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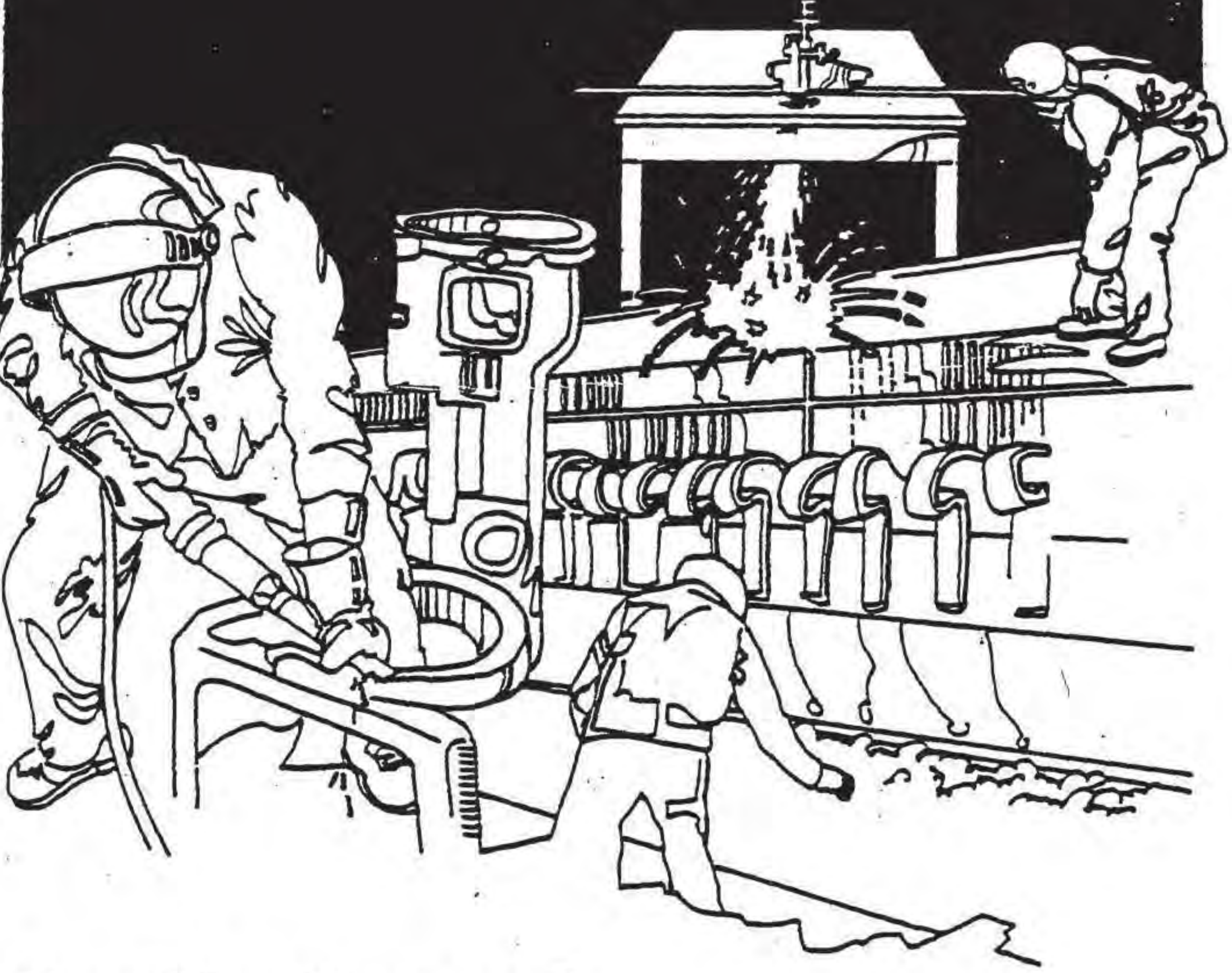

Health Hazard Evaluation Report

HETA 82-341-1682
GREAT LAKES CARBON
WILMINGTON, CALIFORNIA

PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

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GREAT LAKES CARBON
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I. SUMMARY

In July 1982, the National Institute for Occupational Safety and Health (NIOSH) received a request for a Health Hazard Evaluation at Great Lakes Carbon Corporation (GLC), Wilmington, California. Workers requested that NIOSH evaluate possible adverse respiratory effects due to exposure to petroleum coke dust during the calcining process.

NIOSH investigators conducted an environmental survey in February 1984, consisting of personal and area air sampling for total coke dust, polynuclear aromatic hydrocarbons (PNAs), and oil mist. Among the 75 total employees, 75% were administered the NIOSH questionnaire by a GLC nurse. A private contractor provided pulmonary function test (PFTs) to 69% of the workers and chest x-rays to 64%. All medical test results were reviewed and evaluated by NIOSH.

Personal breathing-zone concentrations of total airborne dust ranged from 0.1 to 12 mg/m^3 with a median of 1.6 mg/m^3, among 10 air samples collected from workers engaged in a variety of typical daily jobs. Particle sizing of airborne dust by cascade impactors indicated a mass median diameter of about 8 micrometers. Four very high personal breathing-zone (PBZ) concentrations of coke dust were found during a semimonthly cleanup job in the underground coke pits. These levels ranged from 98 to 190 mg/m^3 with a mean of 140 mg/m^3. Respiratory protection was worn. Three PBZ air samples for oil mist were nondetectable (< 0.5 mg/m^3).

Exposures to polynuclear aromatic compounds (PNAs) were below the analytical limit of detection (<0.25 ug/m^3) among workers doing routine jobs.

The medical evaluation revealed abnormal PFT results (1 restrictive and 5 obstructive) among 12% of those tested. The questionnaire identified five (10%) cases of chronic bronchitis and seven (13%) cases of chronic cough among those interviewed. The abnormal (obstructive) PFT and questionnaire results appeared to be more closely associated with cigarette smoking than employment category (salaried, operator assistants, and other production workers). Chest x-rays showed no evidence of pneumoconiosis.

Thirty eight percent of interviewed employees reported skin problems since beginning work at GLC. It appeared that these problems (red skin, pimples, blackheads and blisters) were caused by a variety of agents (dusts, oils, heat, sun, or a combination of these).

A laboratory study of sieved (<7um) and rafter samples of petroleum coke dust was conducted to determine if PNAs can be extracted by a simulated lung fluid (SLF). Although PNAs were found to be soluble in SLF, there was no indication of the SLF's ability to elute bound PNAs from the surface of petroleum coke. These results tend to reduce the concern over the presence of PNAs in petroleum coke.

On the basis of the data obtained in this evaluation, NIOSH determined that there were potentially hazardous exposures to high dust levels generated during semimonthly coke pit cleaning jobs. Recommendations for improved respiratory protection are included in Section VII of this report.

KEYWORDS: SIC 2999 (Products of Petroleum and Coal), calcined petroleum coke, calcine, coke dust, polynuclear aromatic compounds, PNAs, pulmonary function, pneumoconiosis, chronic bronchitis, simulated lung fluid.

II. INTRODUCTION

In July 1982, the National Institute for Occupational Safety and Health (NIOSH) received a request for a Health Hazard Evaluation at Great Lakes Carbon Corporation (GLC) in Wilmington, California. The Oil, Chemical, and Atomic Workers International Union and its Local 1-128 requested that NIOSH evaluate environmental conditions and possible adverse health effects (respiratory effects in particular) among workers exposed to coke dust at the Wilmington plant. The request was prompted, in part, by the fact that NIOSH was conducting a health hazard evaluation of a similiar calcining operation, at the GLC plant in Port Arthur, Texas. NIOSH postponed the study at Wilmington until completing the study at Port Arthur in January 1983.[1] NIOSH made an initial visit to the Wilmington plant in June 1983. In December 1983, NIOSH was provided with the results of a NIOSH questionnaire administered to workers by a GLC nurse along with pulmonary function tests (PFTs) and chest x-rays conducted by a private contractor. NIOSH investigators conducted an environmental survey in February 1984, and submitted recommendations for proper selection and use of respirators for workers exposed to high dust levels. An interim report of environmental and medical results was distributed in July 1984.

III. BACKGROUND

The GLC plant in Wilmington began the calcining operation in the 1940s. The raw material, petroleum coke, is procured from a nearby refinery and transported to the plant in trucks. The coke is emptied from the trucks into a raw coke hopper and then transported through a system of conveyors to large, horizontal, rotary kilns where it is heated to temperatures greater than 2000°F. The plant has four kilns, although one of the four has been down since 1975. The calcined coke is then cooled with water, sprayed with dedusting oil, and moved by conveyor belts to various calcine storage silos to await transport by truck or railcar. The process at the Wilmington plant is similar to that at the Port Arthur facility except that the Wilmington plant uses feed silos for raw materials, rather than having open storage mounds and mobile equipment to transport the petroleum coke to the kiln areas.

Workers at the Port Arthur plant were found to be exposed to airborne total particulate levels ranging from 1.2 to 6.1 mg/m^3 with a mean of 3.4 mg/m^3. Fourteen polynuclear aromatic compounds (PNAs) were identified or quantified in personal breathing-zone air samples. Cumulative PNA concentrations ranged from 0.1 to 36 ug/m^3. The medical evaluation revealed abnormal PFT results (1 restrictive, 2 obstructive, and 5 combination of both) among 9 (10%) current employees. PFT abnormalities were significantly related to dust exposure as measured by lenth of employment, age, and a history of working for five years or longer in the mobile equipment department. Chest x-rays showed no evidence of pneumoconiosis.[1]

In addition to a concern over the pulmonary effects of exposure to petroleum coke dust, workers at the Wilmington plant expressed concern over skin problems first noted in 1975, after the introduction of the dedusting oil, "Tex 1666". In 1980, the union conducted a skin questionnaire survey of the workforce.

In June 1983, the plant employed 52 hourly and 23 salaried workers. The plant medical program included preplacement pulmonary function tests (PFTs), chest x-rays (both being offered over the past 3-5 years), and a physical examination. No periodic medical examination program was in effect at the time of the request.

IV. METHODS

A. Environmental

On February 7-9, 1984, NIOSH investigators collected 15 full-shift personal breathing-zone (PBZ) air samples for petroleum coke dust at a flow rate of 1.0 liters per minute on teflon filters followed by Orbo 43 sorbent tubes. Three PBZ air samples for oil mist were collected on polyvinyl chloride filters at 1.5 liters per minute and analyzed by infra-red spectroscopy according to NIOSH P&CAM 283[2].

Bulk samples of raw coke, calcine, rafter samples, dedusting oil, and waste dust were collected and analysed for benzene soluble fraction, cyclohexane soluble fraction and acetonitrile soluble fraction. PNAs were analysed by high performance liquid chromatography following NIOSH Technical Bulletin TB-001, issued December 1, 1982.

Fifteen triplicate sets of side-by-side area air samples of petroleum coke were collected at 2.0 liters per minute on teflon filters for the purpose of determining which one of three solvents (benzene, cyclohexane, or acetonitrile) was superior for extracting polynuclear aromatic compounds (PNAs). Benzene was found to be the most efficient solvent, so the PBZ coke air samples were analyzed for total weight, benzene soluble fraction, and concentrations of benzene soluble PNAs, according to NIOSH TB-001. Four outdoor area air samples for PNAs were collected upwind from the plant. The samples were drawn at an average flow rate of 1.5 liters per minute for 14 hours and analysed by the same methods as the PBZ samples.

Airborne petroleum coke particle size was studied by two methods. Airborne dust samples were collected on open-face (0.1 um pore size) Nucleopore® filters at 1.0 liters per minute and examined at a magnification of 500x, using a scanning electron microscope. PBZ and area air samples were also collected using Sierra Model 294 (four stage) Cascade Impactors® at 2.0 liters per minute.

B. Medical

In July 1983, questionnaires were administered by the GLC nurse and the chest x-rays and PFTs were performed by the contractor. Fifty-six questionnaires were completed by 18 of 25 (72%) salaried employees, and by 38 of 50 (76%) hourly employees. PFTs were obtained for 52 employees (18 salaried and 34 hourly workers). Forty-eight participants had chest x-rays taken. The data were sent to NIOSH in December 1983.

