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Health Effects of the Gas-Aerosol²⁴ Complex

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Report to Special Committee on Health and Ecological Effects of Increased Coal Utilization

by Bernard D. Goldstein*

Combustion products derived from the burning of coal are definitely capable of producing adverse human health effects. No single component of the combustion product mixture is solely responsible. Rather, effects are due to a group of compounds, both gases and aerosols, in the effluents of stationary source combustion processes. Although incompletely defined, the individual components of the gas-aerosol complex appear to be capable of interacting both in terms of atmospheric chemistry and health effects. The three primary air quality standards pertinent to regulating coal combustion all represent to some extent indirect, although reasonable, measures of this gas-aerosol complex. As a group, these standards appear to be adequate to protect human health. Conventional toxicological considerations suggest that the adverse health effects of any necessary increase in coal combustion effluents would be greatest per unit of coal in those areas which are most heavily populated and have the highest preexisting levels of the gas-aerosol complex. In order to decrease the degree of uncertainty for future decisions of this type, it is important that prospective epidemiological and air monitoring studies be initiated in conjunction with any large scale introduction of coal use.

Introduction

Combustion products derived from the burning of coal are clearly deleterious to human health. The causal relationship between coal emissions from combustion and disease, particularly of the respiratory tract, has been inferred for centuries. Modern appraisal of this relationship can be considered to have begun at the time of the London smog episode of 1952, although a few antecedent studies and local air pollution disasters (e.g., Donora, Pennsylvania in 1948; Meuse Valley in 1937) can be cited.

In 1952 London was characterized as having mul-

multiple emission point sources arising from coal combustion. Coal was used for heating of individual homes as well as for power generation and industry. In December 1952 weather conditions produced a four-day inversion period, which resulted in a marked increase in air pollutant levels. During the smog, and a few days subsequent to it, more than 3000 excess deaths were estimated to have occurred. This galvanized medical authorities in Britain and elsewhere to look very closely into the causes and consequences of air pollution, particularly in relation to coal combustion. The pollutants that were measured were, quite obviously, those that were amenable to analysis with the available technology. This led to a focus on sulfur dioxide and particulates (measured as smokes shade in Great Britain and total suspended particulates in the U.S.). While many studies used the level of these two indices to correlate with observed health effects, it was recognized

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at about the time of the 1952 London disaster that sulfur dioxide and smog were somewhat indirect indicators of the agents responsible for human effects. Since that time, much evidence has accumulated demonstrating that it is a complex of atmospheric products and mixtures of emitted pollutants which play the major causative role in adverse health effects due to fossil fuel combustion products. The group of compounds participating in this process, which will be discussed in more detail below, will be described as the gas-aerosol complex. Although the nature of the available information requires this document to treat this complex in its individual components, it should be kept in mind that it is the interplay of these many components which result in the deleterious human health effects associated with fossil fuel combustion.

Inasmuch as the focus is on coal, this document will stress studies in Great Britain where control of coal combustion effluents has led to a marked improvement in air quality, as well as American studies. Unfortunately, in neither country was there a rigorous attempt to study prospectively the health consequences of the major changes in fuel consumption and emission control that led to the presence of cleaner air. This lack of information is most unfortunate. It is possible to construct a graph depicting the decrease in atmospheric pollution levels in the recent past. Were one able to construct a similar curve showing changes in community health associated with the previous decrease in level of pollutants, it would now be a much simpler proposition to predict what effect, if any, would occur due to increased pollutant levels attendant upon conversion to coal. It is unlikely that retrospective studies in the United States will rectify this serious omission in view of our generally inadequate health statistics base. There is, however, the possibility, worthy of exploration, that pertinent information concerning the effect of decreasing coal use on human health could be obtained by a study of the more complete British health records. As an obvious corollary, a careful study of the effect of reinstitution of coal use should begin as soon as possible before the actual switchover occurs, and continue for some time afterwards. While such a study would be relatively expensive relative to the current funding level for studies of environmentally caused health effects, it is extremely cheap compared to the multibillion dollar impacts arising from decisions concerning the energy program.

It is assumed that those reading this review are reasonably knowledgeable concerning the biomedical effects of pollutants, the inherent limitations of the various types of toxicological studies, and the need for confirmatory information from differing ap-

proaches. A number of reviews describing the health effects of air pollutants have been published in recent years. These should be consulted for detailed information beyond the scope of this document (1-4).

The subject of health effects of photochemical oxidants will not be discussed in this review, although one of the precursors of these pollutants, oxides of nitrogen (NO_x), will be increased by the proposed switch from oil to coal. It is difficult to assess the effect of increased NO_x emissions on photochemical oxidant levels because of the complicated time-dependent set of reaction mechanisms leading to the formation of oxidants.

Constituents of the Gas-Aerosol Complex

The constituents of the gas-aerosol complex derived from stationary source fossil fuel combustion are usually subdivided into particles and gases (the major gases being sulfur oxides and nitrogen oxides). The subject of airborne particles has recently been reviewed by a panel of the National Academy of Sciences (5). Of importance is that the particles formed as a result of fossil fuel combustion tend to be in the respirable size range (i.e., $<1 \mu\text{m}$). The major anionic components of toxicological importance are sulfates and nitrates, and perhaps sulfites and nitrites as well. These are predominantly products formed in the atmosphere from reactions of the emitted gases (i.e., secondary products). More information about the levels of the associated cations is becoming available. These cations include trace levels of various metal elements, ammonium ions, and protons (hydrogen ions). The effects arising from trace elements are considered in a separate document.

Sulfur in fossil fuel is converted mainly into sulfur dioxide during combustion, although a small percentage is emitted directly as sulfate. Sulfur dioxide is a highly soluble gas which exists in solution, either as hydrated SO_2 or as the sulfite or bisulfite ion, depending upon pH. Two general processes associated with polluted atmospheres act to convert sulfur dioxide to sulfate aerosols. In the presence of various trace elements, SO_2 absorbed into aqueous aerosols is catalytically oxidized to H_2SO_4 (sulfuric acid). This process is highly dependent upon humidity, temperature, the type and quantity of trace elements present, and the pH of the aerosol. The second general pathway for the formation of atmospheric sulfates is through a photochemical process in which the action of sunlight on hydrocarbons and oxides of nitrogen generates species capable of oxidizing SO_2 . The complexity of both of these processes requires emphasis. There is a potentially large variety of dif-

ferent sulfates formed depending upon the cations. These sulfates have a wide range of physicochemical properties and, presumably, toxicity. Most are in the respirable size range. Further information concerning the mechanisms of formation, the reaction rates, the atmospheric transport, and the dispersion of sulfur oxides is necessary in order to better understand the toxic properties of the aerosols, and in order to attempt to construct successful control strategies. Of particular value would be a determination of the chemical speciation of sulfates present in ambient air. This would allow epidemiological and controlled human exposure studies to focus on those sulfates most likely to be responsible for toxicity. At present, however, there is little reason to expect that any one sulfur oxide will be solely or mainly responsible for the effects of the gas-aerosols complex. It should be kept in mind that sulfur in fuel and the resultant sulfur dioxide, are the precursors of essentially all anthropogenic sulfur oxide aerosols.

The nitrogen oxides have usually been considered separately from sulfur oxides and particulates in discussion of health effects of air pollutants. This in part is due to the fact that both stationary source and automotive fossil fuel combustion contribute substantially to atmospheric NO_x emissions. In the past, the toxicity of nitrogen oxides has been considered almost solely in terms of nitrogen dioxide. (Nitric oxide, the other major gaseous oxide of nitrogen, does not appear to be toxic at ambient concentrations). Recent information has suggested that aerosols containing nitric acid, organic and inorganic nitrates and nitrites are present in the atmosphere and may contribute to the observed toxicity of the gas-aerosol complex. The evolving evidence suggests a situation analogous to that described above for sulfate, i.e., the presence of nitrates concentrated in the respirable size range, and being derived from atmospheric transformation of gaseous NO_x precursors. There is, however, far less information concerning nitrate air chemistry and toxicology than there is for sulfate. The subject of nitrogen oxide formation and toxicity has recently been thoroughly reviewed by an NAS panel (2).

Basic Biomedical Considerations

Respiratory Tract Response to Inhaled Irritants

The human respiratory tract contains a number of relatively effective defenses against inhaled irritants. The nose is particularly efficient in removing those larger particles which impinge upon the nasal turbinates, and also in scrubbing out soluble gases such as

sulfur dioxide. Pollutant removal within the nose does not completely preclude pulmonary effects, as there is some evidence which suggests that vagal reflexes, leading to bronchoconstriction, may be initiated by nasal receptors. Breathing through the mouth also effectively removes soluble gases and larger particulates, but to a lesser extent than the nose. Smaller particulates, including most anthropogenic sulfates and nitrates, as well as less soluble gases such as NO_2 and O_3 , more readily penetrate deeply into the respiratory tract. In normal adults, mouth breathing usually occurs during periods of high minute volume when the dose delivered to the lower airways would tend to be highest. Such considerations presumably play a role in the susceptibility of children and individuals with pre-existing cardiorespiratory disease to pollution. Mouth breathing and high minute volumes occur relatively frequently in these population segments.

Acute Exposure. Mucociliary clearance is a cleansing process which results in a flow of mucoid material upwards toward the pharynx. There is unfortunately relatively little information concerning the basic determinants of mucociliary clearance rates or the effects of pollutants on this process. Although some studies have obtained indirect evidence of altered pulmonary clearance rates following exposure to components of the gas-aerosol complex, there is no evidence that usual ambient levels have an effect on this process. Of potential interest are recent animal studies suggesting that repetitive acute exposure to sulfuric acid aerosol during a period of months may lead to an alteration in baseline pulmonary clearance (5). Also of interest is the ability of mucosal secretions to buffer inhaled acid aerosols. This has been highlighted by recent studies suggesting that ammonia may be a constituent of the respiratory tract (6). If neutralization of acid aerosols does prevent toxicity, then it is conceivable that the buffering capacity of the respiratory tract is the basis for a true threshold for the acute effects of acid aerosols, although possibly subject to individual or temporal variability. This is, of course, speculative but represents an intriguing area of potential significance.

The alveolar macrophage is an important component of pulmonary defense. There is some evidence suggesting that the basis for the potentiation of respiratory tract infections by nitrogen dioxide may be an interference in the ability of alveolar macrophage to kill inhaled microorganisms (7, 8). Such evidence is not available for sulfur oxides. More information concerning the effect of inhaled particulates on alveolar macrophage function is needed. A better understanding of the mechanism of the bacteriocidal

mechanisms employed by the macrophage is also required.

The major physiological response to sulfur oxides in controlled short-term human and animal exposure studies is an increase in airway resistance. In animal studies, sulfuric acid aerosol has been shown to be a stronger potentiator of bronchoconstriction than ammonium sulfate aerosol which is stronger than SO_2 gas (9). The pathways mediating bronchoconstriction, which is generally believed to be the basis for this response, include vagal reflexes set off by receptors located in various parts of the respiratory tract. However, studies have shown that bronchoconstriction can occur even when the vagus nerve has been inactivated. It is hypothesized that humoral factors are capable of acting on airway smooth muscle, or may potentiate the effect of such factors. *In vitro* studies have shown that acid salts are enhancers of histamine release from cells (10). This bronchoconstrictive response could account for many of the adverse health consequences associated in epidemiological studies with the gas-aerosol complex. Controlled human studies on asthmatics have shown that short-term NO_2 exposure potentiated the bronchoconstrictive effect of carbachol (11).

Long-Term Exposure. Studies of the effects of long-term exposure of animals to sulfate aerosol have produced evidence of some effects, but in general, the findings have not been dramatic. Slight bronchial epithelial proliferation, edema and alveolar wall thickening in animals exposed to at least $500 \mu\text{g}/\text{m}^3$ of sulfuric acid has been reported, as has a decrease in CO lung diffusion capacity in beagles continually exposed to H_2SO_4 for up to two years (12).

Monkeys continually exposed to H_2SO_4 levels of $100 \mu\text{g}/\text{m}^3$ for one year have shown no evident lung abnormalities. At H_2SO_4 exposure levels of about $1000 \mu\text{g}/\text{m}^3$ in conjunction with about $500 \mu\text{g}/\text{m}^3$ fly ash particles, bronchiolar wall thickening was observed (13). Occupational studies of workers chronically exposed to H_2SO_4 levels above $10,000 \mu\text{g}/\text{m}^3$ have not indicated excess chronic disease incidence, but have indicated an excess number of acute attacks in those individuals already suffering from chronic respiratory disease, such as bronchitis. These results yield an unclear picture of possible long-term acid sulfate aerosol exposure effects. The real problem is that the underlying biochemistry of the disease etiology is not well understood for sulfates.

