks were featureless. As shown in Table 2, the major species were C₁₉-C₃₆ n-paraffins and phthalates. In contrast to the vapor phase organics, the particulate phase organics appeared to be more aliphatic and approximately 2 to 3 orders of magnitude lower in concentration. N-paraffins ranged from 1 to 40 ng/m³; the most concentrated particulate phase organic

Table 2. TENTATIVE IDENTIFICATION AND RANGE OF CONCENTRATIONS OF VAPOR AND PARTICULATE PHASE CONSTITUENTS IN SAMPLES COLLECTED NEAR YUGOSLAVIAN GASIFIER^e

VAPOR PHASE		PARTICULATE PHASE	
TENTATIVE IDENTIFICATION	RANGE OF CONCENTRATION ^a , μg/m ³	TENTATIVE IDENTIFICATION	RANGE OF CONCENTRATIONS, ng/m ³
BENZENE	0.33-1.8	BIPHENYL	0.29-4.2
n-C ₉ H ₂₀	0.16-1.0	n-C ₁₉ H ₄₀	1.8-11
TOLUENE	0.74-9.0	PHENANTHRENE	_b
n-C ₁₀ H ₂₂	0.16-0.60	n-C ₂₀ H ₄₂	0.44-2.0
ETHYL BENZENE	0.46-1.3	C ₁₄ -BENZENE	_c
m-XYLENE	0.20-1.3	n-C ₂₁ H ₄₄	1.0-4.7
p-XYLENE	0.38-3.2	C ₁₄ -BENZENE	_c
o-XYLENE	0.24-1.6	n-C ₂₂ H ₄₆	8.5-28
CUMENE	0.02-0.38	FLUORANTHENE (+ HYDROCARBON)	0.93-4.1
C ₃ -BENZENE	0.11-0.52	n-C ₂₃ H ₄₈	5.4-13
C ₃ -BENZENE	0.25-2.0	n-C ₂₄ H ₅₀	1.6-8.8
MESITYLENE	0.06-0.58	MW 256 + 274	-
C ₃ -BENZENE	ND-0.51	n-C ₂₅ H ₅₂	6.2-18
C ₃ -BENZENE	0.21-2.2	n-C ₂₆ H ₅₄	3.9-16
C ₃ -BENZENE	0.10-0.81	BIS-(2-ETHYL HEXYL)PHTHALATE	43-120
o-METHYL STYRENE	ND-0.11	MW 226 ^d	-
BENZALDEHYDE	1.1-2.8	n-C ₂₇ H ₅₆	19-40
ACETOPHENONE	1.3-3.0	n-C ₂₈ H ₅₈	13-42
NAPHTHALENE	0.02-1.5	C ₄ -QUINOLINE	_c
2-METHYL NAPHTHALENE	0.03-0.25	n-C ₂₉ H ₆₀	11-21
1-METHYL NAPHTHALENE	0.01-0.15	n-C ₃₀ H ₆₂	2.2-7.9
PHENOL	0.16-2.3	BENZO(b, j, OR k)FLUORANTHENE	2.3-6.2
o-CRESOL	ND-1.0	n-C ₃₁ H ₆₄	7.4-13
BIPHENYL	0.04-0.09	n-C ₃₂ H ₆₆	1.4-7.2
INDOLE	0.02-0.13	n-C ₃₃ H ₆₈	2.2-6.5
p-CRESOL	ND-0.24	n-C ₃₄ H ₇₀	1.1-3.6
m-CRESOL	ND-0.36	n-C ₃₅ H ₇₂	0.8-2.9
p-ETHYL PHENOL	ND-0.16		

^aND = NOT DETECTED.

^bINCOMPLETE RESOLUTION PREVENTS QUANTITATION.

^cSTANDARD NOT AVAILABLE FOR QUANTITATION.

^dNOT BENZO(ghi)FLUORANTHENE.

^eFROM REFERENCE 17.

observed, bis-(2-ethyl hexyl) phthalate, ranged from 43 to 121 ng/m³. Polycyclic aromatic hydrocarbons were approximately 10⁻¹ as concentrated as the paraffins. Oak Ridge results were not weighted by percent downwind. Differences between upwind and downwind aerosol phase organics were not as apparent as those for the vapor phase organics. This result suggests that the vapor phase organics are a more sensitive indicator of the gasification plant's impact. However, further fractionation of the particulate phase organics may reveal more substantial differences than those observed from the profiles of the gross filter extracts.

CONCLUSIONS

Each of the Yugoslav ambient air study objectives was met. The adverse impact on the surrounding atmosphere of the Kosovo Industrial Complex, especially downwind, is unmistakable as described in the following conclusions:

- Aerosols in the form of coal dust are a significant pollutant from the coal handling operation.
- Aerosol emissions from the gasification process are overshadowed by aerosol emissions from coal handling.
- Ambient aerosol levels exceed the primary and secondary U.S. National Ambient Air Quality Standards.
- Aerosols appear to be carriers of PAH's.
- The source of the PAH's in the aerosol collections is as yet unknown but may be the flare.
- The level of benzo(a)pyrene exceeds the A-MEG's by a factor of 1000.

-Even though the light organic compounds were lost during sampling, benzene probably exceeds the A-MEG's by a factor of 10 to 100.

-Organic pollutants can be traced to the gasification plant.

-There is a broad range of organic compounds in the ambient air. The classes include aromatic and aliphatic hydrocarbons as well as their oxygen-, sulfur-, and nitrogen-containing derivatives.

Even though proposed U.S. facilities will be "better controlled" due to the use of state-of-the-art control technology and U.S. regulations, this study revealed areas of special concern on which emphasis should be placed when making decisions about the development, control, and placement of such facilities in the U.S. Such aspects as coal mining, processing, transport, and storage; process by-product storage and venting; fugitive emissions of organics throughout the process; and the storage of gasifier (and power plant) ash should be carefully reviewed. The Kosovo complex is a commercial scale facility, but only one tenth the size of proposed U.S. facilities. This study suggests that it is possible to differentiate between the emissions from a gasification plant and those from other sources near an industrial complex, and it also provides a unique data base for researchers as well as policy makers.

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