C. Experimental Investigation of the Bioavailability of PNAs from Petroleum Coke

This study was conducted (Appendix) to investigate the physiological significance of PNAs associated with petroleum coke.

V. EVALUATION CRITERIA

A. Environmental Criteria

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects if their expsoures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the evaluation criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: 1) NIOSH Criteria Documents and recommendations, 2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLV's), and 3) the U.S. Department of Labor (OSHA) occupational health standards. Often, the NIOSH recommendations and ACGIH TLV's are lower than the corresponding OSHA standards. Both NIOSH recommendations and ACGIH TLV's usually are based on more recent information than are the OSHA standards. The OSHA standards also may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH-recommended standards, by contrast, are based primarily on concerns relating to the prevention of occupational disease. In evaluating the exposure levels and the recommendations for reducing these levels found in this report, it should be noted that industry is legally required to meet only those levels specified by an OSHA standard.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended short-term exposure limits or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high short-term exposures.
Listed below are the evaluation criteria referred to in this investigation:

	NIOSH Recommended Criteria	ACGIH TLV	OSHA Standard
Total Particulates	----	10 mg/m^3	15 mg/m^3
Respirable Particulates	----	5 mg/m^3	5 mg/m^3
Carbon Black	3.5 mg/m^3 or 0.1 mg/m^3 PNA content (cyclohexane extractable fraction)	3.5 mg/m^3	3.5 mg/m^3
Coal Tar Pitch Volatiles	0.1 mg/m^3 (cyclohexane solubles)	0.2 mg/m^3 (benzene solubles)	0.2 mg/m^3 (benzene solubles)

All values are time-weighted averages.
NIOSH criteria are based on a 10-hour workday.
ACGIH and OSHA are based on an 8-hour workday.

B. Coke Dust

Coke is the solid product resulting from the destructive distillation of coal (coal coke), or the heavy petroleum fraction resulting from the refinery of petroleum products (petroleum coke).

Coke consists primarily of pure carbon (generally 99%), with the balance consisting of such impurities as hydrogen or mineral impurities.[3] Coke usually contains little or no detectable silica.

Currently, there are no NIOSH criteria, OSHA standard, or ACGIH TLV for coke dust. Therefore, for the purpose of this study, environmental criteria for total (nuisance) particulates, respirable particulates, carbon black, and coal tar pitch volatiles (CTPV) are referred to in evaluating occupational exposure to coke dust.

For most industrial purposes, carbon black and petroleum coke are substantially different materials. However there are similarities, especially in their PNA content, that justify some comparisons when evaluating their potential health effects. The major chemical property that has been thoroughly investigated is their percentage of carbon which is usually at least 99% in both substances. The major physical difference between the two substances which relates to potential health effects is probably their particle size and adsorptive characteristics. Most carbon blacks generally consist of very fine particles with diameters less than 0.5 um.[4] In one recent study of petroleum refinery workers, the investigators found that petroleum coke dust from four refineries had a particle mass median diameter of 8 um.[5] Particles less than 10 um are generally considered to be in the respirable size range. Thus, it appears that the PNA content of these and similiar materials is one of the most important constituents to be studied. In fact, both the NIOSH and ACGIH recommended standards for carbon black were primarily designed to minimize worker exposure to PNA compounds. The ACGIH TLV Committee found considerable variation in the benzene extractable content among the different types of carbon black. For instance, channel black was found to contain very little material removable by hot benzene extraction, whereas furnace black had a 0.28% benzene extractable fraction. The Committee concluded that "the 3.5 mg/m^3 TLV would keep the absorbed values of polycyclic aromatic hydrocarbons well below their limit of 0.2 mg/m^3.[6] The NIOSH approach of the recommended standard specifies that exposure to any type of carbon black should not exceed 3.5 mg/m^3 or 0.1 mg/m^3, measured as the cyclohexane extractable fraction.[4]

Table I compares the PNA content of petroleum coke and calcine samples taken from Great Lakes Carbon versus the PNA content of several varieties of carbon black.[7] The results show that petroleum coke contains greater amounts of PNA compounds than many of the carbon blacks. Therefore, the carbon black standard may be useful as a guide to controlling petroleum coke exposures but may or may not provide adequate protection.

It should be noted that considerable controversy arose from the development of the carbon black criteria that could have future relevance to other carbon products, including petroleum coke. Some opponents of the current carbon black standard believe that the "alleged" carcinogenic potential of carbon black was based on incorrect analogies with various carcinogenic coal tar products. One of their major arguments is that PNAs are strongly adsorbed on commercial carbon black particles and cannot significantly be eluted by biological systems, whereas many coal tar products often contain unadsorbed PNA molecules.[8] Further negative evidence includes several epidemiologic studies of workers exposed to carbon black dust in North America and Western Europe which show no excess in mortality or morbidity due to cancer, heart disease, or respiratory disease.

C. PNAs and Benzene or Cyclohexane Solubles

PNAs are condensed ring aromatic hydrocarbons normally arising from the combustion of organic matter. They are commonly emitted into the air when coal tar, coal tar pitch, or their products are heated, but can result from burning the heavy petroleum fraction used in petroleum coke.[9] A number of PNAs, including benzo(a)pyrene and anthracene are carcinogenic (lung and skin). There are no federal standards pertaining to airborne concentrations of individual PNAs. However, The Standard Advisory Committee on Coke Oven Emissions (Federal Register July 31, 1985, 29 CFR 1910.1029) has recommended that worker exposure not exceed 0.2 ug/m^3.

In 1967, the ACGIH adopted a TLV of 0.2 mg/m^3 for CTPV, described as a "benzene-soluble" fraction, and listed certain carcinogenic components of CTPV. The TLV was established to minimize exposure to the listed substances believed to be carcinogens, viz, anthracene, BaP [benzo(a)pyrene], phenanthrene, acridine, chyrsene, and pyrene. CTPV's are among the seven substances listed as "Human Carcinogens" in Appendix A of the current ACGIH TLV's. This group consists of "a substance, or substances, associated with industrial processes, recognized to have carcinogenic or cocarcinogenic potential with an assigned TLV". The TLV was promulgated as a federal standard under the Occupational Safety and Health Act of 1970 (29 CFR 1910.1000).[10] In 1972, the Federal Register (37:24749, November 21, 1972) contained an interpretative rule of the term "coal tar pitch volatiles": "... coal tar pitch volatiles include the fused polycyclic hydrocarbons which volatilize from the distillation residues of coal, petroleum, wood and other organic matter". This has been reprinted as 29 CFR 1910.1002. The general philosophy behind this interpretation was that "all of these volatiles have the same basic composition and ... present the same dangers to a person's health".[11]

In the development of the NIOSH recommended standard, it was concluded that CTPV's are carcinogenic and can increase the risk of lung cancer in workers. Since no absolutely safe concentration can be established for a carcinogen, NIOSH recommended the exposure limit be the lowest concentration that can be reliably detected by the recommended method of environmental monitoring. At that time (September 1977) the lowest detectable concentration for CPTV's was 0.1 mg/m^3.

Although the benzene or cyclohexane extractable fraction offers an easier, less expensive method of analysis than actual PNA quantitation, there is no certainty that there is a correlation between the two. The analytical method for measuring the benzene-soluble fraction is not limited to PNAs but will include all other organic compounds collected on the filter and soluble in benzene.

D. Respiratory Effects

Coke Dust

There are currently no published studies of the respiratory effects of workers in the petroleum coke industry. However, there are several studies which provide documentation of pneumoconiosis related to carbon dust exposure which is indistinguishable from that seen in coalworkers.

A study by Watson et al (1959) gives an account of a clinical survey of 15 carbon electrode makers, of whom 4 suffered from complicated and 5 from simple pneumoconiosis. The authors concluded that carbon electrode makers may develop simple pneumoconiosis with focal emphysema, and a complicated form of the disease, which are indistinguishable from the corresponding conditions in coalworkers.[12] In this study, the dust consisted of mainly coal and coke particles. Meiklejohn's (1957) study of workers employed in the manufacture and handling of carbon black suggests that the inhalation of nearly pure carbon over prolonged employment resulted in radiologic evidence of very early simple pneumoconiosis of the coalworkers' type but without clinical effects.[3] Both of these studies were based on radiological and/or pathological findings of pneumoconiosis. Okutani (1963) found (graphite) pneumoconiosis among 112 (43% of those examined) carbon electrode makers exposed to average dust levels of 57.6 mg/m in Japan.[3] A survey[13] of respiratory disease in carbon black workers in the U.K. and the U.S.A. (Crosbie, 1976) showed no evidence of harmful effects from the inhalation of carbon dust.[14]

A chronic inhalation toxicity study of petroleum coke was recently conducted on rats and monkeys. The animals were exposed to concentrations of 1, 10.2, or 30.7 mg/m^3, 6 hours/day, 5 days/week for 2 years. Body weight, physical appearance, ophthalmologic, hematologic, serum biochemical, cytogenic (rats only) and histologic evaluations were conducted. Significant exposure related effects were limited to increased lung weights, and deposition and phagocytosis of dust in lungs. Rats in the 30.7 mg/m^3-exposure group also had microscopic pulmonary alterations, including chronic inflammation, sclerotic and metaplastic changes, and the presence of keratin cysts. The authors concluded that the inhalation of petroleum coke dust produced neither oncogenicity in rats nor significant toxicity in monkeys.[15]

VI. RESULTS AND DISCUSSION

A. Environmental

Three PBZ air samples for oil mist were below the limit of detection (0.5 mg/m^3). Fifteen PBZ air samples for total particulates ranged from 0.1 to 190 mg/m^3 (Table II). Four very high potential exposures occurred during a semimonthly cleanup job involving 2-3 workers who shoveled up raw petroleum coke which had spilled from open conveyors in the underground coke pits. These dust concentrations ranged from 98 to 190 mg/m^3 with a mean of 140 mg/m^3. Disposable 3M #8710 respirators were worn. The GLC written respirator program includes general guidelines for selection, use, maintenance, training, and recordkeeping, but does not include detailed requirements for specific jobs, such as coke pit cleaning.

Workers engaged in typical daily jobs were exposed to dust concentrations ranging from 0.1 to 12 mg/m^3 with a median of 1.6 mg/m^3.

Particle Size Distribution

The effective cutoff diameter and cumulative mass percent were plotted on logarithmic probability graph paper, such that the particle mass distribution for any size range can be readily noted (Figures 1-4). The mass median diameter of airborne dust was about 8 um in a Silo Penthouse area sample and two Raw Coke Pit PBZ samples. The mass median diameter was about 13 um in a Front-End Loader PBZ sample.

The scanning electron microscope showed a wide range of particle sizes in the air samples. Many of the larger particles were aggregates. The count median diameter was 1.4 um in a Silo Penthouse area air sample. Approximately 1.75% of the particles were greater than 7 um.

PNAs

Of the three solvents tested, benzene extracted the most material from the bulk samples (Table III). Four bulk samples of raw coke had cumulative PNA concentrations ranging from 110 to 330 ppm with a mean of 210 ppm. Of the 17 PNAs quantitated, chrysene was found in the highest concentration followed by benz(a)anthracene, benzofluoranthene, and benzo(e)pyrene. No PNAs were found in calcine or waste dust.

The air sample analyses failed to characterize particulate-borne PNA exposure among workers routine jobs (Table II). These results are partiularly disappointing considering that the new (NIOSH TB-001) sampling and analytical method was employed, presumably for the purpose of improving older methods. In reality, the newer method produced PNA detection limits that were 50 times higher than limits of detection obtained over two years earlier when NIOSH conducted a survey of the Great Lakes Carbon plant in Port Arthur, Texas (Table IV). At that time air samples were collected on glass fiber/silver membrane filters and extracted with benzene. The extract volume was reduced by blowdown with nitrogen before analysis by high resolution gas chromatography/mass spectromety. The limit of detection was 2 ng/sample. The newer method used teflon filters which were also extracted with benzene. The extract was solvent exchanged to acetonitrile for analysis by high performance liquid chromatography. The limit of detection was 100 ng/sample.