Considerably more research is required to definitively pin down the role of individual coal-derived pollutants in the causation of chronic disease. The biomolecular mechanisms must be elucidated as well as the dose-response relationships.

Individual Variability

The concept of individual variability in the susceptibility to pollutants is important for understanding the health impact of the gas-aerosol complex. Such variability must be considered to be operative both among different individuals, leading to some members of the population being inherently more vulnerable, and within a single individual at different time periods. Inter-individual differences represent inherited factors, including presumably the reactivity of the bronchial tract to external agents, and acquired factors, such as preexisting cardiorespiratory disease. Intra-individual variability includes such temporal factors as the presence of microbial respiratory tract infection and age. Controlled exposure studies have clearly demonstrated widely differing responses in groups of animals to bronchoconstrictive pollutants. Inasmuch as animals used in these studies generally have a common genetic and environmental heritage, it is not surprising that, based on the few available studies, there appears to be at least as great a variability in human response. A marked variability in human response is also suggested by some epidemiological studies.

Unfortunately, there are as of yet inadequate data to statistically characterize the degree of human variability in response to pollutants. This would be of value in determining the validity of extrapolating results of controlled human exposure studies (which generally utilize a small number of healthy subjects) to high risk populations.

Physicochemical Characteristics of Pollutants in Relation to Respiratory Response

Studies in animals exposed to defined components of the gas-aerosol complex have clearly demonstrated that there is a marked difference in the ability of individual pollutants or combinations to elicit an acute bronchoconstrictive response. This is particularly evident in the series of studies performed by Amdur and her colleagues on guinea pigs (9, 14). The physicochemical characteristics which appear to be particularly significant are size, solubility, pH, and chemical reactivity. For example, particles in the respirable ($< 1 \mu\text{m}$) size range appear to exert a greater bronchoconstrictive response than larger particles given a similar mass concentration. Many aerosols of the appropriate size are, however, inert with respect to bronchoconstriction. In some cases the absence of response appears to be due to lack of "chemical reactivity" (e.g., NaCl), in others it is due to the relative insolubility of the compound which

presumably allows clearance before any chemical reaction can occur. The pH of the aerosol also is of importance. In general, the greater the acidity, the higher the likelihood of a bronchoconstrictive response. More information is needed on the role of particle shape and hygroscopicity in determining regional airway deposition and subsequent bronchoconstrictive impact (15).

Knowledge concerning the role of these physico-chemical characteristics in mediating airway response to aerosols has been of great value in understanding pollution effects and predicting response. Simple manipulations of these parameters does not, however, totally explain the response of guinea pig airways to inhaled irritants. A better basic understanding of the biochemistry underlying the physiology of airway response would be of great value. Another research area of related importance is the determination of the responsiveness of the human respiratory tract to these pollutants. Such studies would consist of short-term acute exposures with the aim of establishing a hierarchy of responsiveness to individual components of the gas-aerosol complex, as well as determining appropriate no-effect levels. In addition, more information is required concerning potential synergistic interactions of these air contaminants. In particular, animal studies of sulfur dioxide effects in the presence of inert respirable particles and photochemical pollutants including ozone, NO_2 , and organic irritants such as acrolein should be extended to man.

Observed Health Effects of the Gas-Aerosol Complex in Humans

Mortality

There is no question that exposure to past ambient levels of the gas-aerosol complex has led to increased mortality during acute air pollution episodes. Those individuals who died during such episodes were mainly the elderly, the infirm, and, in some episodes, the very young. Controversy does exist concerning the extent, if any, to which current pollutant levels are responsible for daily variations in mortality. To study this problem it is necessary to carefully adjust for many variables, including meteorological and seasonal effects.

In recent years a number of investigators have evaluated New York City mortality data in relation to air pollution levels (16-21).

The studies are in general agreement as to the existence of a residual variation in daily mortality

that is explainable by pollution levels. There is, however, a lack of consensus concerning whether the effect correlates more strongly with sulfur dioxide or total suspended particulates. This is not surprising in view of the interrelationship of these two measures of the gas-aerosol complex. There is also controversy concerning the interpretation of these studies; the results of one investigation suggesting little or no threshold for the association of mortality with sulfur dioxide levels (20), while a more recent analysis (21) reports no change in the excess mortality associated with pollution during a period in which there was substantial improvement in ambient sulfur dioxide levels.

A deficiency in most of these investigations, as well as air pollution-related epidemiological studies in general, is the use of only one monitoring station to characterize the pollutant exposure of a large population. This adds to the uncertainty of the results. It should be noted that studies of daily mortality in relation to daily air pollution levels are unlikely to discover a life-shortening effect that is due to the causation of a chronic disease by these air pollutants.

Morbidity

Acute Effects. There are literally dozens of types of adverse health effects which have been reported to be associated with inhalation of the gas-aerosol complex or its components. For many of these effects (e.g., behavioral, immune) the information is inconclusive or at best, peripheral. Epidemiologic studies of respiratory tract effects of these pollutants have utilized a variety of different measured parameters. These studies have tended to focus on population groups believed to be at high risk for pulmonary effects, including children, asthmatics, the elderly, and individuals with pre-existing cardiorespiratory disease.

The impact of air pollutants on children has been studied extensively [see for example reviews by the American Academy of Pediatrics (22), Wehrle and Hammer (23), and NAS (4)]. A relation between the gas-aerosol complex and lower respiratory illness has been established. Epidemiological studies in Great Britain, including evaluation of up to 10,000 individuals, have reasonably clearly demonstrated an effect of air pollution on bronchitis incidence (24-26).

Of particular interest are two studies in which cohorts were evaluated at varying time intervals. In a study of 5-year-olds living in four different areas, the incidence of chronic cough correlated well with existing air pollution levels, and there was a significant decrease in pulmonary function in the residents of

the most polluted area during the first study period. Four years later, in 1969, these same children were restudied. During this period there had been a marked improvement in air pollution levels (45-80% decrease in smokes, 10-25% decrease in sulfur dioxide) with an abolition of the pollutant gradient between the four areas. Appreciable decreases in observed respiratory effects were observed and there were no longer differences between the areas (27, 28). Another study of a cohort of children born in 1946 noted an association of the history of lower respiratory tract infection with air pollution (25). When this group was thoroughly evaluated at age 20, cigarette smoking was found to be the dominant factor in the presence of respiratory symptoms, while air pollution had at most a minimal effect. Other British and American studies have reported a lesser prevalence of respiratory problems in association with improvement of air quality (29-31).

Studies in the United States and elsewhere, including the CHES studies (32), have evaluated the association of sulfur oxides and particulates with childhood respiratory tract illness. With some exceptions, lower respiratory tract illness has been positively correlated with those pollutants at levels somewhat above the current U.S. standards, but not at lower levels. Studies of childhood pulmonary function in relation to sulfur oxides and particulates have shown less consistent results.

Ambient levels of nitrogen dioxide have been implicated in the potentiation of upper respiratory tract infection in children and their families. This is in contrast to sulfur oxides which, while clearly associated with lower respiratory tract bacterial illness, have not been consistently found to be associated with upper respiratory viral infections. Epidemiological evidence of a relationship between NO_2 and respiratory infection was noted in school children and their families in a study performed in Chattanooga (33). This took advantage of a relatively unique point source of nitrogen dioxide. Replication of this study, which is a major base of the U.S. air quality standard, would be of great value, but is difficult due to the entanglement of nitrogen dioxide with other pollutants in most areas. Recent studies demonstrating relatively high nitrogen dioxide levels in kitchens with gas as compared to electric stoves (34, 35) may provide a basis for re-evaluation of the epidemiological association of nitrogen dioxide with respiratory tract infection.

There is some controversy concerning the susceptibility of asthmatics to the gas-aerosol complex. Basic biomedical considerations lead to a strong suspicion that individuals with a hyperactive bronchoconstrictive response should be particularly

sensitive to inhaled air contaminants. There are a number of epidemiological studies which appear to support this contention, as well as the recent controlled human study on NO_2 and carbachol (11). The epidemiological studies are, however, open to various degrees of criticism which appear to reflect the fact that asthmatics are a particularly difficult group to study. It is difficult to obtain a large study population, and there are numerous confounding variables, particularly meteorological and seasonal factors, which complicate interpretation of the effects of air pollutants.

The retrospective observation that 87.6% of asthmatics reported respiratory symptoms during the Donora air pollution disaster (36), as compared to 42.7% of the general population, indicates that asthmatics do respond adversely to air pollution. The question at present, which is similar for other susceptible populations, is to what extent do current or foreseeable pollutant levels produce asthma attacks. Relatively low level effects were reported in the CHES studies and in an EPA study performed in New Cumberland, West Virginia (37). The latter is one of the few U.S. studies of effects due to an uncontrolled coal-fired power plant. These studies have been heavily criticized, mainly on the basis of the data collection and analysis techniques which were used (38). At present, it would appear warranted to place a relatively wide error band around any extrapolation relating potentiation of asthma attacks to current or projected levels of stationary source fossil fuel combustion products.

It should be emphasized that asthma attacks represent an acute effect, and are therefore particularly significant during high short-term peak levels of pollutants. The causation of the basic underlying effect leading to classical allergic asthma does not appear to be related to chronic pollutant exposure. The relation of air pollution to asthma attacks has been the subject of a number of reviews (4, 39, 40).

Exacerbation of pre-existing cardiorespiratory disease has been clearly demonstrated to be a consequence of exposure to the gas-aerosol complex. Controlled animal and human exposure studies have suggested that bronchoconstriction is the basis for the observed acute effects. There may also be an element of pollutant-induced increased mucous production leading to worsening of disease, particularly in the chronic bronchitic.

Numerous epidemiological studies have focused on individuals with chronic pulmonary disease (chronic bronchitis, emphysema, and nomenclature variants thereof). Diary studies of this group (in Britain) readily demonstrated an association of worsening symptoms with short-term pollution

levels. This has recently been less evident following institution of control measures leading to a marked abatement in particulate levels and lesser decreases in sulfur dioxide (29, 30, 41, 42).

Similar studies in the United States have produced somewhat contradictory results. For example, Burrows et al. (43), found little or no correlation of sulfur dioxide levels in Chicago with daily symptoms of patients with chronic respiratory disease, although Carnow et al. (44), using a similar, but somewhat more extensive approach in Chicago, reported that symptoms were related to sulfur dioxide levels extending down to the range of the current air quality standard. The CHES program has utilized panels of elderly subjects, with and without chronic cardiopulmonary disease, to study daily pollution effects (32). While a positive correlation with current ambient sulfate levels was reported, the high dropout rate and other technical difficulties complicated interpretation of these results.

Chronic Effects. The bulk of the studies discussed above deal with the ability of the inhaled gas-aerosol complex to produce acute disease or an acceleration of an already existing chronic disorder. The present section focusses on the possibility that long-term inhalation of these pollutants may act to cause the production of chronic disease, particularly chronic respiratory disease. The potential impact of a role for air pollutants in the causation of chronic respiratory disease may perhaps be greater than that of acute disease. It is, however, a more difficult problem to study. Evaluation of day-to-day variations of pollutants in relation to health effects does not provide any direct information. Nor are usual prospective studies of value in a situation where it may require many decades of exposure for the development of measurable chronic damage.

Studies approaching this problem have generally utilized a geographic comparison in which the prevalence of chronic respiratory disease among a population in a polluted area is compared to the prevalence in a nonpolluted area. In order to make such a comparison successfully it is necessary that the populations in the study areas be as similar as possible in other respects. The major confounding variable in such studies is the extent of cigarette smoking, which is the most important causative factor in chronic respiratory disease. Other factors, particularly occupation, but also life style and social class, could conceivably play a role in the causation of chronic respiratory disease and should be evaluated in the study design.

Using such measures as death rates, reason for disability, and questionnaires concerning cough and sputum production, many studies have clearly dem-

onstrated a higher prevalence of chronic respiratory disease in polluted areas. When originally studied in the 1950's, air pollution appeared to account for a substantial proportion of the total incidence and disability due to chronic bronchitis in Britain. A relation of air pollution to the prevalence of respiratory disease has also been noted in American and Canadian studies. The largest American study of this type was performed by CHES in various parts of the country by use of a self-administered questionnaire (32). There was a reasonable consistent finding of a higher prevalence of chronic respiratory disease in the more polluted communities. This is among the least controversial of the CHES findings. However, inasmuch as the observed effect presumably represents long-term exposure to air pollution, including the much higher levels of the past, the data can not be readily used to estimate effects due to current ambient levels. It would be useful to analyze subsequent years of the CHES studies to determine whether there was a decrease in the prevalence of chronic respiratory disease which parallels the previous fall in air pollution levels.