Phenanthrene was the only compound detected on the sorbent tubes. PBZ concentrations of phenanthrene vapor ranged from non-detectable (<0.1 ug/m^3) to 0.4 ug/m^3 (Table V). It is interesting to note that those workers with the highest petroleum coke exposures had no detectable phenanthrene exposure. It is possible that the large amounts of coke dust loaded on the filter samples could have adsorbed the phenanthrene vapor before it reached the sorbent tubes.

Possible sources of phenanthrene vapor are the GLC calcining process, and other industrial sources in the area. The four air samples taken upwind of the Wilmington plant ranged from 0.04 to 0.06 ug/m^3 with a mean of 0.05 ug/m^3. Phenanthrene was the only compound detected in these samples.

Phenanthrene vapor exposure levels at the Port Arthur plant ranged from non-detectable to 0.23 ug/m^3 with a mean of 0.07 ug/m^3 (Table VI).

B. Medical

Demographic information collected during the interviews provided the following background information on the work force. Sixty-two percent of the 56 workers interviewed were white, 14% were black, 16% were hispanic, and 7% were classified as others. Ninety-three percent were males. The average age of those interviewed was 39 years (range: 20-62 years). The median length of employment was 9 years (range: 1-37 years). Twenty-two (39%) reported that they currently smoked cigarettes, 15 (27%) reported that they were ex-smokers, and 19 (34%) stated that they had never smoked.

Respiratory System Evaluation

Review of the chest x-rays by two B readers (physicians trained and certified in interpreting x-rays for pneumonconiosis) showed no evidence of pneumoconiosis.

NIOSH analyzed the results of those PFTs which measured the forced vital capacity (FVC), the one-second forced expiratory flow (FEV_1), and the ratio of the FEV_1 to FVC. Other measurements of pulmonary function were not considered in this analysis. One worker had a slight decrement in FVC, which is indicative of a restrictive abnormality. [Restrictive abnormalities are often associated with connective tissue disease or fibrotic disease (pneumoconiosis).] This worker had worked at the Wilmington plant for at least 15 years and was currently a salaried employee. He was a non-smoker. Five workers had obstructive abnormalities as indicated by an FEV_1/FVC of <70% of predicted. This abnormality is commonly associated with cigarette smoking, but can also be caused by exposure to coal dust. When workers with abnormal results were stratified by work groups (salaried, operator assistants, and other production workers) and smoking history, the abnormal results appeared to be associated with cigarette smoking but not employment category (Table VII).

The respiratory questionnaire identified five workers with chronic bronchitis (productive cough on most days for three months out of the year, for two or more consecutive years). Seven workers reported chronic cough which did not meet the case definition of chronic bronchitis. Both chronic cough and chronic bronchitis were associated with smoking history but not employment category (Tables VIII and IX).

Skin Disorders

1980 Union Survey

Of 37 employees completing the survey questionnaire, 16 reported no skin problems; 15 reported problems, but did not see a doctor; and six workers reported seeking medical attention for a skin problem. The majority of workers with complaints associated the skin problems with working near the baghouse and/or waste dusts. Workers reported being exposed when waste dusts were emptied into containers by the OL Waste and during repair and maintenance of the baghouse.

1983 Company Interviews

In the 1983 interviews conducted by the GLC nurse, 21 (38%) of the workers reported skin problems since beginning work at GLC. Thirteen workers reported red itching skin, 12 reported dry cracked skin, 8 reported blisters, 15 reported blackheads, and 12 reported pimples. Workers reported skin problems on most body parts, with more than five workers reporting problems on the face, arms, legs, and hands.

Only two of these 21 reported having these problems prior to working at GLC. Fifteen had the problem prior to one year preceeding the interviews and 19 said that the problem still persisted. Six workers reported seeing a physician for this problem; two of them consulted dermatologists. Thirteen workers associated the skin problem with a particular job. Six associated it with work in the baghouse, two with waste dust, and the others with a variety of work areas or exposures.

Since the time of the company interviews the NIOSH medical investigator has spoken to a company representative and one of two workers whom the company sent to a dermatologist. Both stated that the dermatologist was unable to identify any work-related sensitivities in either of the two workers.

VII. CONCLUSIONS AND DISCUSSION

Most airborne dust exposures among workers doing routine jobs are less than 2 mg/m^3. Average dust exposures are about half of the exposure levels found at the Port Arthur plant, primarily because the coke is stored in silos instead of the open storage mounds used at Port Arthur.

The medical evaluation found little evidence for the current presence of respiratory hazards at the Wilmington GLC facility.

The results of the SLF-PNA elution study tend to reduce the concern over the prescence of PNAs in petroleum coke. Although PNAs were found to have some solubility in SLF, there was no indication of the SLF's ability to extract bound PNAs from the surface of petroleum coke. However, this is only a preliminary study of the biological availability of PNAs in coke, using a simulated lung fluid that has not been used extensively in previous PNA elution studies. While the evidence suggests that petroleum coke should not be included in the same class of "soot-like" substances associated with unadsorbed PNA compounds, the potential carcinogenicity of petroleum coke should not be completely ruled out until further studies are conducted. In the interim, exposures should be kept as low as possible.

Although the NIOSH medical officer did not conduct the interviews which elicited the reports of skin problems or examine the workers, a review of questionnaire responses indicates that workers (38% of those who participated in the survey) have experienced skin problems; most were possibly related to their work at GLC. A combination of heat and dust may cause some rashes. Often, harsh detergents or solvents are used to clean skin. These agents can remove the protective oil and outer layer of the skin, contributing to skin problems. Since the reported skin problems included a variety of manifestations (red skin, pimples, blackheads, blisters) it appears likely that they represent a number of conditions which could be caused by various agents (dust, oil, heat, sun, or a combinations of these). It appears unlikely that the dedusting oil (pure mineral oil according to ther manufacturer) is the direct source of the skin irritation. However, oils can block follicular openings in the skin, resulting in blackheads and perifollicular inflammation. Various dusts are also known to mechanically block these openings.

VIII. RECOMMENDATIONS

The very high dust levels generated during coke pit clean-up should be reduced or eliminated, preferably by repairing or replacing conveying machinery so it does not spill so much coke. In the interim, facepiece respirators with standard dust filter cartridges should be used, since they provide greater protection than the disposable dust masks. Respirators for coke pit workers should have a protection factor of 100, whereas the disposable dust masks are only rated a protection factor of 5. Most of the past problems with worker acceptance of the available half facepiece respirators probably were caused by attempts to use high efficiency particulate (HEPA) cartridges in the coke pits. These filters load up too quickly when used against high dust concentrations, resulting in discomfort and possible face seal leaks due to the increased breathing effort.

It is possible to use HEPA filters for high dust levels only when a standard dust prefilter is used. The prefilters can be frequently replaced while the more expensive HEPA filters can be kept in place for long use. Actually, the choice of filter systems is a trivial matter (99% efficiency for standard filter vs. 99.97% efficiency for HEPA filter) in comparison to the much more important issue of facepiece fit. Even with quantitative fit testing, half facepiece respirators should be considered to have a maximum protection factor of 100, regardless of the filters used. If quantitative fit testing can not be made available to coke pit workers, then full facepiece respirators with qualitative fit testing should be used.

Skin problems should be reported to the person responsible for health and safety at the plant, so that the problem can be monitored and better characterized. The company should make arrangements for employees to have ready access to a dermatologist who is familiar with the materials used in the plant and their effects on the skin. Protective clothing should be made available to workers. Pre-employemnt physical examinations with special emphasis directed toward the skin should be provided to all employees.

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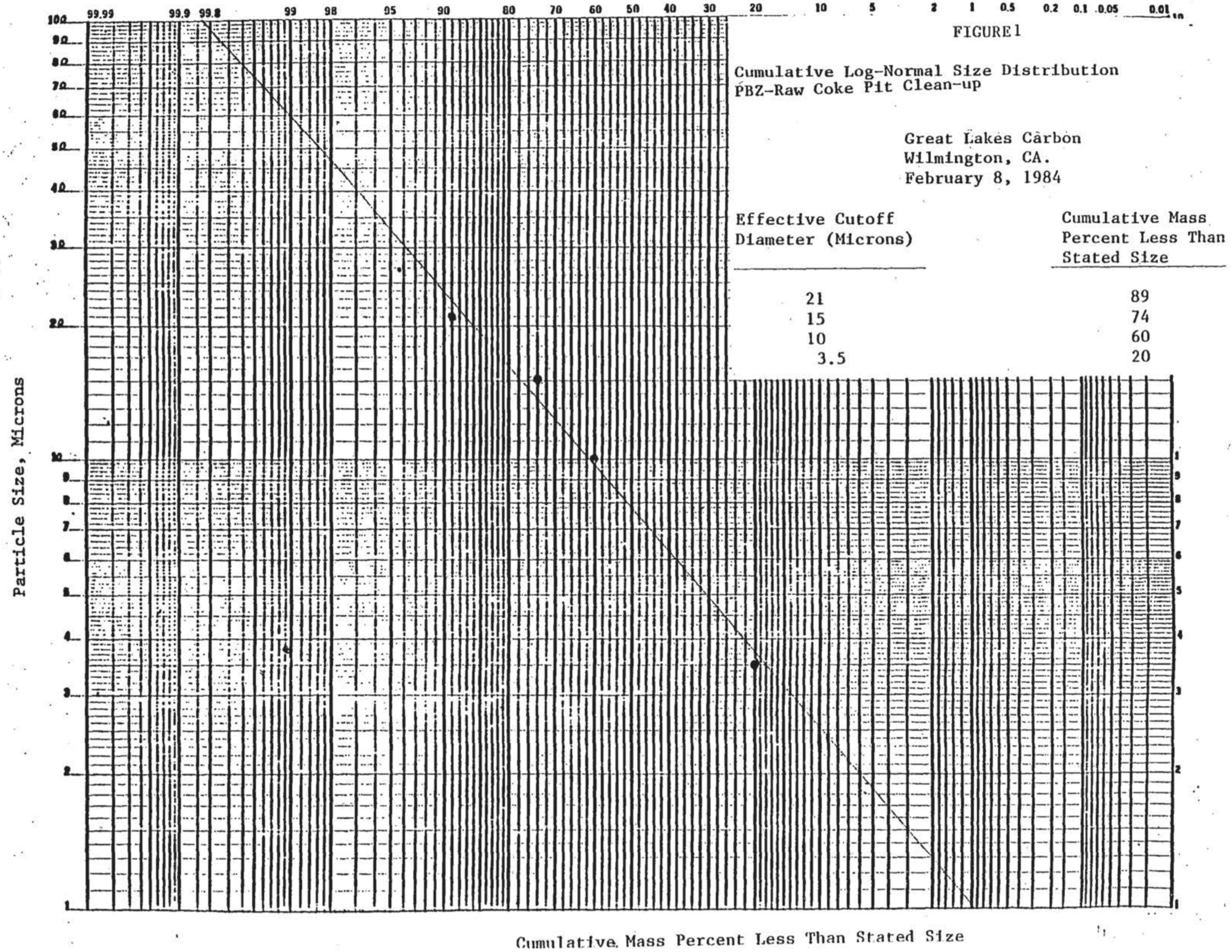

FIGURE 1

Cumulative Log-Normal Size Distribution
PBZ-Raw Coke Pit Clean-up

Great Lakes Carbon
Wilmington, CA.
February 8, 1984

Effective Cutoff Diameter (Microns)	Cumulative Mass Percent Less Than Stated Size
21	89
15	74
10	60
3.5	20

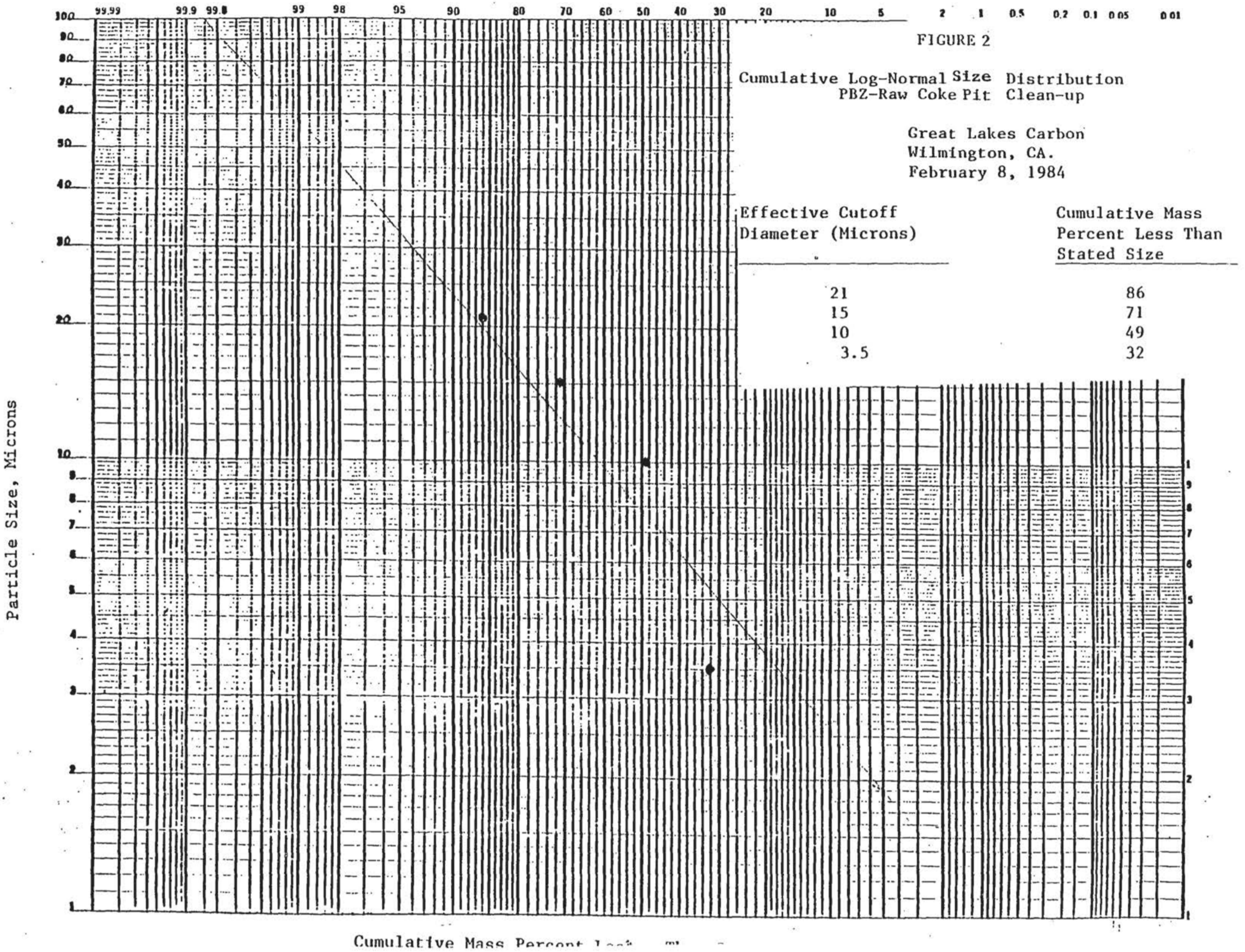

FIGURE 2

Cumulative Log-Normal Size Distribution
PBZ-Raw Coke Pit Clean-up

Great Lakes Carbon
Wilmington, CA.
February 8, 1984

Effective Cutoff Diameter (Microns)	Cumulative Mass Percent Less Than Stated Size
21	86
15	71
10	49
3.5	32

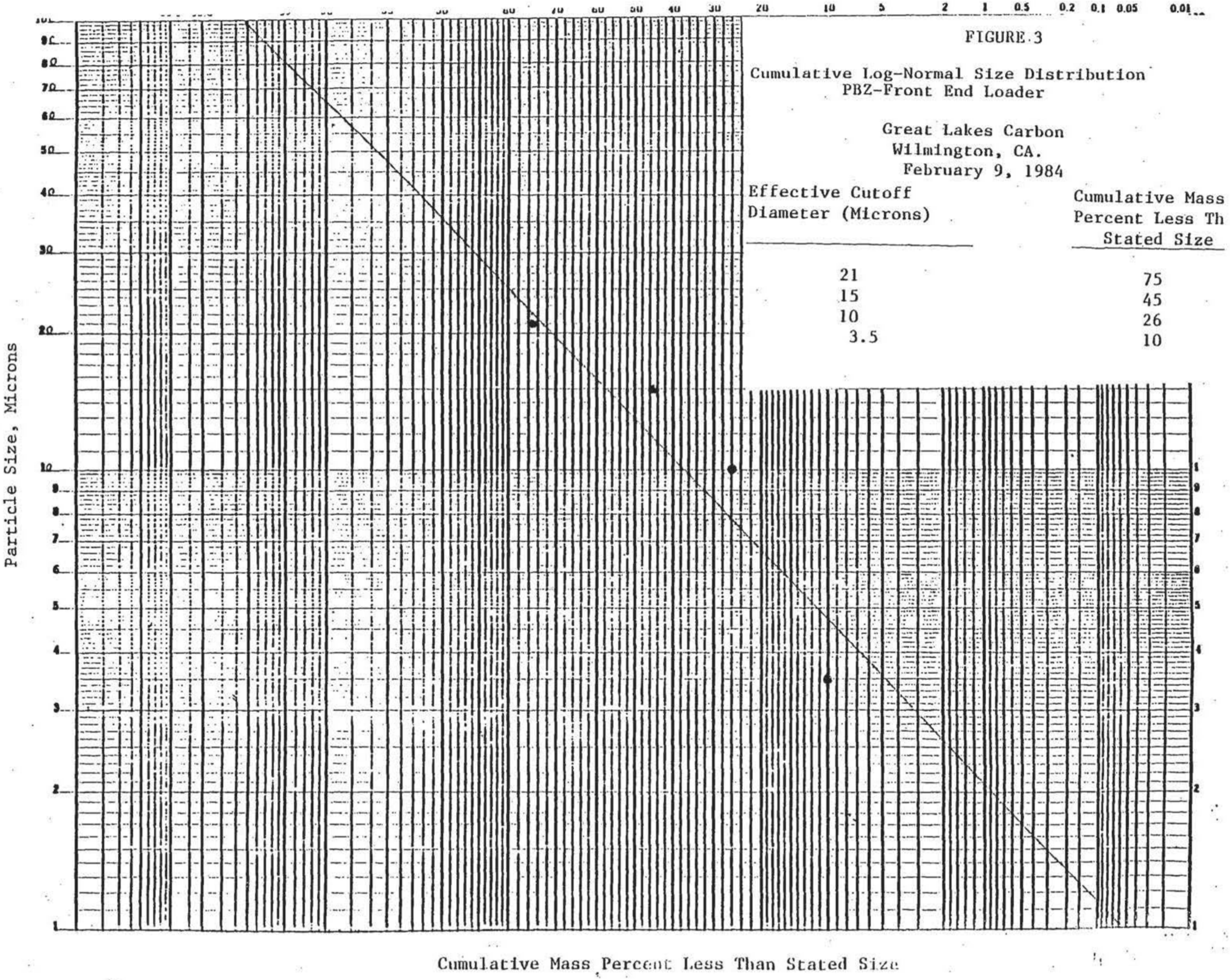

FIGURE 3

Cumulative Log-Normal Size Distribution
PBZ-Front End Loader

Great Lakes Carbon
Wilmington, CA.
February 9, 1984

Effective Cutoff Diameter (Microns)	Cumulative Mass Percent Less Th Stated Size
21	75
15	45
10	26
3.5	10

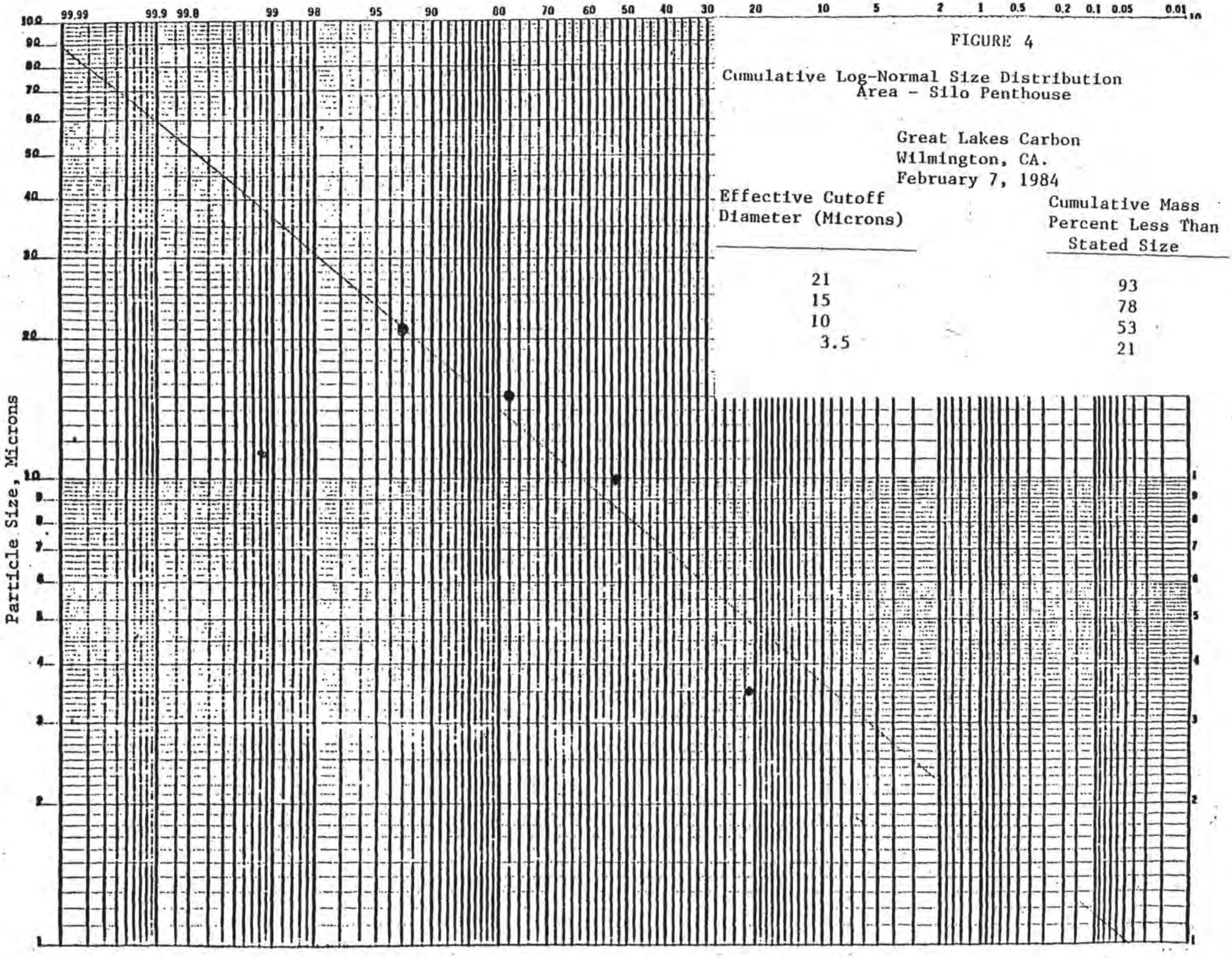

FIGURE 4

Cumulative Log-Normal Size Distribution
Area - Silo Penthouse

Great Lakes Carbon
Wilmington, CA.
February 7, 1984

Effective Cutoff Diameter (Microns)	Cumulative Mass Percent Less Than Stated Size
21	93
15	78
10	53
3.5	21