A study comparing the prevalence of histologically determined emphysema prevalence on autopsy subjects showed that the disease was three times as prevalent among nonsmokers in St. Louis as in Winnipeg, Canada (45). The variable used to explain the difference was fossil-fuel combustion product derived air pollution. No specific substances were correlated with the disease, rather only total emissions of SO_2 , particulates, and NO_x .

There is the possibility that components of the gas-aerosol complex might play a causative role in the increased levels of lung cancer observed in urban areas. Bisulfite has been shown to be mutagenic in a number of systems, presumably by deaminating cytosine (46, 47). It is, however, questionable whether this reaction can occur at physiological pH. Tumor formation in animals exposed to sulfur dioxide has been reported, most notably in a study demonstrating higher levels of lung tumors in animals exposed to sulfur dioxide and benzpyrene as compared to benzpyrene alone (48). In conjunction with arsenic exposure, sulfur dioxide exposure appeared to increase the risk of lung cancer in smelter workers (49). Nitrogen oxides have also been suggested to be potential carcinogens, mainly based on reactions with other agents which might form nitrosamines which are known to be very potent carcinogens (50). Recent studies have demonstrated that these reactions can take place in polluted atmospheres, especially during the nighttime hours.

While further research concerning the possible mutagenic effects of components of the gas-aerosol

complex would be of interest, it is unlikely to provide information in the near future specifically applicable to human exposure.

Dose-Response Analyses

The estimation of human dose response to the gas-aerosol is an arcane art. The major difficulties are derived from the dose side of this equation. The most commonly measured pollutant, sulfur dioxide, is an indicator of varying reliability of the entire gas-aerosol complex. To complicate the problem, sulfur dioxide is also a major precursor of more toxic components and its own toxicity can vary depending on its combination with other pollutants. This multiple role for sulfur dioxide is the basis for the apparent discrepancy between epidemiological studies and controlled human and animal exposure experiments, the latter requiring much higher levels of sulfur dioxide in clean air in order to observe effects. The common methods of particulate measurement are also only indirectly related to those agents actually causing adverse effects. In addition, one must carefully disentangle the effects of other variables (e.g., cigarette smoking, weather, and occupation) from those due to pollution. There is accordingly an essentially inherent degree of uncertainty in the assigned dose for each level of response. There are also difficulties in the measurement of response, including adequate characterization of populations, the validity of measuring techniques, and the selection of subjects for study. These problems are compounded by the requirement for multiple points in the plotting of a dose-response curve.

There are a number of complex statistical techniques which have been developed or refined in recent years to handle the variables in individual studies and to formulate dose-response curves. There is, however, a crossover point at which the uncertainty caused by the multiplicity of pollutants and other variables is replaced by uncertainty about the validity of the complex statistical procedures used to disentangle these variables. Furthermore, there is no consensus in the scientific community concerning where this crossover point is located.

Dose-response information can be more simply derived from controlled human exposure experiments involving defined responses to measured doses. The major drawback of this approach, as is evident in the case of sulfur dioxide, is that the exposure does not replicate the complex mixture present in urban air. In addition, it is difficult to study the response of susceptible populations. Animal exposure experiments, although advantageous in other ways, suffer the same limitations with the added drawback of interspecies differences.

The above caveats should be kept in mind when considering the available literature concerning the effects of the gas-aerosol complex. Among the most frequently quoted studies is that of Lave and Seskinen (51) who in 1970 estimated that a 50% production of all urban air pollution would result in a 25-50% decrement in the excess urban mortality and morbidity from bronchitis, 25% of lung cancers, 25% of respiratory disease, 10% of cardiovascular morbidity and mortality, as well as a 15% decrement in the overall prevalence rate. These figures have been utilized by a number of other authors as the basis for further calculations. It should be emphasized that the analysis refers to all air pollutants and is applicable to the increment of these effects observed in urban areas.

A frequently employed data set for extrapolating the effects of various levels of stationary source fossil fuel combustion products is derived from use of the CHESSE studies (52). These studies have been the subject of much controversy, including a generally critical congressional review as well as frequent criticism by other researchers. The CHESSE dose-response estimations were based on measured levels of atmospheric sulfates. As pointed out by the authors, they clearly represent a first approximation containing a large degree of uncertainty. It should be noted that the major reason for extrapolating a dose-response curve from the original CHESSE data was a need for making regulatory decisions based on presently available evidence. This remains true today.

Among the subsequent analyses, using the CHESSE extrapolations, is a report by the National Academy of Science to the U.S. Senate Public Works Subcommittee (4) in which the impact of alternate fuel use strategies was evaluated. This includes estimates for the health impacts associated with individual plants depending on siting. A series of studies of a similar nature have been performed at Brookhaven National Laboratory including estimation of mortality due to coal utilization. The authors clearly indicate that their model is greatly simplified due to the lack of solid baseline data from which to calculate the health effects of coal combustion products. Specific criticisms of their approach include the use of a non-threshold model (based on Lave and Seskinen) which employs an annual average pollutant dose to impute mortality rather than short-term peak levels; the lack of characterization of populations at risk; and assumed constant sulfur dioxide oxidation rates. In order to improve the validity of these predictive models it is necessary to develop more accurate dose-response functions based on appropriate averaging times for the pollutant dose. In addition, better means of predicting the levels of secondarily formed pollutants would be of value.

Environmental Health Perspectives

Summary of Issues

It does not appear possible to readily subdivide the issues concerning health effects of the gas-aerosol complex into those for which there is a consensus of opinion and those for which there exist uncertainties or controversy. There is no concrete borderline where reasonable men may or may not differ. Rather there is a continuum ranging from questions for which the answer appears certain, to where there is disagreement as to even how to phrase the question. Following are a partial list of issues that appear pertinent to the problem of health effects due to the gas-aerosol complex. Inherent in such an exercise is the author's judgment concerning what are the issues of particular importance, what are the bounds of reasonable differences in interpretation of existing data, and which are the areas where further information, in the relatively near future, is likely to be of crucial importance.

Can the Gas-Aerosol Complex Derived from the Combustion of Coal Produce Acutely Harmful Effects in Man? The answer to this question is a definite yes. Past experience in the United States, Great Britain, and elsewhere, provides more than ample evidence that atmospheric sulfur oxides and particulates are causally related to adverse health effects. These include increased mortality, particularly during prolonged periods of atmospheric inversion. This situation affects mainly the very young, the old and the ill. Also included is an increased morbidity inclusive of exacerbation of preexisting cardiorespiratory disease and potentiation of lower respiratory tract infection, and, more than likely, the production of asthmatic attacks in susceptible individuals.

Can the Gas-Aerosol Complex Derived from the Combustion of Coal Produce Chronic Disease in Man? There is reasonably good evidence that long-term exposure to these pollutants can play a causative role in the production of chronic respiratory disease. Supporting this hypothesis is evidence indicating a higher prevalence of chronic respiratory disease in polluted areas that does not appear to be accounted for by differences in cigarette smoking rates, occupational exposure or other confounding variables. There are, however, differences of opinion concerning the interpretation of these data and it would not be unreasonable to state that the hypothesis is unproven. In the judgment of this author, the scientific evidence that long-term exposure to stationary source fossil fuel combustion products can be involved in the causation of chronic respiratory disease appears compelling. This assumption would also appear to be in keeping with a prudent public health point of view. There is far less evidence

that nonorganic coal combustion products may cause cancer. Such a hypothesis is supported primarily, by basic research indicating that derivatives of sulfur dioxide and nitrogen dioxide could produce mutagenic effects, and by epidemiological evidence indicating a higher incidence of lung cancer in urban areas. Much more research is required to assess the relation of the basic research findings concerning mutagenesis to human cancer. In respect to the epidemiological evidence, if it in fact reflects a causative role of air pollution in urban lung cancer, the evidence at present more strongly supports a role for organic fossil fuel combustion products.

To What Extent Does the Available Information Permit Accurate Prediction of the Adverse Health Consequences Due to Given Levels of Coal Combustion? There is ample historical evidence that ambient levels of stationary source fossil fuel combustion products have produced serious health effects in exposed populations. This is particularly true for situations in which there were relatively high pollutant concentrations. In recent years there has generally been a decrease in ambient levels of most of these pollutants, exclusive of nitrogen oxides whose emissions have continued to increase. The extent to which present ambient levels of the gas-aerosol complex produce adverse health consequences is a matter of controversy. Reasonable interpretations of the data range from no, or negligible, pollutant effects at present, to the position that any level of the gas-aerosol complex is capable of producing harm.

These widely differing interpretations reflect uncertainties concerning the validity of the existing data. As described above, there have been a number of dose-response estimations performed in recent years. They have been based for the most part on data developed by the CHES program. This controversial program contains the most comprehensive attempt to establish the levels of measurable components of the gas-aerosol complex which produce adverse health effects. There are other studies which provide information useful for approximating a dose-response curve. These, however, are few in number and are derived from different countries, laboratories, scientific approaches, and circumstances. This greatly complicates the problems of extrapolation and leads to the necessity of assigning a relatively high degree of uncertainty to any derived dose-response curve. Accordingly, if the CHES data are interpreted as being meaningless, one is left with a very wide range of possible interpretations, particularly concerning the effects of current ambient pollutant levels and those likely to be achieved with the proposed conversion of power plants to coal.

If the CHES data are accepted as being pertinent,

there are then a number of analyses based on these data which can provide dose-response estimations useful for estimating health effects due to the gas-aerosol complex. One of the more extensive analyses is that of the National Academy of Science discussed above. It has the advantage of providing data for individual power plants located at various distances from urban populations. This author participated in the health effects aspects of the NAS analysis and estimated that a reasonable error-band for the dose-response curve for sulfate used in the computations ranged from an underestimation by a factor of two to an overestimation by a factor of 10. There appears to be no new information justifying a change in this conclusion.

It is also unlikely that any newly instituted research effort will provide information which will substantially change the boundaries of this analysis or the certainty of any prediction of dose-response before the anticipated switchover of utilities from oil and gas to coal. There is, however, every reason to begin such further studies as soon as possible, and preferably in conjunction with any fuel conversion efforts, so as to provide information pertinent to determining the extent to which further conversion affects air quality and public health.

There is one source of information pertinent to this problem which could be available within the near future. This is the remaining unanalyzed portions of the CHES program. Only the first, and part of the second year of this five-year program have been completely analyzed. Many, although not all, of the criticisms of this program reflected problems inherent in the institution of a complex epidemiological study. Some of these were rectified in subsequent study years. If the findings in the latter years of the CHES study replicate the initial findings, this would lend a great deal of credence to the derived dose-response formulations. The converse would also be true. Accordingly, a rapid and thorough analysis of the remaining CHES data, preferably by those not intimately connected with the study or its criticism, could be of great value.

To What Extent Are Average Pollution Levels and Average Human Response Predictors of the Health Impact of the Gas-Aerosol Complex in a Population? It is misleading to consider average pollution levels and average response in the formulation of control strategies. There is a large degree of variability in the response of humans to air pollutants. In general, regulatory actions in this country have specified that the most sensitive groups should be protected. Accordingly, there is a particular need for information concerning the effect of the gas-aerosol complex on susceptible individuals. Information on

this subject has been obtained in epidemiological studies, although this is very often complicated by problems in obtaining sufficient numbers of individuals for study and for appropriate control groups. Controlled human exposure studies of susceptible individuals have only rarely been performed. This is in part due to ethical considerations. Even when ethically appropriate, the performance of these studies is often hampered by the spectre of litigation which makes university review boards reluctant to permit such studies. Unless some answer to this problem is forthcoming, perhaps through federally guaranteed insurance, it is unlikely that information pertinent to the understanding of human variability will be attained in the near future.

Short-term peak pollutant levels are obviously most important in reference to causation of acute effects. It should be emphasized that prolonged meteorological inversions which have the capacity for developing highest pollution levels may occur at intervals of only every few years. Inasmuch as these episodes represent the greatest potential for acute effects, these infrequent occurrences should be considered as a major basis for determination of appropriate control strategies. Such an approach does not substantially differ from that of assignment of flood plain areas based on the concept of the "100 year flood."

What is the Relative Impact on Health of the Gas-Aerosol Mixture Present in the Local Area of a Power Plant Fueled by Coal, Compared to the Gas-Aerosol Mixture Present after Long-Range Transport of Power Plant Emissions? A number of processes act to modify the components of power plant emissions as they travel downwind. These are discussed in detail above. In general, the emitted gases are oxidized to acidic aerosols which appear to be of greater potential harm than the parent compounds. Presumably buffering substances, such as NH_3 , are also added over time and these may alter the potential toxicity of the gas-aerosol complex. Obviously, dispersal of the plume over distance leads to a dilution in pollutant concentrations. In areas such as the Northeast, there may, however, be additive effects from multiple point sources.