TABLE I

PNA Content of Petroleum Coke, Calcine, and Various Carbon Blacks* (ppm)

Substance	Extraction (solvent/hours)	Anthracene	Fluoranthene	Pyrene	Pyrene			Benzo (GHI) Perylene
					Benzo (a)	Benzo (e)	Indeno (123CD)	
Petroleum Coke	Benzene/24	2.9	2.9	19	12	23	1.9	11
Petroleum Coke	Cyclohexane/24	1.7	3.9	18	6.7	13	0.7	3.8
Calcine	Benzene/24	0.9	1.6	2.5	0.7	0.7	N.D.**	0.6
Calcine	Cyclohexane/24	0.3	0.2	1.6	0.3	0.3	N.D.	N.D.
Channel Black ASTM RCC	Toluene/48	N.D.	0.2	0.3	0.1	0.1	N.D.	0.7
Channel Black ASTM S301	Toluene/48	N.D.	0.5	0.3	0.11	0.2	0.1	0.5
Furnace Black ASTM N472	Toluene/48	N.D.	1.0	0.5	N.D.	-†	N.D.	N.D.
Furnace Black ASTM N375	Benzene/250	45	58	315	20††		24	166
Furnace Black ASTM N326	Benzene/250	-	9	58	1.0††		1.0	16
Furnace Black ASTM 330	Benzene/250	2.0	10	48	3.0††		0.3	25
Thermal Black ASTM N990	Benzene/24	300	200	600	190	145	-	220

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*Rivin, D. et al. "Environmental Health Aspects of Carbon Black", Rubber Chemistry and Technology, Vol. 55, No. 3, 1982

**N.D. = none detected

†- = not analyzed

†† = a and e isomers were not separated

TABLE II

Petroleum Coke Exposure Levels - Total Dust (mg/m^3), Benzene Soluble Fraction (mg/m^3), and PNAs (ug/m^3)

Great Lakes Carbon Corporation
Wilmington, California
HETA 82-341
February 8-9, 1984

Job	Sampling Period	Total Dust	Benzene Soluble Fraction	Acenaphthene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benz (A) Anthracene	Chrysene	Fluoranthene		Pyrene		Indeno (123CD) Pyrene	Dibenz (A,H) Anthracere	Benzo (GHI) Perylene
											Benzo (B)	Benzo (K)	Benzo (E)	Benzo (A)			
Calcine Operator	703-1413	0.1	ND*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Calcine Operator	700-1420	0.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Front End Loader	708-1418	1.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Lab Helper	711-1420		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Lab Helper	714-1400	12	ND	0.9	1.1	ND	ND	ND	ND	ND	ND	ND	0.3	ND	ND	ND	ND
Maint. Mechanic	712-1408	1.5	ND	0.3	0.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Maint. Mechanic	715-1416	1.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Maint. Mechanic	658-1432	2.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Maint. Mechanic	702-1409	1.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Utility	652-1404	1.1	ND	0.4	0.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Yard Labor	723-1430	1.7	0.5	ND	ND	ND	ND	ND	ND	2.6	0.6		1.1	2.9	ND	2.6	2.2

ND=NONE DETECTED

CONTINUED

TABLE II
(continued)
Petroleum Coke Exposure Levels - Total Dust (mg/m^3),
Benzene Soluble Fraction (mg/m^3), and PNAs (ug/m^3)

Great Lakes Carbon Corporation
Wilmington, California
HETA 82-341
February 8-9, 1984

Job	Sampling Period	Total Dust	Benzene Soluble Fraction	Acenaphthene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benz (A) Anthracene	Chrysene	Fluoranthene		Pyrene		Indeno (123CD) Pyrene	Dibenz (A,H) Anthracene	Benzo (GHI) Perylene
											Benzo (B)	Benzo (K)	Benzo (E)	Benzo (A)			
Coke Pit	718-1420	110	3.2	ND	2.4	ND	1.8	4.4	6.9	13	6.0		7.9	6.2	4.8	8.9	9.5
Coke Pit	709 1411	98	5.1	ND	2.5	ND	1.6	4.6	9.9	14	7.0		13	9.0	4.6	9.0	12
Coke Pit	711 1404	150	7.1	ND	3.8	ND	3.3	8.0	12	19	14		16	13	8.3	11	15
Coke Pit	716-1406	190	6.5	ND	3.0	ND	6.5	11	14	23	14		18	15	8.4	11	17

ND=NONE DETECTED

TABLE III

Bulk Samples - Soluble Fractions and PNA Content (ppm)

Great Lakes Carbon Corporation
Wilmington, California
HETA 82-341
February 8-9, 1984

Substance	Acetonitrile Soluble Fraction (mg/g)	Cyclohexane Soluble Fraction (mg/g)	Benzene Soluble Fraction (mg/g)	acenaphthylene	acenaphthene	fluorene	phenanthrene	anthracene	fluoranthene	pyrene	B(c)P	B(a)A	chrysene	B(b)F + B(k)F	B(e)P	B(a)P	indeno (123-cd) pyrene	dibenz(ah)anthracene	benzo(ghi)perylene	Cumulative PNA concentration
Fresh coke from Mobile[ω]	4.2	3.4	8.8	<1	2	<1	5	3	5	8	2	22	30	15	10	6	<2	<2	6	110
Fresh coke from IVEC[ω]	5.5	3.6	11	<1	<1	<1	6	3	5	7	2	25	21	25	11	8	<2	2	9	120
Conveyor Pit rafter sample	8.8	7.5	19	<1	5	2	15	7	13	26	5	68	79	30	30	18	4	5	22	330
Silo rafter sample	12	7.9	21	<1	2	<1	14	5	12	22	5	41	65	34	32	18	4	7	21	280
Calcine-directly from kiln (no oil)	0.5	0.3	0.3	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<2	<2	<2	<2	<2	<2	N.D.
Texaco 1666[ω] "dedusting oil"	57	1000	1000	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<200	<200	<200	<200	<200	<200	N.D.
Calcine-final product (oiled)	1.5	3.5	3.2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<2	<2	<2	<2	<2	<2	N.D.
Waste dust from baghouse	2.9	0.6	0.5	<1	<1	<1	<	<1	<1	<1	<1	<1	<1	<2	<2	<2	<2	<2	<2	N.D.

TABLE IV

Airborne Particulate PNA Sampling Results in ug/m^3

Great Lakes Carbon Corporation
Port Arthur, Texas
HETA 81-421

January 26-27, 1982

Job/Location	Sampling Period	Benzene Soluble Fraction Concentration	Cumulative PNA Concentration	Phenanthrene*	Anthracene*	Fluoranthene	Pyrene*	Benz (A) Anthracene*	Chrysene*	Fluoranthene		Pyrene*		Perylene	Indeno* (123CD) Pyrene	Benzo* (GHI) Perylene	Dibenz* (AH) Anthracene
										Benzo (B)	Benzo (K)	Benzo (E)	Benzo (A)				
Front End Loader	8:06-14:45	1600	1.1	0.07	0.02	0.02	0.07	0.09	0.16	0.09	N.D.*	0.13	0.09	0.01	0.04	0.09	0.05
Front End Loader	8:10-14:45	280	3.5	0.20	0.01	0.13	0.18	0.34	0.52	0.27	N.D.	0.46	0.38	0.02	0.09	0.26	0.45
Front End Loader	15:00-21:32	<70	0.76	0.03	0.02	0.02	0.07	0.08	0.12	0.07	N.D.	0.10	0.08	0.01	0.03	0.05	0.08
Front End Loader	7:41-14:38	<70	0.56	0.04	0.02	0.02	0.07	0.03	0.04	0.06	N.D.	0.10	0.09	0.10	0.01	0.05	0.05
B Operator	7:23-14:50	170	0.44	0.03	0.01	0.01	0.02	0.04	0.06	0.04	N.D.	0.05	0.04	0.01	0.01	0.05	0.02
B Operator	7:31-14:50	80	0.65	0.04	0.01	0.01	0.05	0.06	0.09	0.05	N.D.	0.08	0.07	0.01	0.03	0.06	0.03
Operator Helper	7:35-14:51	1100	6.9	0.31	0.15	0.12	0.54	0.57	1.2	0.66	N.D	0.95	0.80	0.11	0.28	0.80	0.36
Operator Helper	7:55-14:54	<70	0.37	0.02	0.01	0.01	0.03	0.03	0.05	0.03	N.D.	0.04	0.03	0.01	0.01	0.03	0.02
Car Unloader	14:50-21:35	<70	0.74	0.06	0.01	0.02	0.07	0.07	0.12	0.06	N.D.	0.01	0.08	0.01	0.02	0.05	0.07
Car Unloader	15:05-21:35	70	1.2	0.07	0.02	0.05	0.10	0.10	0.19	0.09	N.D.	0.13	0.10	0.02	0.05	0.10	0.06
Unloading Opr.	7:38-14:37	<70	0.29	N.D.	0.01	0.01	0.02	0.02	0.04	0.02	N.D.	0.03	0.02	0.01	0.01	0.02	0.01
Unloading Opr.	14:57-21:30	<70	0.10	0.02	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Silo Operator	15:10-21:50	320	2.9	0.14	0.10	0.05	0.24	0.22	0.47	0.22	N.D.	0.37	0.35	0.05	0.11	0.34	0.18
Sample Operator	8:22-14:45	<70	1.4	0.17	0.03	0.40	0.12	0.09	0.19	0.19	N.D.	0.15	0.12	0.01	0.04	0.11	0.06
Maintenance Helper	7:26-14:59	5100	36	2.4	0.90	0.70	3.3	3.6	6.2	3.0	N.D.	4.7	3.9	0.42	1.6	3.3	2.1
Area Sample Calcine Transfer House	8:10-13:18	1600	0.20	0.06	0.03	N.D.	N.D.	N.D.	0.02	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.01
Area Sample Dedusting Oil Station	8:15-13:15	3300	1.1	0.09	0.20	0.14	0.14	0.16	0.16	0.03	N.D.	0.07	0.06	N.D.	0.01	N.D.	N.D.
Area Sample Lunchroom	8:10-15:00	230	0.43	0.02	0.01	0.01	0.02	0.02	0.04	0.02	N.D.	0.03	0.02	0.01	0.01	0.02	0.01

* These compounds are listed as having some cancer-causing potential in the 1980 NIOSH Registry of Toxic Effects of Chemical Substances.