The importance of this issue lies in its pertinence to decisions concerning which electric power plants should be converted from oil to coal. If, as has generally been assumed, the local effects predominate by virtue of higher concentrations, then clearly the extent of the adverse health impact of a given level of coal combustion would be proportional to the density of the local population. This effect would be magnified by the fact that existing air pollution levels tend to be highest in dense urban areas. Therefore,

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Health Effects of Coal Mining and Combustion: Carcinogens and Cofactors

by Hans L. Falk* and William Jurgelski, Jr.*

Some polynuclear aromatics (PNA) have been found to be potent carcinogens for all tissue, and organs of experimental animals that have been exposed to them, but different dose levels are needed for these effects. They have been known for decades to cause cancer at the site of application but also at certain sites distant from the area of contact. Although some hydrocarbons are potent and complete carcinogens, the majority of related hydrocarbons was originally found to be inactive. Since they generally appear together, it was important to know more about their interaction, particularly whether they would synergize, or antagonize.

The polycyclic hydrocarbons have been studied by subcutaneous injection, where they prove very potent carcinogens. They are also very active on the skin of mice where they produce cancer on prolonged application. Inhalation studies, require larger doses yielded negative results until particulate matter was introduced which facilitated the development of lung tumors. Although iron oxide dust was used initially, other dusts were also capable of enhancing the response of the tissue to benzo(a)pyrene carcinogenesis. This point is of importance, particularly since the inhalation of PNA in situations of air pollution or coal mining involves particulates, although of a different type.

Soot is not a homogeneous substance and several factors determine its properties. Soots will lose some of the absorbed chemicals during their residence in air, but they retain their PNAs for long periods of time when they reach the soil.

The carcinogenicity of PNAs in the adsorbed state may be completely absent, depending on particle size of the soot and availability of eluting capability of the tissues or cells in contact with the soot. Whenever the carcinogenic polynuclear aromatics can be eluted they will be active in producing cancer if their residence is adequate.

There seems to be no reason to assume that a large increase in coal combustion in the future will by necessity lead to greater risks of cancer to the coal miners or the general urban dweller, because activities to be started now can take into consideration the requirements necessary for control of air pollution in mines as well as in cities. If new uses of coal will be developed, it will be a completely different situation, and statements about the carcinogenic risk from coal utilization do not apply there. Although some of the same carcinogenic PNAs are involved in the health hazards from those processes, other carcinogens and also cocarcinogens will be present, and the exposed workers will not have the apparent benefits of adsorption of PNAs on soot.

Introduction

Polynuclear aromatics (PNA) have been known as carcinogens for many laboratory species since the thirties, and efforts have been expended to correlate structure and carcinogenic activity for many members of that group. It was not completely successful, but certain conclusions are still accepted about the limits of structure/activity correlations. This allows the researcher in the field to make educated guesses regarding the possible carcinogenicity of polycyclics with specific arrangement of the ring system, but it

becomes impossible to predict the range of activity when alkyl derivatives are involved. Carcinogenicity of alkyl derivatives may be far greater than that of the parent compound, depending on the location of the alkyl group.

Carcinogenic Polycyclic and Heterocyclic Aromatic Compounds

Presence in Coal and Soot

Coals have not been analyzed very often for their composition as far as organic constituents are con-

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cerned. There are data on the atomic ratio of hydrogen to carbon which for a sample of coal (Illinois #6) was found to be 0.86. A highly imaginative structure was given by Wadden (1) (Fig. 1). It allows the creation of an image of what variety of structures may be present in coal. Completely realistic, however, is the analysis of an extract of powdered bituminous coal which identifies the polycyclic aromatic hydrocarbons by means of absorption spectroscopy and the degree of alkylation by mass spectrometry. This analysis gives a quantitative picture of the various groups present. Of interest with regard to potential carcinogenicity are the groups: benzo(a)pyrene, chrysene, cyclopentano-chrysene, and benz(a)anthracene derivatives (2). It is clear that the process of pulverization and extraction would not have contributed to the formation of these compounds which therefore must be assumed to be present as such in coal (Table 1).

When coal is burned, many changes occur in the composition of these polynuclear aromatics. At the high temperature reached, chemical bonds are bro-

ken and free radicals are formed. Under conditions of incomplete combustion soot is liberated together with a collection of adsorbed polynuclear aromatics consisting of the same structures that were present in coal, but not necessarily the same molecules. During the process of combustion the polycyclic aromatics are broken down or may lose their alkyl sidechain, so that the chemicals that can be recovered from the soot are more generally the parent substances, i.e., those without alkyl groups belonging preferentially to the peri-condensed group of aromatics. Some data on the pyrolytic process will be given later in this paper. So far no mention was made of heterocyclic compounds, but independent of the presence of these compounds in coal the pyrolytic process during combustion will allow the formation of nitrogen-containing polycyclic compounds and a number of them have been found in air pollution particulate matter (Table 2) (3). Their carcinogenicity also depends on structure, but different rules seem to govern structure and carcinogenicity in this case. Some are quite potent; but an increase in the number of

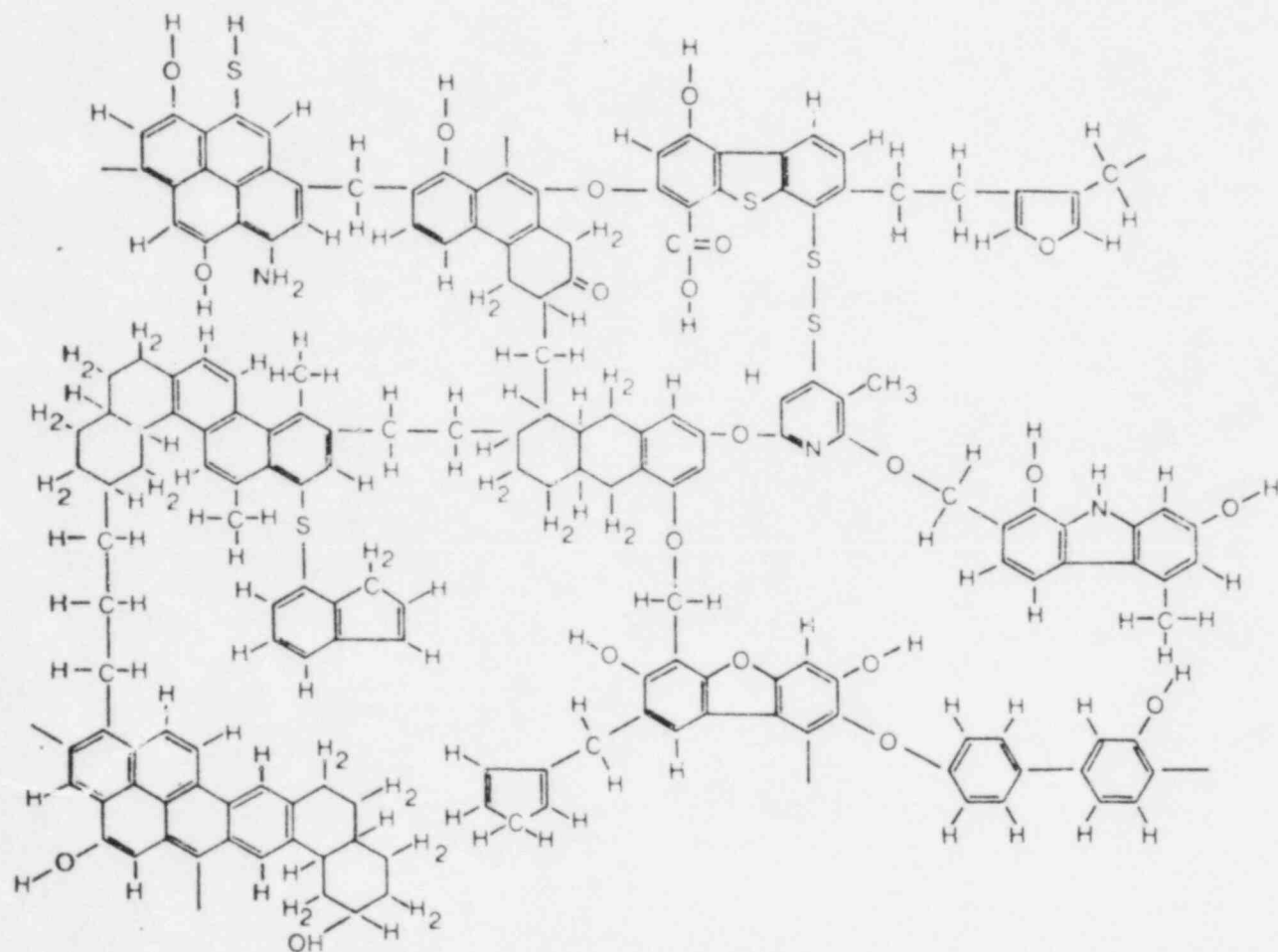


FIGURE 1. A representative bituminous coal structure (1).

nitrogen atoms in the ring system tends to decrease potency abruptly.

The analysis of coal mentioned above did not extend beyond the polycyclic aromatic hydrocarbons, but studies on coal tar revealed the presence of many other heterocyclic compounds where nitrogen, oxygen, or sulfur is built into the ring systems. It is necessary to dissociate these findings from both, the composition of coal and the composition of soot, because these compounds may be formed under different conditions. However, they help us to an un-

derstanding of what kind of structures we could expect to be present in coal, which might be formed subsequently on tar formation, and which might lead to new structures on combustion. Structures containing a thiophene ring instead of an aromatic ring in the polycyclic structure may also be quite carcinogenic.

Table 3 shows the concentrations of some polycyclic aromatic hydrocarbons and related compounds found in coal and in urban air. The concentration range of some of these compounds in city air has been determined by Sawicki et al. (4). Figure 2 gives the structure and name of a number of important FNAs. One group of polycyclic hydrocarbons which was not mentioned in the coal analysis is that of benzfluoranthenes. These compounds are present in soot and in air pollution, and may contribute to the carcinogenic burden of urban populations. Figure 3 shows seasonal variation in air pollution, based on the presence of benzo(a)pyrene.

Inorganic Compounds

Some inorganic carcinogens exist in coal and reach the atmosphere following combustion. The concentration of these elements in coal are given in Table 4 (5). They are mentioned here only for the sake of completeness. As most of them will be removed before reaching the air by electrostatic precipitation, the carcinogenic risk may not be very great, however, elements such as arsenic, cadmium, lead, and selenium may pass the precipitator and thus reach the environment as fallout from the air. Others may represent a disposal problem of fly ash and clinkers. This topic will be dealt with in another paper.

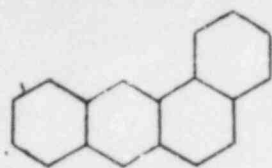
N-Nitrosamines

The last group of carcinogens to be mentioned are the *N*-nitrosamines. They are not present in coal, but it might be anticipated that they would be formed during the process of combustion of coal under special conditions. An analysis of the problem has been made by Henschler and Ross (6), who exposed mice to 40 ppm NO₂ for various time intervals observing proliferation of alveolar cells but no suggestion of development of cancer. The report was an interim report as many of the animals were still alive, but it enabled the authors to conclude that a carcinogenic risk from *N*-nitrosamine formation from oxides of nitrogen in the air and amines present in the tissues of the mice seemed unlikely. By contrast, Pitts (7) observed *N*-nitrosamine formation on allowing a reaction to occur between secondary amines added to air containing 0.3 ppm NO_x in darkness, while nitramines were formed in daylight. The amine concen-

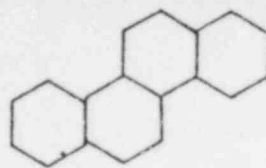
Table 1. Composition of the part of coal extract not reactive with maleic anhydride^a

Mass	Possible nuclei	Concentration, % of extract
142	Benzenes	0.30
156		0.55
170		0.44
184		0.30
168	Cyclopentanaphthalenes	0.13
182		0.24
196		0.26
210		0.18
178		0.16
192	Phenanthrenes	0.21
206		0.20
220		0.11
234		0.03
248		0.02
218		0.05
232	Cyclopentanophenanthrenes	0.08
246		0.07
260		0.06
274		0.03
202		0.03
216	Pyrenes	0.08
230		0.12
244		0.00
258		0.06
272		0.04
286		0.01
228	Chrysenes	0.04
242		0.04
256		0.06
270		0.05
284		0.02
298		0.02
268	Cyclopentano-chrysenes	0.04
282		0.05
296		0.04
310		0.03
252	Benzo(a)pyrenes	0.06
266		0.06
280		0.05
294		0.03
308		0.01
322		0.01

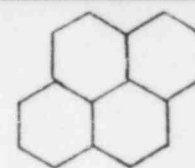
^aData of Tye et al. (2).