** N.D. = none detected

TABLE V

Exposure to Phenanthrene Vapor

Great Lakes Carbon
Wilmington, California
HETA 82-341
February 8-9, 1984

Job	Sampling Period	Phenanthrene (ug/M^3)
Calcine Operator	703-1413	ND
Calcine Operator	700-1420	ND
Front End Loader	708-1418	0.1
Lab Helper	711-1420	ND
Lab Helper	714-1400	0.3
Maintenance Mechanic	712-1408	0.3
Maintencance Mechanic	715-1416	0.2
Maintenance Mechanic	658-1432	0.4
Maintenance Mechanic	702-1409	0.1
Utility	652-1404	ND
Yard Labor	723-1430	ND
Coke Pit	718-1420	ND
Coke Pit	709-1411	ND
Coke Pit	711-1404	ND
Coke Pit	716-1406	ND

ND = None detected (<0.1 ug/M^3)

TABLE VI

Exposure to Phenanthrene Vapor

Great Lakes Carbon Corporation
Port Arthur, Texas
HETA 81-421
Janury 26-27, 1982

Job/Location	Sampling Period	Phenanthrene(ug/m^3)
Front End Loader	806-1445	0.23
Front End Loader	810-1445	0.10
Front End Loader	1500-2132	N.D.
Front End Loader	741-1438	N.D.
B Operator	723-1450	0.06
B Operator	731-1450	0.06
Operator Helper	735-1451	0.05
Operator Helper	755-1454	0.05
Car Unloader	1450-2135	N.D.
Car Unloader	1505-2135	0.08
Unloading Operator	738-1437	0.08
Unloading Operator	1510-2150	0.08
Silo Operator	1510-2150	0.03
Sample Operator	822-1445	0.03
Maintenance Helper	726-1459	0.09
Area Sample - Calcine Transfer House	810-1318	0.08
Area Sample - Dedusting Oil Station	815-1315	0.07
Area Sample - Lunchroom	810-1500	0.19

N.D. - non detectable (<0.02 ug/m^3)

TABLE VII

NUMBER OF WORKERS WITH FEV_1/FVC LESS THAN .70 BY CURRENT JOB AREA AND SMOKING HISTORY

Great Lakes Carbon Corporation
Wilmington, California
HETA 82-341
July 1983

	HOURLY	OPERATOR TRAINEE	SALARIED
CURRENT SMOKER	2	0	2
X-SMOKER	0	0	0
NON-SMOKER	0	0	1
	2	0	3

TABLE VIII

NUMBER OF WORKERS REPORTING CHRONIC COUGH BY CURRENT JOB AREA AND SMOKING HISTORY

Great Lakes Carbon Corporation
Wilmington, California
HETA 82-341
July 1983

	HOURLY	OPERATOR TRAINEE	SALARIED
CURRENT SMOKER	1	2	2
X-SMOKER	0	1	1
NON-SMOKER	0	0	0
	1	3	3

TABLE IX

NUMBER OF WORKERS WITH CHRONIC BRONCHITIS* BY CURRENT JOB AREA AND SMOKING HISTORY

Great Lakes Carbon Corporation
Wilmington, California
HETA 82-341
July 1983

	HOURLY	OPERATOR TRAINEE	SALARIED
CURRENT SMOKER	1	0	2
X-SMOKER	0	1	1
NON-SMOKER	0	0	0
	1	1	3

*See text for definition

APPENDIX

Experimental Laboratory Investigation of the Bioavailability of PNAs from Petroleum Coke

A study designed to learn more about the physiological significance of PNAs in petroleum coke was conducted. A portion of a coke rafter sample was sieved to the respirable size (<7um) and both the respirable and rafter samples were investigated for their extract content, adsorptive capacity, and potential for elution of selected PNAs by a simulated lung fluid. Dipalmitoyl phosphahdycholine (DPPC) vesicles provide a reasonable model of pulmonary surfactant which lines the alveoli and is composed of about 50% DPPC.[1]

I. Methods

The first task performed was the exhaustive extraction from both petroleum cokes of the adsorbed organic compounds. Two Soxhlet extraction systems were cleaned with toluene. Aliquots of 11.7300 g rafter petroleum coke and 6.1327 g of respirable petroleum coke were placed individually into Whatman cellulose extraction thimbles (I.D. 27mm, external length 80 mm) that had been washed with toluene. The two cokes were extracted for 100 hours with hot toluene. Essentially, all PNAs with molecular weights up to 300 daltons are extracted from furnace blacks in 48 hours with toluene.[2] Benzo[a]pyrene contains approximately 252 daltons. This extraction efficiency and the ease of solvent removal was the basis for the choice of toluene as the extraction liquid.

The sample extracts in toluene were transferred to 250 mL actintic volumetric flasks. The extraction round bottom flasks were rinsed serially three times with toluene and the washings added to the extracted samples. The extracts were then taken to 250 mL total volume. Both fractions of the petroleum coke were extracted in the same manner with fresh toluene to insure that the organics were removed from the coke's surface.

The extracted lots of the petroleum coke were used as blank media for the spiking and recovery study. Aliquots of approximately 100 mg of each coke were placed into individual 50 x 6 mm culture tubes. The blank petroleum coke in the tubes was dried in an oven overnight at a temperature of 85°C to drive off the residual toluene and activate the surface of the petroleum coke.

GC/MS Analysis:

The content of the organic compounds extracted from both petroleum cokes was determined. The analysis was performed on a VG 7070 HS mass spectrometer interfaced with a HP 5840 gas chromatograph and a VG 2250 data system. The gas chromatograph was equipped with a 30 meter capillary DB5 column with splitless injection of 1 uL. The carrier gas flow was 1.8 mL/min. The injection temperature was 300°C and the interface temperature was 290°C. The column temperature was programmed from 60 to 300°C at 12° per minute with a final hold of 10 minutes. The mass spectrometer parameters were an ion source temperature of 280°C, an emission current of 200 uA, a scan rate of 1 second per decade over a mass range of 360 to 24 amu, and resolution of 2000 (10% valley definition).

Simulated Lung Fluid:

An artificial lung fluid was used rather than fluid extracted from lungs of slaughtered animals. This choice allowed greater control of the experiment, eliminated the variability introduced by the natural fluids, and allowed the experiment to be reproducible.

The composition of canine pulmonary surfactant is 50% dipalmitoylphosphatidylcholine, 25% unsaturated phosphatidylcholines, 5-10% phosphatidyglycerol, 5% cholesterol, and 8-10% proteins.[3] The biochemical composition of adult human lung surfactant is similar except that the phosphatidylglycerol surfactant contains considerably less saturated fatty acids.[4]

Lakowicz, England, and Hidmark prepared a simulated lung fluid in their work involving transport of PNAs from particulate to lipid layers.[5] They prepared phospholipid vesicles of dipalmitoyl-L- -phosphatidylcholine suspended in buffer at a lipid concentration of 10 mg/mL. The buffer was 0.01 M Tris/0.05 M KCl/pH 7.5. This procedure for preparing simulated lung fluid was chosen for this study.

The simulated lung fluid was prepared in the following manner. A 100 mg aliquot of dipalmitoyl-L-a-phosphatidylcholine (DPPC) was weighed into a 20 mL scintillation vial. The stock was purchased from Sigma Chemical Corporation, St. Louis, Missouri, and was received as a white powder. The powder was dissolved in chloroform, the cholorform evaporated, and the DPPC recovered in the crystalline form. Ten mL of a buffer consisting of 0.01M Tris/0.05 M KCl/pH 7.5 was added. The solution was agitated in an ultra-sonic bath at a temperature of 50°C for four hours with occasional swirling. The solutions were allowed to stand overnight and the excess DPPC settled to the bottom. The supernatant was removed and used as the simulated lung fluid. It is a cloudy liquid with no native fluorescence.

Fluorescence Measurements:

All fluorescence measurements were performed on a Perkin-Elmer 650-40 Fluorescence Spectrophotometer interfaced to a XY recorder. The source was a 150 watt xenon lamp. All measurements were made in 1 cm cuvettes and both excitation and emission slit widths were initially 3nm. The slit widths were increased to attain greater sensitivity when warranted. The emission spectrum was determined by scanning emission wavelengths with the excitation wavelength set at a maximum. The excitation spectrum was determined by scanning excitation wavelengths with the emission wavelength set at a maximum. These maxima were determined instrumentally in the pre-scan mode of the instrument. Data were collected from the scans by monitoring the fluorometric response of the samples at several maxima.

Benz(a)Anthracene Study:

The initial work concerned the elution of benz(a)anthracene (BaA). A study to ensure that the measurements would be a reflection of the uptake of BaA by the phospholipid vesicles rather than residual or undissolved BaA in the microcrystalline form was completed. A spiking solution was prepared at a concentration of 151.8 ug/mL in toluene. Using a microsyringe, 100 uL of the BaA spiking solution was added to a series of 4 mL sampling vials and the toluene was allowed to evaporate.

The amount added to each vial was 15.8 ug. The BaA remaining was dissolved in 3 mL of the simulated lung fluid (SLF), the Tris buffer solution, toluene, methanol, or water. These samples were agitated for 4 hours in an ultrasonic bath at 50°C. The Tris buffer and water solutions gave emission maxima at 403 nm, 420 nm, and 485 nm as shown in Figure 1. The SLF, toluene, and methanol solutions gave emission maxima at 390 nm, and 436 nm as shown in Figure 2. This spectral shift was used to differentiate between the BaA taken up by the SLF and any microparticulate present as a result of its limited solubility. Filtering the water and Tris effectively eliminated all fluorometric response but the response remained when the SLF was filtered. This experiment effectively demonstrated the ability of SLF to dissolve BaA.

An aliquot of 100 uL of the BaA solution was spiked into six of the respirable petroleum coke tubes, six of the native petroleum coke tubes, and six of the 4 mL vials. Each of the tubes contained approximately 100 mg of coke. Care was taken to spike the petroleum coke in the center to minimize wetting the tube walls. After allowing the toluene to evaporate, the petroleum coke was transferred into 4 mL vials. Three mL of SLF was added to each vial and agitated for 4 hours by an ultrasonic bath at a temperature of 50°C. The vials were swirled periodically to ensure complete wetting of the petroleum coke. The vials werea llowed to stand overnight to allow particulate to settle.

The samples were divided into six sets with each set consisting of a respirable spike, native spike, vial spike, and a SLF blank. The supernatant was transferred into a 1 cm cuvette and measured fluorometrically.

Benzo(a)pyrene Study:

The next phase of the study involved the elution of Benzo(a)pyrene (BaP). A standard solution of BaP was prepared at a concentration of 4.046 mg/mL in toluene. Nine respirable petroleum coke tubes, nine native petroleum coke tubes, six empty 4 mL vials, and three 4 mL vials containing 3 mL of toluene were spiked with 25 uL of the standard solution. Care was taken to spike the petroleum coke in the center to minimize the wetting of the tube walls. The amount spiked onto each medium was 101.15 ug/sample. The solvent was allowed to evaporate from the tubes and empty vials and the petroleum coke was transferred to 4 mL vials.

Six sample sets were extracted with 3 mL of SLF. Each of these sample sets consisted of a SLF extract of respirable petroleum coke, a SLF extract of native petroleum coke, a SLF extract of a vial spiked with BaP, and a SLF blank. Three more sample sets were made by extracting the remaining petroleum coke spikes with 3 mL of toluene. Each of these samples sets included the toluene extract of the respirable petroleum coke, the toluene extract of the rafter petroleum coke, a BaP spike into toluene and a toluene blank. All of the sample sets were extracted by agitation by a sonic bath for 4 hours at 50^{o}C.

16 PNAs Study:

The next phase of the study concerned the elution from petroleum coke of 16 of the most common PNAs. Sets of samples the same as that of the BaP study were spiked with 50 uL of a commercial polynuclear aromatic hydrocarbon mix. The mixture contained 2000 ug/mL each of acenaphthene, anthracene, benzo(a)pyrene, benzo(ghi)perylene, chrysene, fluoranthene, indeno(1,2,3-cd)pyrene, phenanthrene, acenaphthylene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthrancene, fluorene, naphthalene, and pyrene. This corresponds to 100 ug of each PNA per sample or a total of 1600 ug of PNA per sample.

II. Results

GC/MS Analysis

The compounds that were identified by GC/MS analysis from the toluene extracts are given in Table I. No differences in composition between the respirable and rafter petroleum coke were observed. No compounds were detected from a second extraction with toluene. A semi-quantitation of the concentrations of benz(a)anthracene and benzopyrene was calculated. These determinations were based on the area exhibited by the molecular ion. The concentration of benzopyrene in the respirable portion was 4.5 ug/g while that of the rafter was 3.4 ug/g. The concentration of benz(a)anthracene was 2.7 ug/g for the sieved portion and 2.1 ug/g for the rafter portion.

Benz(a)Anthracene

Figure 2 shows the fluorometric analysis of a representative sample set. The emission wavelength was set at 344 nm and an excitation scan was monitored over the range of 355 to 600 nm. The fluorometric response was measured at the excitation maxima of 390 nm, 412 nm, and 436 nm. The scan marked SLF shows the BaA taken up by the phospholipid vesicles. Comparison of the six sets showed an agreement within 10%. The scan marked R shows the analysis of the respirable petroleum coke spike while N shows that of the native petroleum coke spike. Measurement of the fluorometric response showed no elution of the BaA from either size of the petroleum coke. This held true for the other sets. The scans marked R2 and N2 show the R and N scans at a greater sensitivity. The increased sensitivity was achieved by reducing the recorder scale and widening the slit widths to 10 nm. No BaA was detected from any of the samples of either size petroleum coke when extracted with the simulated lung fluid. An analytical detection limit for BaA was determined to be 2.5 ng/mL in toluene.