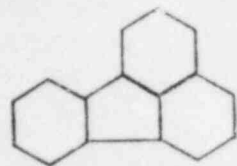
Benz(a)anthracene



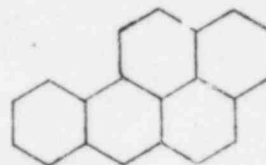
Chrysene



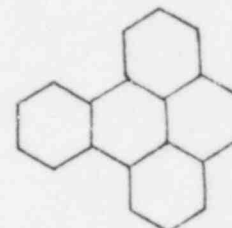
Pyrene



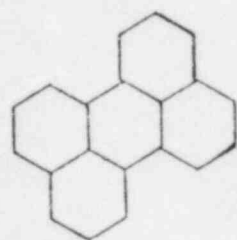
Fluoranthene



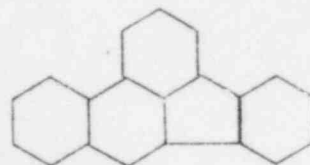
Benzo(a)pyrene



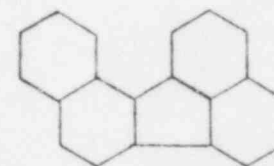
Benzo(e)pyrene



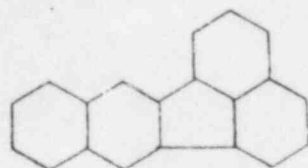
Perylene



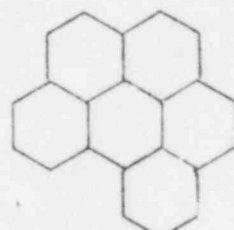
Benzo(b)fluoranthene



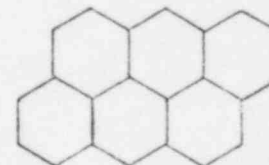
Benzo(j)fluoranthene



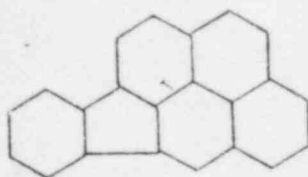
Benzo(k)fluoranthene



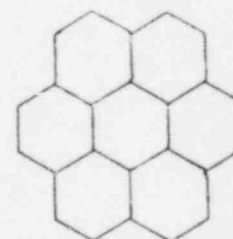
Benzo(ghi)perylene



Anthanthrene



Indeno(1,2,3-cd)pyrene



Coronene

FIGURE 2. PNA components of air pollution.

Table 2. Approximate concentrations of aza heterocyclic compounds in benzene-soluble fraction of selected urban atmospheres ^a

Compound	Concn. $\mu\text{g/g}$					
	Atlanta	Cincinnati	Los Angeles	Nashville	New Orleans	Philadelphia
Benzo(b)quinoline	200	80	6	100	7	26
Benzo(h)quinoline	20	20	1	30	1	7
Benzo(a)acridine	200	80	3	70	20	30
Benzo(c)acridine	30	10	1	8	2	6
1H-Indeno(1,2-b)-quinoline	30	40	4	20	8	10
Dibenz(a,h)acridine	8	2	a	6	0.6	6

^aEPA data (3).

a Undetectable in the amount of sample analyzed.

Table 3. Four to six-ring PNAs and their activities in carcinogenesis.

Compound	Initiator	Cocarcinogen with BaP	Complete carcinogen	Anti-carcinogen
Benzo(a)anthracene	+++		+	
Chrysene	+++		+	++
Pyrene	±	++	-	S.C.
Fluoranthene	-		-	+
Benzo(a)pyrene	+++		+++	S.C.
Benzo(e)pyrene	-	+++	-	
Perylene	±		-	++
				S.C.
				++
				skin
Benzo(b)fluoranthene			++	
Benzo(j)fluoranthene			++	
Benzo(k)fluoranthene			-	++
				S.C.
Benzo(ghi)perylene	±	++	-	-
				S.C.
Anthanthrene	-		-	-
				S.C.
Indeno(1,2,3-cd)pyrene			+	-
				S.C.
Coronene	±		-	-
				S.C.

Table 4. Tabulation of carcinogenic elemental concentrations in coal.^a

Element	Concentration, ppm	Mass flow, g/min
Arsenic ^b	3.8 - 18	4.7 - 23
Beryllium ^c	0.3 - <5	0.4 - <6.3
Calcium ^d	0.44 - 0.50 ^d	0.55 - 0.63
Chromium ^b	21 - 23	26 - 29
Cobalt ^b	3.3 - 5	4.1 - 6.3
Lead ^d	<5 - 30	<6.3 - 37
Nickel ^d	<100 - 150	<130 - 190
Selenium ^b	2.6 - 3.2	3.3 - 4.0
Uranium ^b	1.67 - 3.3	2.09 - 4.1

^aData of Bolton et al. (5).^bNeutron activation analysis.^cSpark source mass spectrometry.^dIsotope dilution SSMS.

tration was high, i.e., 50 ppb, for the reaction to occur and these levels may not generally be found in urban air, but may exist at certain locations. The formation of NO_x during combustion has been studied and quantitated and the evidence for *N*-nitrosamine formation in the air or in the organism needs further clarification.

Cocarcinogens Associated with Coal Combustion

Lately the problem of synergism between chemicals in their toxicologic effect has been emphasized, and some weight has been attached to its possible contribution to cancer induction, but as yet no exhaustive studies of the effect have been made. Orig-

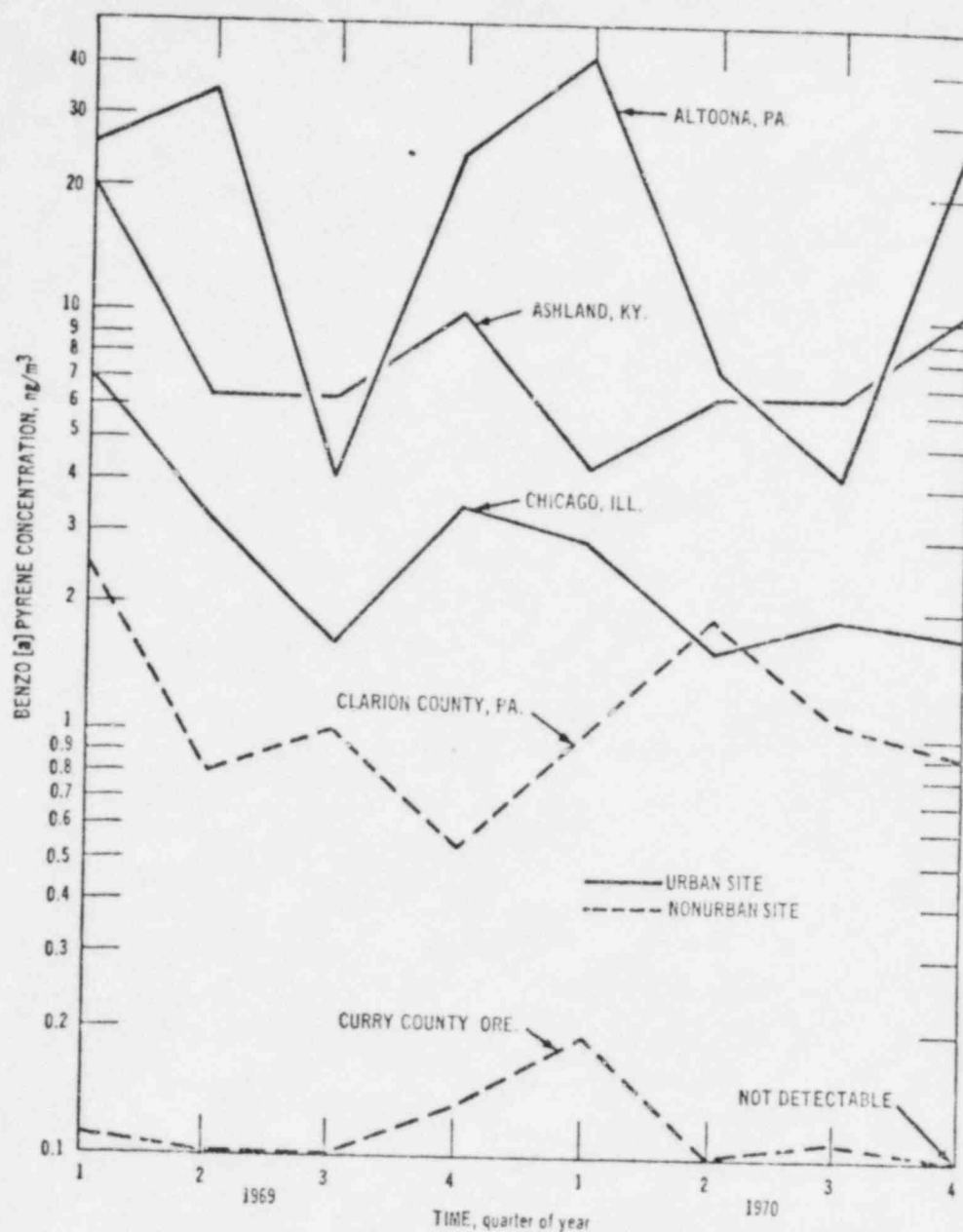


FIGURE 3. Seasonal variations of benzo(a)pyrene concentrations in ambient air at selected NASN stations (3).

nally it was considered a tool for the study of mechanisms of carcinogenesis, but soon was recognized as being involved in human cancer, such as the incidence of skin cancer in the oil industry, and lung cancer in heavy smokers, particularly those who also live in urban areas, work with asbestos, or earn their living as uranium miners.

In all these cases there is a greater than expected cancer incidence, but an understanding of the mechanism is still lacking. Even the agents responsible for

the synergistic effect have not been identified in most situations. It is realized that it is not necessary that the agent responsible for the synergistic effect is present at the same time, but may be separated by time intervals of several days which makes their study more difficult. There seem to be definite limits to this cocarcinogenic effect as observed in animal studies. If we can extrapolate to humans on this basis, it may be possible to describe many of the specific synergistic situations as only applicable in

extreme occupational situations which have been remedied as soon as they were discovered, but we will be left with one perfect example: the habit of cigarette smoking 2 packs or more per day. As will be discussed under the heading of epidemiology, smoking cigarettes may be considered a cocarcinogenic hazard in association with coal combustion.

Initiators or Incomplete Carcinogens

Recently some of the "inactive" polycyclic compounds were retested in combination with a synergist, or promoter of carcinogenesis, usually croton resin or one of its components in pure form, i.e., phorbol myristate acetate. The species of choice was the mouse, and the polycyclic hydrocarbon was applied to the skin with subsequent treatment with the promoter, as will be described in some detail later on. Some became effective initiators of carcinogenesis under these conditions while without promotion treatment they had been inactive or were very weakly carcinogenic. They were then called incomplete carcinogens or initiators of carcinogenesis. However, not all previously "inactive" compounds were active under these conditions.

Although it is not to be implied that those incomplete carcinogens should be weighted the same way as the complete carcinogens, nonetheless they may play an important role towards understanding of the carcinogenic process. Table 3 gives the chemicals that have been identified this way as incomplete carcinogens, but they have never been tested in relation to lung tumor induction in animals. It should also be noted that the compounds studied are only the major polycyclic hydrocarbons on soot, and do not represent all of the adsorbed PNAs.

There is little evidence for the presence of promoters in coal or soots. Promoters found in petroleum fractions are long-chain saturated or unsaturated hydrocarbons and sulfur-containing compounds. Although they are absent from coal itself, they could be formed during its liquefaction.

Cocarcinogens Associated with Coal Combustion

Sulfur Dioxide. Sulfur dioxide was found to be a promoter of carcinogenesis by Laskin et al., who exposed rats for 6 hr/day to 10 ppm SO₂ or to clean air and also for 1 hr/day to air containing 10 mg BaP/m³ and 3.5 ppm SO₂ for 5 days/week (8). The experiments were continued for 98 weeks and produced no lung cancers in the animals exposed to clean air, compared to 5 rats of 21 with squamous cell carcinomas on exposure to the carcinogen and SO₂

plus the additional 6 hr/day on the high concentration of SO₂. These experiments used too few animals for the evaluation of the effect of SO₂ alone. Two other studies are of interest also. In one study, rats were exposed chronically to 4-8 ppm SO₂. No lung tumors were observed in these animals. (9). However, in a study by Peacock and Spence, on mice of a strain highly susceptible to lung tumor formation (LX) the lung tumor incidence was doubled in males exposed to 500 ppm SO₂ for just 5 min/day, 5 days/week for a period of 300 days. In females of that strain who do not show lung tumors spontaneously, lung tumors were also observed (10).