Benzo(a)Pyrene

All the sample sets were measured fluorometrically. The excitation was set at 396 nm and the emission spectra from 400 to 600 nm was obtained. Figure 3 shows the emission spectra of a representative SLF extracted set. The fluorometric response was measured at 410 nm, 432 nm, and 458 nm for the BaP taken in toluene. No response for BaP was detected from the extraction of either size petroleum coke with SLF. The spectrum marked R shows the emission scan for the respirable petroleum coke extract while N marks the spectrum for the extracted native petroleum coke. Figure 4 shows a representative scan at a greater sensitivity than that of Figure 3. Again, the spectra marked R2 and N2 showed no response for BaP. An analytical detection limit for BaP was determined to be 8 ng/mL in toluene.

Extraction of the petroleum cokes with toluene did recover some of the BaP. Using the BaP spike in toluene as a standard, calculations based on an emission wavelength of 432 nm and an excitation wavelength of 396 nm gave a recovery of approximately 56% from the native petroleum coke and 41% from the respirable petroleum coke. This is an indication that PNAs are more tightly bound to smaller particle size petroleum coke. The exhaustive extraction of the coke demonstrated that more BaP were recovered from the respirable fraction. This may be a surface area phenomenom. With equivalent masses of materials, the smaller particle size would have a greater surface area and more adsorbed material could be recovered with rigorous extraction. The amount of BaP that was taken up by the phospholipid was calculated in the same manner. The amount of BaP taken up by the phospholipid vesicles from the vial was approximately 34%.

16 PNAs

The same extraction and analytic procedure was used as previously described. The excitation wavelength was set at 399 nm and the emission spectrum from 400 to 600 nm was obtained. Figure 5 shows representative spectra of a SLF extracted sample set with the spectrum marking the same. The emission maxima at 413 nm, 480 nm, and 508 nm were measured. The spectra of the SLF uptake was similar to that of toluene extracts. No fluorometric response was detected from the SLF extracted petroleum cokes at either sensitivity.

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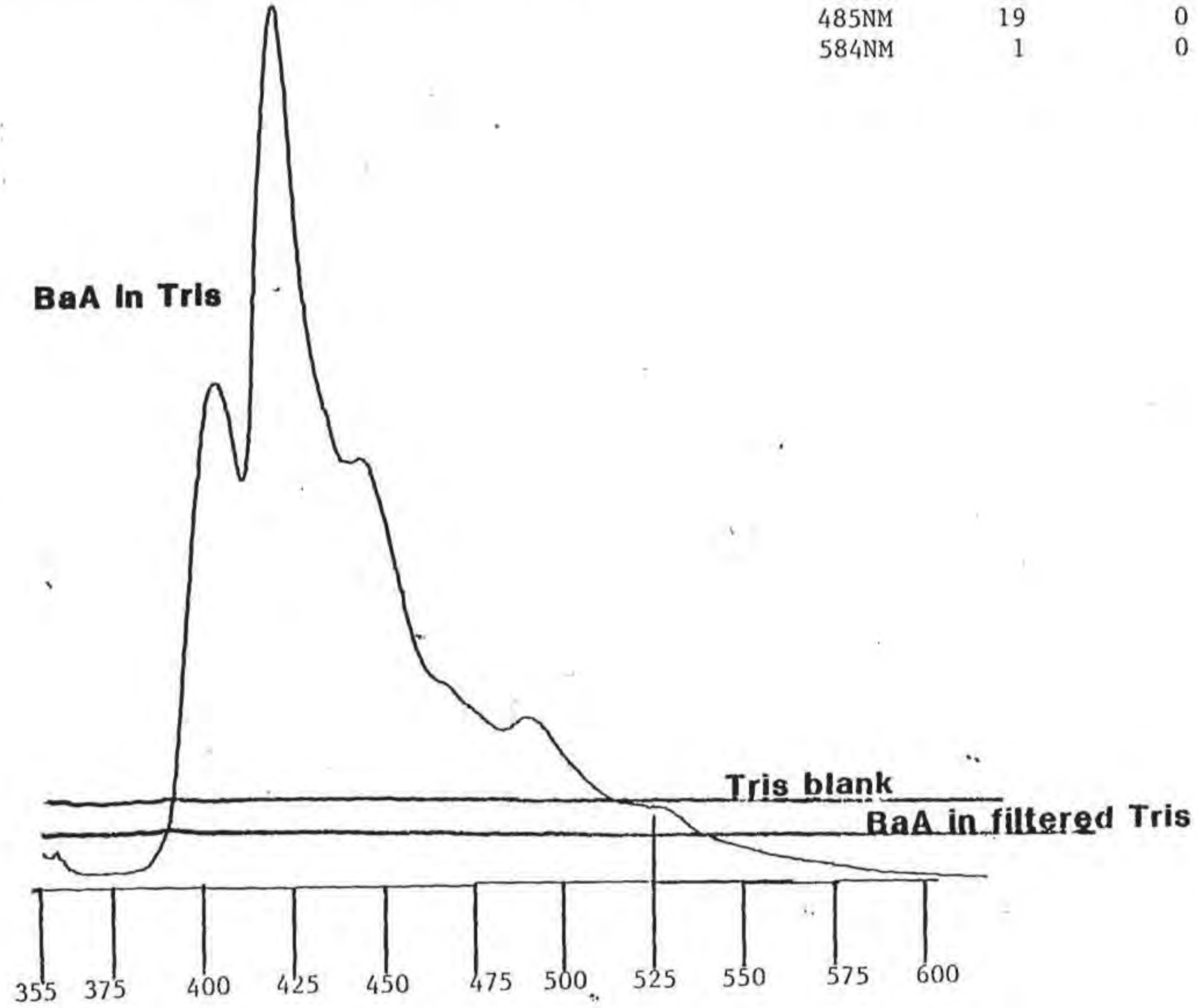
Ex 344
Em 355-600NM
Range 73.3

FIGURE 1

BAA IN TRIS BUFFER

Em λ	Mixed	Fil	Bk
390NM	3	0	0
403NM	25	0	0
420NM	41	0	0
485NM	19	0	0
584NM	1	0	0



Em 344

Ex 355-600
Range 137
Range 2 6.8

FIGURE 2

Ex	SLF	R	N
390	70	0	0
412	65	0	0
436	30	0	0
500	10	0	0
591	1	0	0

BAA EXTRACTED WITH SLF

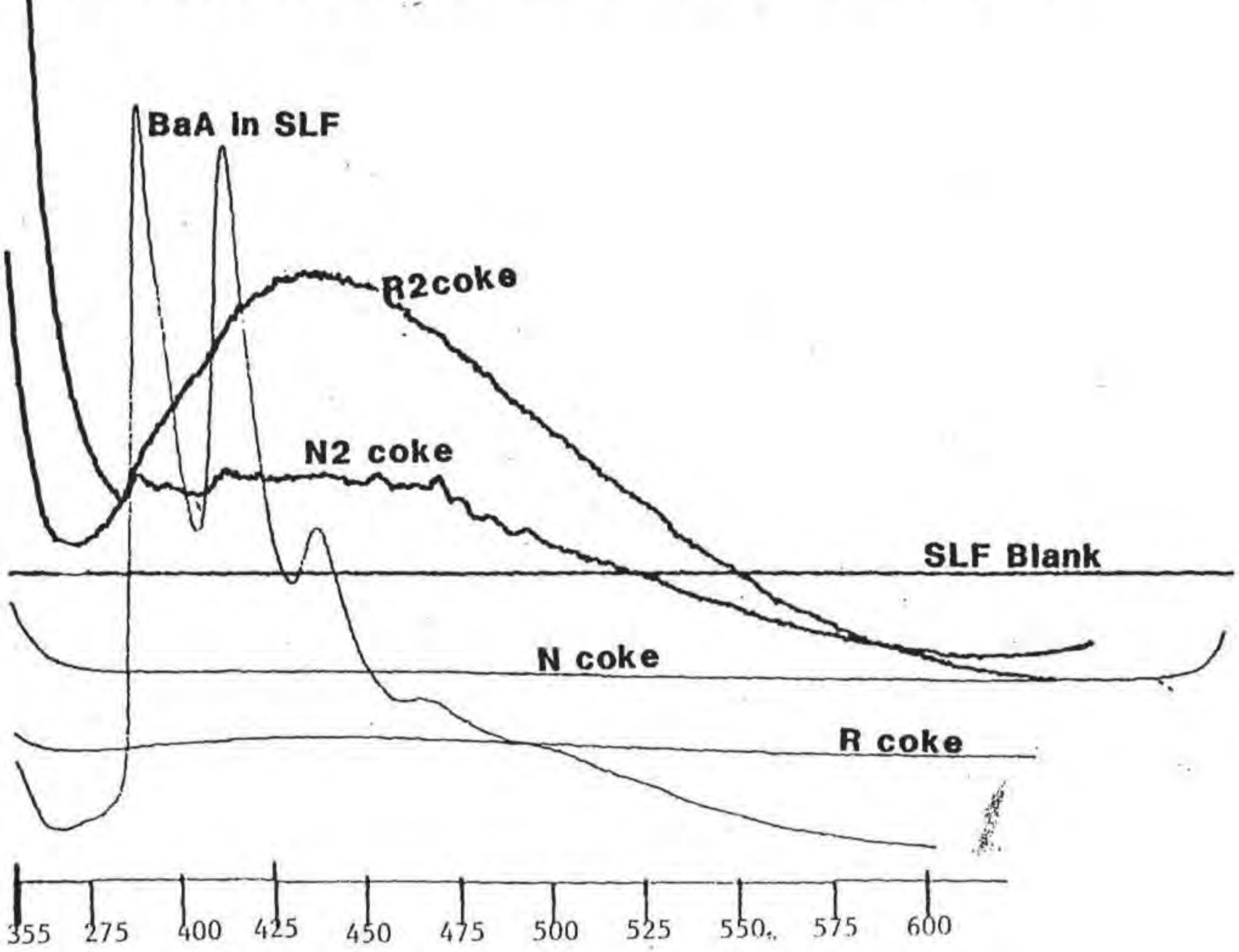
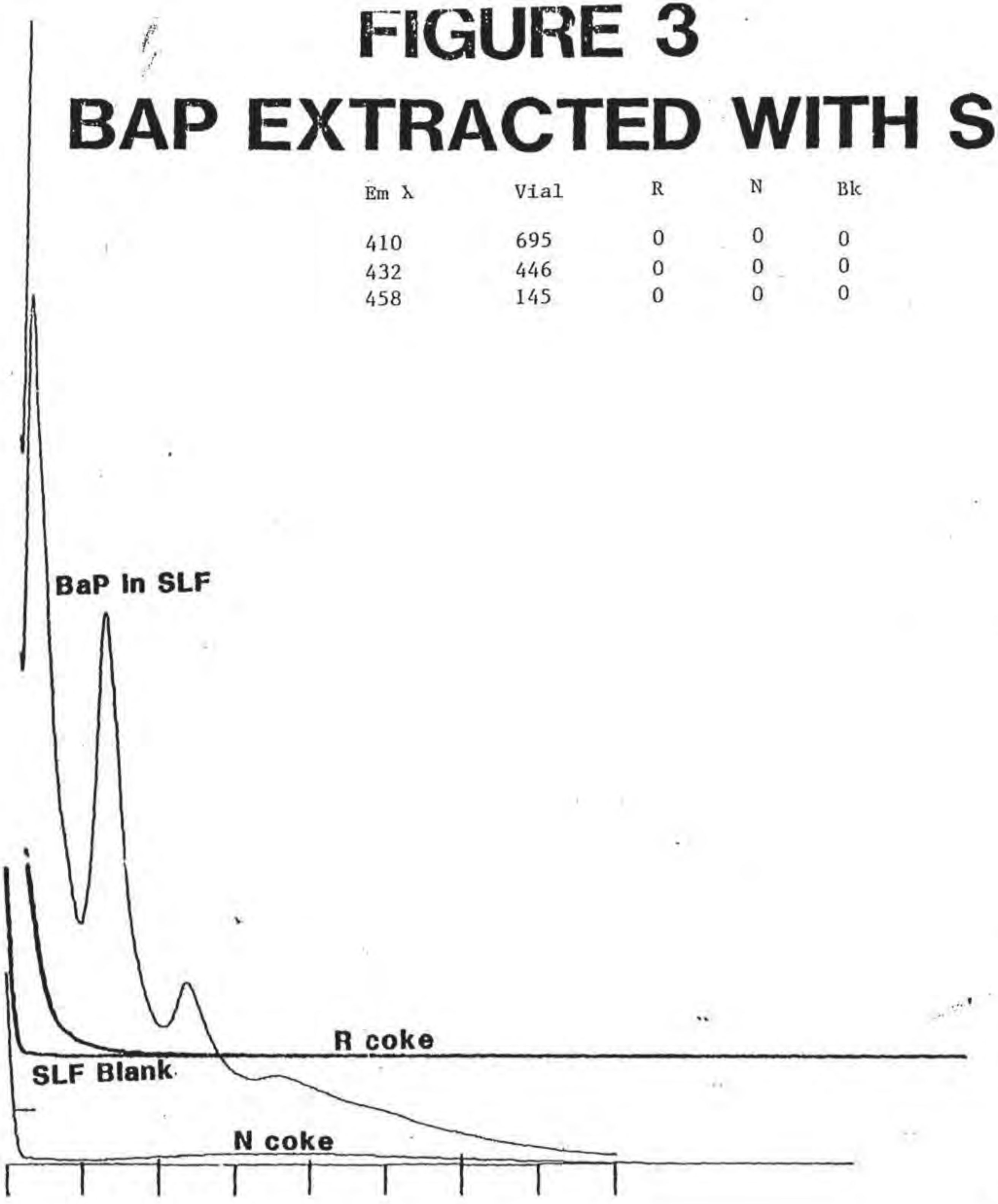