It may be of interest to note that sodium bisulfite was found to be mutagenic to lambda phage, and the mechanism of action has been studied showing that bisulfite reacts with uracil and cytosine-forming addition compounds (11). In another study it was found that bisulfite leads to the deamination of cytosine. High concentrations of bisulfite were used in these studies (12).

Particulates. Particulates play an important role in all aspects of air pollution's adverse effects. They may help to carry adsorbed gases to greater depth for deposition in the lung, or they may overwhelm the mucociliary defenses of the respiratory tract leading to longer residence of toxic materials in critical areas. However, they may also serve to prevent exposure of tissue to some carcinogenic chemicals if these can be adsorbed strongly on particulates such as soots.

In our concern about coal dust and soot as contributors to human lung cancer, we need to be aware of the importance of surface area to their capacity for adsorption. It has been found that particle size is a controlling factor in determining whether adsorbed polycyclic aromatic hydrocarbons will be eluted or not. In a study of different particle size carbon blacks, it was found that the critical average particle size was 40 nm, below which even the best solvent would not elute any PNA, but at a particle size of 80 nm elution was effective. In a study in which BaP was added at increasing concentrations to 100 mg of each carbon black in 6 ml benzene it was found that up to 200 µg BaP could be completely adsorbed to particles with 10 nm diameter and only 1 µg BaP remained in solution when 500 µg BaP was added to that solution. As the particle size was increased to 30 nm, adsorption was no longer complete even with the lowest concentration (5 µg BaP) added and 10% remained in solution. With a carbon black sample of 80 nm no adsorption took place, but the originally held BaP and other PNA were eluted (13).

It is also true that in mixtures of carbon blacks of different particle size the smaller particles will adsorb readily what has been eluted from the larger

particles so that none can be detected.

These findings serve to suggest an explanation for the different observations made in laboratory experiments as well as on humans exposed to soot or carbon blacks. When soot is allowed to come in contact with skin and its sebaceous secretion, it may give rise to cancer if contact is allowed to persist and the particle size is large enough. The same soot may not have any effect on inhalation in the lung. However, if a solvent system were available in the lung — and it is likely that cigarette smoke condensate may serve this purpose — elution may take place in the lung. This theory would need experimental confirmation of the capabilities of tobacco condensates, but elution of PNA from soot also occurs under normal conditions by serum proteins, specifically the lipoprotein fraction, which may account for the observation that carbon deposits in human lungs when recovered at autopsy are devoid of most polycyclic aromatic hydrocarbons (14). Additional evidence will be given below on the importance of adsorption of carcinogens on soot.

It is also of importance to note that adsorption on particulate matter such as soot will protect PNA from quick destruction by light and air (15).

Epidemiologic Evidence of Carcinogenic Risks in Coal Mining and Combustion

Coal Mining

Carcinoma of the Stomach. Several epidemiological studies imply that the incidence of gastric carcinoma in coal miners is elevated above that of comparable segments of the general population not engaged in mining of coal.

Thus, Stocks (16) found that the death rates from cancer of the stomach in nine mining areas in England and Wales among coal miners of working age in the period 1949-1953 exceeded that of nonminers in the same counties with the same distribution by age and urbanization of place of residence. In every area the rate of stomach cancer in coal miners exceeded that of nonminers but the excess incidence showed pronounced geographical differences, the average difference being 125 per million with a range from 65 to 226 per million. It is high in mountainous areas of heavy rainfall. The greatest excess in the rate shown by miners over nonminers occurred in Wales in Brecknock, Carmarthen, and Pembroke, where it was 226 per million. It was of interest that 82% of the miners in the area were engaged in the mining of anthracite at the time of the census. However, it was also found that in North Wales mortality from stomach cancer was particularly high in farmers,

quarry workers in slate and igneous rock and in coal workers suggesting that direct contact with soil in areas with high mortality might have been an important factor (Table 5). Another puzzling finding in the study was the excess mortality of about 50% from stomach cancer in wives of coal miners as compared with all married women in England and Wales. In the coal fields as a whole, when the rates for nonminers were weighted by the miners' population, the overall rate of stomach cancer was 294 per million. This mortality in men aged 20-64, was about 10 percent above that of all males in England and Wales. It was speculated that the excess rate of carcinoma of the stomach in the wives of miners might be due to some contaminant in the home such as coal dust.

Similar conclusions on coal miners derive from one recent American paper. Matolo et al. (17) found that the age- and sex-adjusted incidence of gastric cancer from January 1965 to January 1969 in the only two coal mining regions in Utah was four times that of the State of Utah; three times that in residents who were not coal miners living in counties with coal mining and at least eight times that of males in counties with no coal mining. It was further found that 59% of the male patients with gastric cancer were coal miners. All homes of patients affected with gastric cancer were heated with coal, and in some of the homes coal was used for cooking. Although American wives of miners, like English miner's wives, showed an excess rate of gastric carcinoma, the excess rate for American females was not found to be significant. Neither diet, socioeconomic class distribution, nor ethnic, religious, or social background appeared to be related to the increased cancer incidence.

Table 5. Age-adjusted mean annual death rates per million from cancer of the stomach in coal miners and nonminers aged 20-64 in nine areas of England and Wales in 1949-1953.^a

County areas containing coalfields	Age-adjusted rates (per million)		
	Miners	Non-miners	Difference
Brecknock, Carmarthen, Pembroke	538	312	+ 226
Glamorgan	520	325	+ 195
Monmouth	412	255	+ 157
Durham and Northumberland	432	329	+ 103
Cheshire, Lancashire	389	288	+ 101
Yorkshire (West Riding)	346	230	+ 114
Stafford, Shropshire and Worcester	384	319	+ 65
Nottingham	367	269	+ 98
Derbyshire, Leicester and Warwick	268	193	+ 75

^aData of Stocks (16).

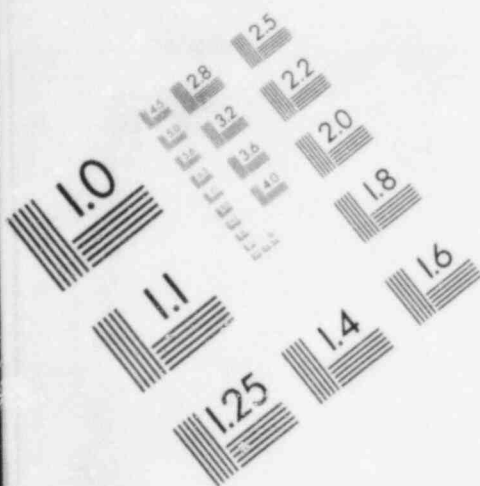


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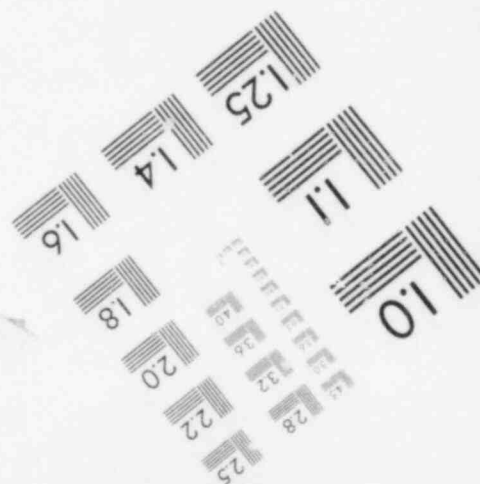
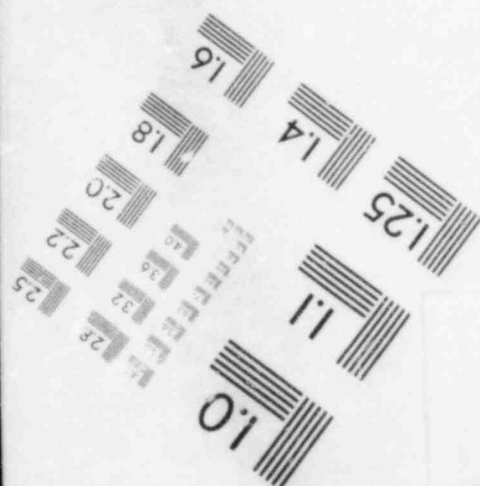
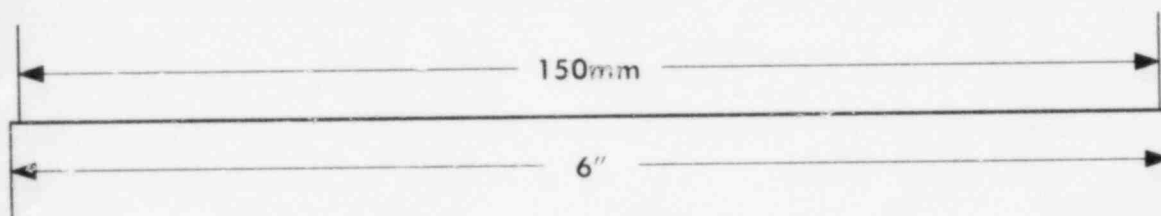
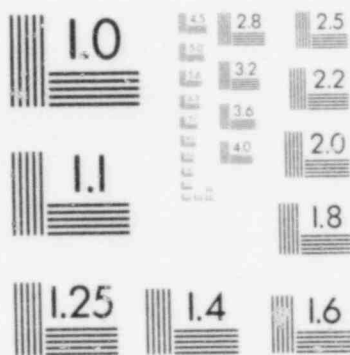
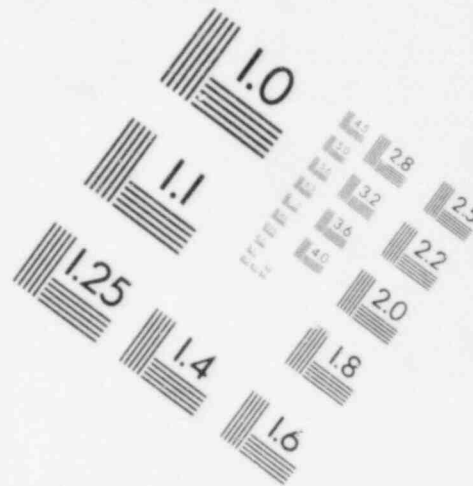
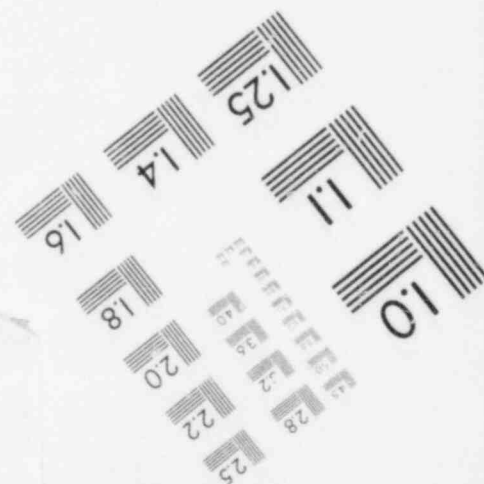
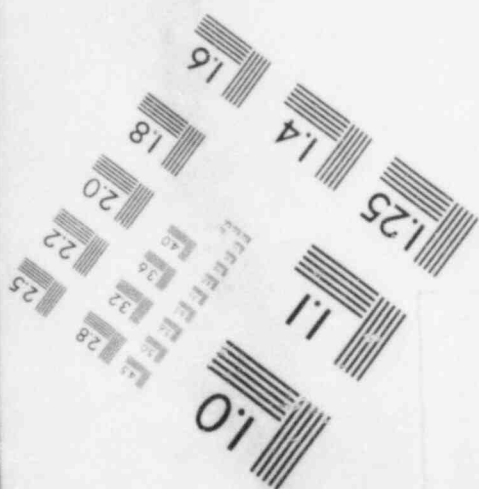
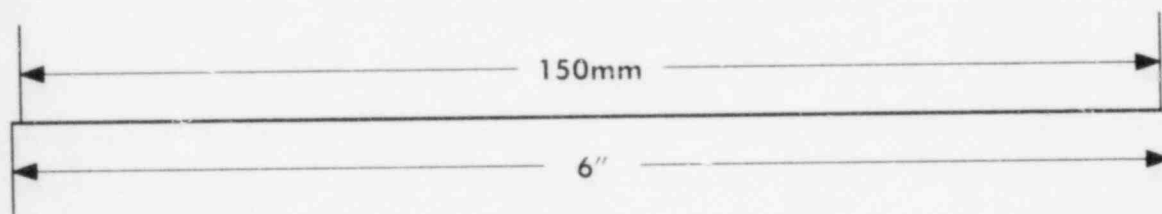
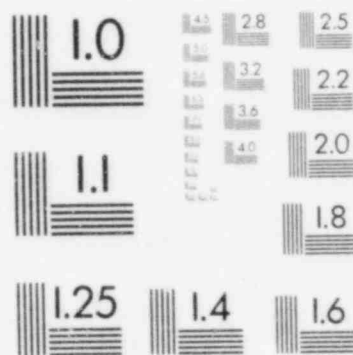
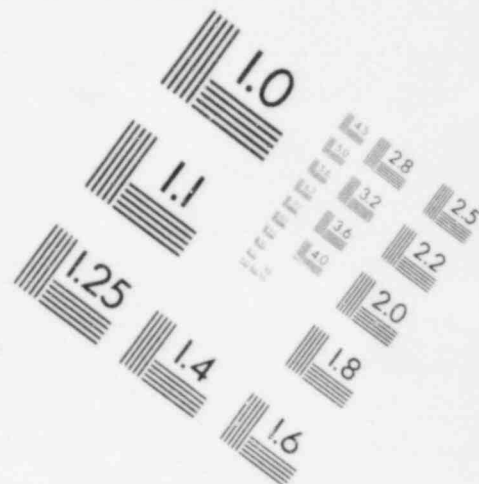
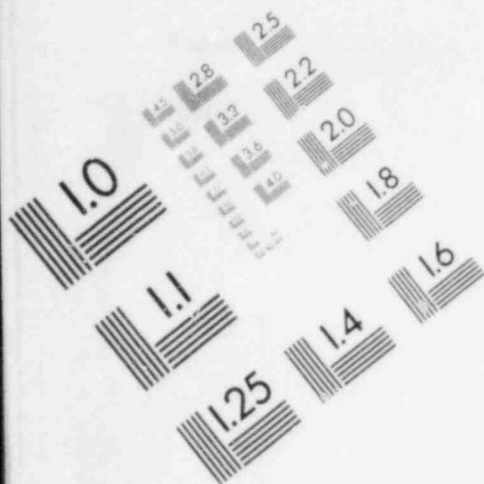


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A later American study by Creagen et al. (18) disputes an association between mining and an increased rate of cancer of the stomach and suggests that the correlation is with socioeconomic class rather than with occupation. In this work, mortality from gastric cancer in 23 coal mining counties in seven states of the United States during the period 1950 to 1969 was compared with other counties. Populations were carefully matched by educational level and median income. While observed deaths from gastric cancer were 20% to 30% greater than expected for men and women (statistically highly significant) a similar excess was noted for lung and cervical cancer, tumors related to low socioeconomic class. Fewer deaths occurred as a result of leukemia, and breast and colon cancers, tumors which are associated with higher social class.

The authors dismissed the excess stomach cancer rate on the basis of a socioeconomic association; yet they stressed that the miners and nonminers were in fact closely matched on the basis of schooling completed and median family income.

In a recent mortality study, Rockette (19) found a 35% excess of stomach cancer among a population of 22,998 coal miners, representing a 10% probability sample of all coal miners eligible for benefits from the United Mine Workers of American Welfare and Retirement Funds as of January 1, 1959. The sample population was traced through the year 1971, and was compared to all males in the U.S. for 1959-71 as a control.

A definitive conclusion on the association between coal mining and increased risk of cancer of the stomach is not possible from the published epidemiological data. However, when the available data are taken on balance, it would appear that the excess rate of cancer of the stomach in coal miners over nonminers cannot be dismissed wholly on a socioeconomic basis. While the existing data imply that an increase in coal mining might result in an increased incidence of cancer of the stomach among coal miners and perhaps their immediate families, further work to identify the effects of conflicting variables is required before such an association can be either confirmed or denied.

Carcinoma of the Lung. Available epidemiologic studies suggest that the death rate of coal miners from cancer of the lung is appreciably lower than the rate for nonminers of comparable age. In the earliest reported study, Kennaway and Kennaway et al. (20) examined the death certificates of men aged 20 years and over who died in England and Wales during 1921-32 of cancer of the lung and larynx. They calculated age-standardized death rates for 63 occupations and noted specifically low rates in agriculture and coal miners. This finding was corroborated by

data in the Registrar General's Decennial Supplement on Occupational Mortality for 1949-1953 (21). Doll (22) found a similar association in the death records of 15,000 men who had been residents in four districts of South Wales during 1948-56. The ratio of deaths from lung cancer to deaths from other causes was calculated for several occupational groups and found to be particularly low for coal miners. It was shown that if cancer had accounted for the same proportion of all deaths in coal miners as it did in other men, that 152 deaths from lung cancer would have been expected in coal miners whereas only 73 were recorded, a deficit of 52%.

Several studies of necropsy incidence of lung cancer in coal miners have been reported. Of these, the best controlled is that of James (23), who compared the results of necropsies on 1827 coal miners and 1531 male nonminers of similar age from South Wales. Lung cancer was present in 3.3% of the miners and in 5.4% of the nonminers. However, it was suggested that pneumoconiosis was a competing cause of death leading to the low necropsy incidence of lung cancer among these workers. In more recent papers, Goldman (24) has presented further support for these earlier observations. He reported that the standardized mortality ratios for cancer of the lung of underground miners and ex-miners employed by the National Coal Board of England was 74 in comparison to 100 expected deaths from this cause. The mortality in surface workers was found to be higher (Table 6). Mortality rates for cancer of the lung for a small coal mining valley and the mortality figures for lung cancer in several towns which are situated in mining and nonmining areas supported these figures. The author also summarized the data available on the relationship between smoking and lung cancer in coal miners. He concluded that numerous investigators have found little difference in smoking habits between coal miners and nonminers and found no indication that the low incidence of lung cancer among coal miners resulted from unusually low cigarette consumption. He speculated that a reduced

Table 6. Standardized mortality ratios (SMR) of miners and ex-miners employed by the British National Coal Board, for cancer of the lung and for other neoplasms, 1955.*

	Underground workers		Surface workers	
	Lung cancer	Other neoplasms	Lung cancer	Other neoplasms
Observed deaths	216	459	54	93
Expected deaths	308	450	59	82
SMR ^b	70.1	102.0	91.5	113.4

*Data of Goldman (24).

^bEngland and Wales, males = 100.

risk of acquiring lung cancer is a specific effect of working in a coal mine, and that an occupational factor such as inhalation of coal dust may block the induction of pulmonary malignant change.

One of two initial studies in the United States failed to corroborate the British findings. Thus Enterline (25), using occupational data from the National Office of Vital Statistics of the U.S. Public Health Service for 1950, calculated standardized mortality ratios for several selected causes of death in coal miners aged 20-64 and 20-59. In the age group 20-64 there were 161 observed deaths caused by cancer of the trachea, bronchus, and lung with 84 expected deaths giving a SMR of 192; i.e., 192 deaths compared to 100 expected. In the 20-59 age groups the SMR was 164. This study can be attacked on the grounds that the expected deaths are based on populations reported in the 1950 census estimates which recorded the last occupation preceeding the date the census was taken; i.e., men who once mined coal but changed occupations were not classified as coal miners.

In the positive American study, Searano et al. (26) found that cancer of the lung was diagnosed in 7% of anthracosilicotics and in 1.08% of nonanthracosilicotics, this difference being highly significant. However, no data on the ages of miners versus nonminers were published, again rendering the conclusion suspect.

In the most recent study of mortality from lung cancer in U.S. coal miners, Costello et al. (27) followed up a cohort of Appalachian coal miners who were included in a 1962-1963 U.S. Public Health Service prevalence study and compared the lung cancer mortality of this sample with the 1968 death rate of the United States males as a whole. Smoking habits were recorded in the population under consid-

Table 7. Observed and expected deaths and standard mortality ratio in a group of 451 Appalachian coal miners who died on or before January 1, 1972.^{a,b}

Age	Observed	Expected
25-29	0	—
30-34	0	1
35-39	1	—
40-44	0	1
45-49	0	3
50-54	2	6
55-59	5	8
60-64	4	16
65-69	11	1
70-74	1	0
75-79	0	0
Total	24	36

*SMR = $(24/36) \times 100 = 67$. From a cohort of 3726 miners randomly selected by the U.S. Public Health Service in 1962-1963.

^bData of Costello (27).

eration. The Standard Mortality Ratio obtained in this study was 67, a figure which agreed well with British figures and corroborated the association reported in the British literature between coal mining and a decreased lung cancer incidence (Table 7). Again no relationship between amount of cigarettes smoked and the decreased rate of lung cancer was found.

The available data strongly suggest that an unknown factor in the coal mine environment, possibly coal dust, exerts a protective effect with regard to cancer of the lung. Accordingly, it would be anticipated that an increase in the scale of coal mining would not increase the incidence of lung cancer in coal miners. However, if coal dust is in fact beneficial with regard to lung cancer, it is also a causative factor in black lung. Thus while lung cancer rates might not increase as a result of an expansion of coal production, black lung and other respiratory diseases would probably become more prevalent.

Coal Combustion

Air Pollution and Cancer. This report considers cancer only; effects of air pollution on respiratory disease are not discussed. Evidence for an association between air pollution and cancer stems from two types of studies. In the first, urban and rural populations have been compared for incidence of lung cancer.

Several small European studies by Stocks and Campbell (28), Daly (29), and Stocks (30) and a number of large-scale American studies standardized with respect to both smoking habits and to age by Hammond and Horn (31), and Haenszel et al. (32) indicate that there is approximately a two-fold higher incidence of lung cancer in urban than in rural areas.

In the second type of study attempts have been made to correlate cancer mortality data with indices of air pollution. However, the evidence linking air pollution and more specifically benzo(a)pyrene (BaP) directly to lung or other cancers is inconsistent. Thus Menck et al. (33) found a correlation between the concentration of benzo(a)pyrene in air and soil and the lung cancer mortality excess of 40% in south central Los Angeles County. The highest benzo(a)pyrene concentration found was five times greater than would have been expected from automobile exhaust alone and the excess was thought to result from the petroleum and chemical industries concentrated in the area. This association is consistent with earlier findings of Stocks (34) from England. It was postulated that the increased rate of lung cancer in the Los Angeles area resulted from a synergistic action between smoking and neighborhood air pollution.

In an extension of the above studies, Henderson et al. (35) measured actual levels of a number of polynuclear aromatic hydrocarbons (PNA) in the suspended airborne particulate matter in South Central Los Angeles County. Four PNAs were found in excess, benzo(a)pyrene (BeP), benzo(a)pyrene (BaP), benzo(ghi)perylene (GEE), and coronene (COR). A correlation was apparent between the geographic distribution of lung cancer cases and the general location of industries which emitted these PNAs.

For the entire county, occupation was an important determinant of a male's lung cancer risk but within the limits of proportional incidence statistics, it did not explain the excess male risk in the region, suggesting that occupational risk may not explain the excess lung cancer in south central Los Angeles. Neither did smoking habits appear to be a valid explanation for the increased lung cancer rate, since only one (esophageal) of the five type of cancers associated with cigarette consumption was in excess and since the greatest excess rate was of adenocarcinoma of the lung, a histological type which does not appear to be related to smoking.

Table 8 which summarizes the evidence for an association between air pollution and lung cancer is taken from a paper by Lave (36) and is based on the work of Buell and Dunn (37). For smokers, death rates (adjusted for age and smoking) ranged from 25 to 123 percent higher in urban areas than in rural areas. For nonsmokers, all differences exceeded 120%.

The incidence of nonrespiratory tract cancers has also been related to air pollution. In a reworking of data from England on rates of death from nonrespiratory tract cancer, Lave and Seskin (37) (Table 9) found that the evidence of stomach cancer was significantly related to a particulate deposit index and a smoke index with nearly identical effects for males and females. Intestinal cancer appeared to be only marginally related to indices of either deposit or

smoke. For 26 areas in northern England and Wales, there appeared to be little relationship between nonrespiratory tract cancers and a smoke index. The single exception occurred in males when the socioeconomic variable was social class: here the smoke index explained a significant amount of the variation in the cancer mortality rate. Regressions 1 through 5 imply that if the quality of air of all boroughs were improved to that of the borough with the best air, the rate of death from lung cancer would fall by between 11 and 44 percent. Regressions 5 and 6 indicate a relationship between air pollution and lung cancer which is either insignificant or inverse.

Winkelstein et al. (38), using as a measure of pollution an index of suspended particulates averaged over a two year period, found the rate of mortality from stomach cancer in Buffalo, New York, and the immediate environs to be more than twice as great in areas of high pollution as in areas of low pollution. However, the authors recognized the necessity of further work which would permit an independent assessment of the possible effects of cigarette smoking, air pollution, and economic or occupational status.

Hagstrom et al. (39), using four measures of air pollution, found the cancer mortality rate to be 25% higher in polluted areas than in areas of relatively clean air among middle class residents of Nashville, Tennessee, between 1949 and 1960. They also found significant mortality rate increases associated with individual categories of cancer such as stomach cancer, cancer of the esophagus and cancer of the bladder.