FIGURE 3
BAP EXTRACTED WITH SLF

Excitation 396NM
Emission Scan
400 - 600NM
Range 1058
Slit 3NM both

Em λ	Vial	R	N	Bk
410	695	0	0	0
432	446	0	0	0
458	145	0	0	0



Excitation 396NM
Emission Scan
400 - 600 NM
Range 14.6

FIGURE 4
BAP EXTRACTED WITH SLF

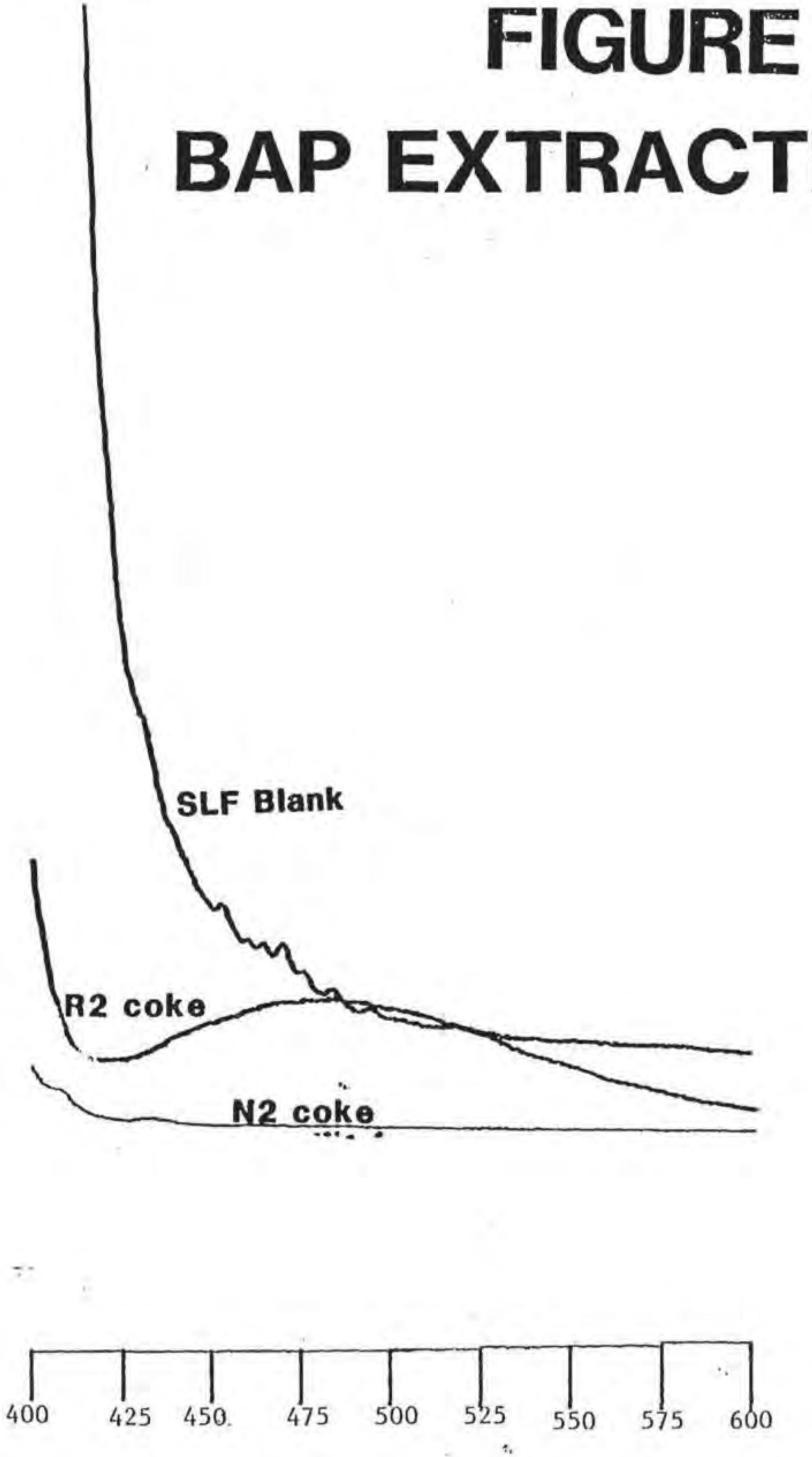


FIGURE 5
16 PNAS EXTRACTED WITH SLF

Ex 399 NM
Em Scan 400 - 600 NM

Em λ	V	N	S	Bk
413	29	0	0	0
480	22	0	0	0
508	25	0	0	0

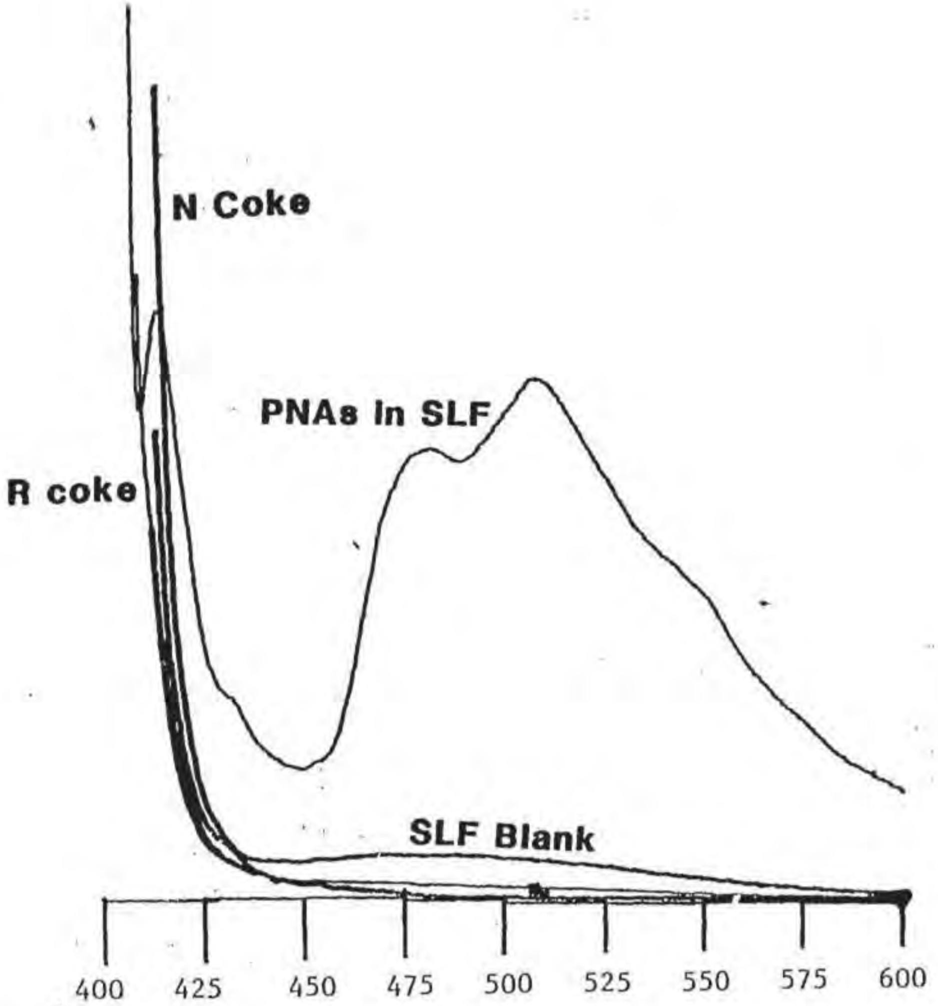


TABLE I

Compounds Identified by GC/MS Analysis

1. Trimethylbenzene (2 isomers)
2. Methyl phenol (3 isomers)
3. C_9 hydrocarbon
4. Tetramethyl benzene (2 isomers)
5. Naphthalene
6. C_{11} hydrocarbon
7. Benzothiozol
8. C_{12} hydrocarbon
9. Methyl naphthalene (2 iosmers)
10. C_{13} hydrocarbon
11. Biphenyl
12. C_{14} hydrocarbon
13. Dimethyl naphthalene (4 isomers)
14. C_{15} isomers
15. C_{15} hydrocarbon
16. Dibenzofuran
17. Trimethyl napnthalene (5 isomers)
18. C_{16} hydrocarbon
19. 9H-fluorene
20. 4-amino biphenyl
21. Branched C_{16} alkane
22. Methyl-9H-fluorene
23. 9H-Fluoren-9-one
24. Dibenzothiophene
25. Branched C_{16} alkane
26. Anthracene
27. Phenanthrene
28. Carbazole
29. Methyldibenzothiophene (2 isomers)
30. C_{17} hydrocarbon
31. Methyl anthracene
32. Branched C_{17} alkane
33. Methyl-9H-carbazole (2 isomers)
34. Methyl phenanthrene
35. Phthalate
36. C_{18} hydrocarbon
37. Phenyl naphthalene
38. Dimethyl-naphtho (2,3,-b) thiophene (2 isomers)
39. Dimethyl phenanthrene (4 isomers)
40. Fluoranthene
41. Methoxy anthracene
42. Pyrene
43. Methyl ethyl carbazole
44. H H Benzo (a) fluorene
45. Methyl pyrene (3 isomers)

TABLE I (continued)

46. Terphenyl (3 isomers)
47. Diphenyl thiophene
48. Benzo (b) naphtho (1,2-d) thiophene (2 isomers)
49. Chrysene
50 Benzocarbazole (2 isomers)
51. Benz (a) anthracene
52. Methyl benzo (b) naphtho (1,2-d) thiophene (3 isomers)
53. Binaphthyl (3 isomers)
54. Dimethyl benzo (b) naphtho (1,2-d) thiophene (2 isomers)
55. Methyl benzo carbazole (2 isomers)
56 Dimethyl benzo anthracene (3 isomers)
57. Benzo pyrene
58. Benzo fluoranthene
59. Perylene

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