Levin et al. (40) reported for all types of cancer the following relationships: the age adjusted cancer evidence rates for urban males was 24 percent higher than for rural males in New York State (exclusive of New York City) (1949-51), 36% higher in Connecticut (1947-51), and 40% higher in Iowa (1950); the incidence for urban females was 14% higher than

Table 8. A comparison of published lung cancer mortality data from rural and urban areas.
Number of deaths from lung cancer per 100,000 population.^a

No. of deaths standardized for age and smoking			No. of deaths in nonsmokers			Study
Urban	Rural	Urban/ rural	Urban	Rural	Urban/ rural	
101	80	1.26	36	11	3.27	California men: death rates by counties
52	39	1.33	15	0	∞	American men
189	85	2.23	50	22	2.27	England and Wales
			38	10	3.80	Northern Ireland
149	69	2.15	23	29	.79	England: no adjustment for smoking
100	50	2.00	16	5	3.20	American men

^aData of Lave (36).

Table 9. Associations between cancer, air pollution, and socioeconomic status. Multiple regressions based on data from England. Numbers in parentheses are the *t* statistic.^a

Category	<i>R</i> ^b	Index ^c	
		Air pollution	Socio-economic
Lung cancer mortality rate			
53 County boroughs ^d (deposit index, persons/acre)	0.545	0.041 (2.09)	0.154 (4.23)
28 County boroughs ^e (smoke, persons/acre)	0.576	0.864 (4.08)	0.161 (3.89)
Male, 26 areas ^f (smoke, persons/acre)	0.781	0.137 (2.86)	0.115 (1.70)
Male, 26 areas ^g (smoke, social class)	0.805	0.161 (5.62)	0.172 (2.47)
53 Urban areas ^h (smoke, persons/acre)	0.344	-0.086 (-2.42)	0.184 (4.83)
53 Urban areas (SO ₂ , persons/acre)	0.378	-0.105 (-3.00)	0.197 (5.23)
Other cancers			
Stomach, male, 53 county boroughs (deposit index, persons/acre)	0.167	0.070 (3.08)	0.005 (0.12)
Stomach, female	0.175	0.070 (3.08)	-0.023 (-0.56)
Stomach, male, 28 county boroughs (smoke, persons/acre)	0.257	0.714 (2.57)	0.065 (1.21)
Stomach, female	0.454	0.883 (4.13)	0.666 (1.60)
Intestinal, 53 county boroughs (deposit index, persons/acre)	0.041	0.018 (1.45)	-0.012 (-0.52)
Intestinal, 28 county boroughs (smoke, persons/acre)	0.129	0.174 (1.26)	0.036 (1.35)
Other cancer, male, 26 areas (smoke, persons/acre)	0.454	0.019 (0.59)	0.073 (1.60)
Other cancer, female, 26 areas (smoke, persons/acre)	0.044	0.039 (0.93)	-0.062 (-1.03)
Other cancer, male, 26 areas (smoke, social class)	0.396	0.060 (2.75)	0.017 (0.33)
Other cancer, female, 26 areas (smoke, social class)	0.002	0.005 (0.17)	-0.013 (-0.19)

^aData of Lave (36).

^bThe coefficient of determination: a value of 0.386 indicates a multiple correlation coefficient of 0.62, and indicates that 39% of the variation in the death rate is "explained" by the regression.

^cThe *t* statistic: for a one-tailed *t*-test with 23 degrees of freedom, a value of 1.71 indicates significance at the 0.05 level; for 25 or 50 degrees of freedom, the critical values are 1.71 and 1.68.

^dPersons per acre (multiplied by 10); the range is 69 to 364, and the mean is 163. Death rates are measured as index numbers, with the mean for all boroughs in England and Wales equal to 100. Ranges within this sample are as follows: bronchitis (males), 73 to 259; bronchitis (females), 72 to 268; lung cancer, 70 to 159; stomach cancer (males), 67 to 168; stomach cancer (females), 84 to 161; intestinal cancer, 87 to 123.

^eData for 28 county boroughs in England and Wales equal to 100. Ranges within this sample are as follows: bronchitis (males), 73 to 259; bronchitis (females), 72 to 268; lung cancer, 70 to 159; stomach cancer (males), 67 to 168; stomach cancer (females), 84 to 161; intestinal cancer, 87 to 123.

^fData for 28 county boroughs in England and Wales as reported by Stocks. Air pollution is measured by a smoke index (suspended matter, in mg/100 m³); the range is 6 to 49. Again, the socioeconomic index is expressed in numbers of persons per acre ($\times 10$); the range is 83 to 342.

^gData for 26 areas in northern England and Wales as reported in Stocks. Air pollution is measured by a smoke index; the range is 15 to 562 mg/1000 m³ and the mean is 260. One socioeconomic variable is the number of persons per acre ($\times 10$); the range is 1 to 342 and the mean is 102. The other socioeconomic variable is social class; the range is 61 to 295. Death rates are measured as for category 1; within this sample, the range for lung cancer is 23 to 165; for other cancer, 6 to 122 (males) and 88 to 154 (females); for bronchitis, 18 to 259 (males) and 12 to 240 (females); for pneumonia, 61 to 227 (males) and 40 to 245 (females).

^hData for 53 areas as reported by Ashley. Air pollution is measured by a smoke index (as for category 3), with a range of 23 to 261 $\mu\text{g}/\text{m}^3$ and a mean of 124, or by an SO₂ index (apparently in the same units), with a range of 33 to 277 and a mean of 124. Death rates are measured as for category 1; within this sample, the range for lung cancer is 70 to 146, and for bronchitis, 64 to 186.

for rural females in New York State, 28% higher in Connecticut, and 34% higher in Iowa. For both males and females the incidence for each of 16 categories of cancer was higher in urban than in rural areas.

Lave and Seskin (37) speculated that approximately 25% of mortality from lung cancer and 15% mortality from all cancer can be eliminated by a 50% reduction in air pollution. In monetary terms, these decreases in cancer rates would represent \$33 million and \$390 million respectively.

On the other hand, Higgins (41) found little correlation between benz(a)pyrene or total suspended particulate levels and lung cancer death rates in some 50 standard Metropolitan Statistical Areas. However, a significant correlation with sulfate levels appeared to exist (Table 10).

A strong relationship of BaP to lung cancer was also absent in a study by Waller (42). He reported that the incidence of lung cancer in gas workers was only about 1.5 times that expected in spite of a 100- to 10,000-fold excess of benz(a)pyrene in the air breathed by those workers in comparison with air to which a normal urban population is exposed.

Perhaps the most convincing support for a relationship between air pollution and lung cancer stems from migrant studies. In this approach, lung cancer death rates in migrants from one country to another were compared with those in their home populations and with those in populations in the countries to which they had immigrated. If such migrants can be considered as equivalent to random or representative samples of the populations of the home countries, differences in death rates from those in the home countries can be ascribed to changes in environmental conditions, since concentrations of pollutants including benz(a)pyrene vary considerably worldwide.

The results of these studies indicated that persons migrating from a more polluted environment to a less polluted environment had an increased risk of lung cancer compared to the native population, but a lower risk than their home populations. The risk

increased with age at time of migration. Unfortunately most of the studies lack data regarding the effect of the smoking factor. However, in several studies such as that of Eastcott (43), an evaluation of migrants from the United Kingdom to New Zealand showed that the migrants had a 35% higher risk of lung cancer than native New Zealanders if they came from the United Kingdom before the age of 30. This was true regardless of the fact that the migrants generally increased the number of cigarettes smoked after arriving in New Zealand.

Dean's studies (44, 45) are also important in this regard. He compared lung cancer rates in British subjects who migrated to South Africa and Australia with those in native born South Africans and Australians.

Australians have heavier smoking habits than persons in the United Kingdom and South Africans are among the heaviest cigarette smokers in the world. British migrants to South Africa tended to increase their consumption of cigarettes markedly. While the butt lengths of cigarettes smoked by British and South African smokers were closely comparable, (25.3 vs. 25.2, respectively) a greater percentage of South Africans inhaled deeply and some South Africans took more puffs per cigarette. In spite of this, migrants from the United Kingdom had a significantly lower lung cancer death rate than persons remaining in England but a higher rate than native South Africans or Australians (Tables 11 and 12). The lung cancer death rates in migrants to Australia from the United Kingdom (45) were also higher than in native Australians but lower than in a cohort group in the United Kingdom.

Similar findings were reported by Reid (46) for migrants from the United Kingdom and Norway to the United States as compared with persons remaining in the home country and with native-born Americans. Again, lung cancer death rates of migrants were intermediate between those of native U.S. residents and those of nonmigrants in the home countries (Table 13).

A recent study relevant to both the urban-rural

Table 10. Epidemiology of lung cancer in the United States^a

Measure of pollution	Death rates from lung cancer 1959-1961			
	Males		Females	
	White	Nonwhite	White	Nonwhite
Total suspended particulates	-0.03	0.25	-0.09	-0.02
Sulfates	0.42	0.39	0.19	-0.05
Benz(a)pyrene	0.17	0.00	0.10	-0.11

^aData of Higgins (41). Correlation coefficient between measures of air pollution and age-standardized death rates from lung cancer (ICD 162-163) in approximately 50 standard metropolitan statistical areas of U.S.

Table 11. Lung cancer death rates for white male natives of England, Wales, and South Africa and United Kingdom migrants to South Africa, 1947-1956.^a

Population group	Annual lung cancer death rate (per 100,000 persons)	
	45-64 years old	65+ years old
Native white South Africans	50	112
United Kingdom migrants to South Africa	112	172
Native white United Kingdom	135	249

^aData of Dean (44).

Table 12. Age-adjusted (40+ years old) lung cancer death rates, 1950-1958.^a

Population group	Lung cancer death rate per 100,000 persons
Native Australians	53
United Kingdom migrants to Australia	94
United Kingdom cohort group	154

^aData of Dean (45).

Table 13. Age-adjusted death rates from lung cancer in Great Britain, Norway, and the United States.^a

Population group	Lung cancer death rate per 100,000 persons	
	Males	Females
Great Britain residents	151.2	19.3
Great Britain-born U.S. residents	93.7	11.5
Norway residents	30.5	5.6
Norway-born U.S. residents	47.5	10.7
Native U.S. residents	72.2	9.8

^aData of Reid et al. (46).

comparison studies and migrant studies is that of Morris et al. (47). In this work, mortality experience was determined over a 13-year period (1960-1972) for sample populations in two small Pennsylvania communities with widely different air pollution levels. A relationship was suggested between mortality rate and length of residence in the polluted community (age adjusted) but not in the control community. An influence of smoking on mortality was clearly evident. While a small (volunteer) population size precluded definitive conclusions, (socioeconomic patterns were also not determined) it appeared that those with over 20 years exposure to air pollution in the polluted community ($151 \mu\text{g}/\text{m}^3$ suspended particulate; $3.7 \text{ mg}/100 \text{ cm}^2/\text{day}$ sulfation rate) had about one-tenth the excess mortality of those smoking one pack of cigarettes a day in the control community ($109 \mu\text{g}/\text{m}^3$ suspended particulates; $0.6 \text{ mg}/100 \text{ cm}^2$

day sulfation rate). The data support the hypothesis that the effects of smoking and air pollution are additive. An important consideration arising from these data which is relevant to migration studies is the hypothesis that immigrants to a polluted community are a self-selected unusually healthy group. These factors require further examination. The above findings provide a strong basis for concluding that differences in lung cancer death rates in different populations are related to more than cigarette smoking i.e., to an urban factor.

Possible Effect on Cancer Incidence of Increased Coal Consumption. Among the polynuclear hydrocarbons produced by coal combustion is benzo(a)pyrene, a carcinogenic hydrocarbon under experimental conditions. Concentrations of benzo(a)pyrene, benzo(e)pyrene, and benz(a)anthracene in the flue gases from coal-fired installations have been published by Diehl et al. (48) (Tables 14 and 15). These results indicate that polynuclear hydrocarbon concentrations in flue gases from coal combustion can be highly variable and that the variation cannot normally be related to identifiable operating parameters.

While BaP cannot be assumed to be the cause of lung or nonrespiratory cancer in man, it can be used as an index of air pollution since its concentration is correlated with other hydrocarbons and sulfur dioxide, and since it appears in solid form in air, usually adsorbed on particles.

A quantitative estimate of the relationship between lung cancer death rates and atmospheric BaP concentrations was attempted by the Committee on Biological Effects of Atmospheric Pollutants of the National Academy of Sciences (49). This committee used the comparison between urban and rural cancer rates (i.e., a male urban lung cancer death rate approximately twice that found in corresponding rural areas) and the urban ($6.6 \mu\text{g}/1000 \text{ m}^3$ BaP) and rural ($0.4 \mu\text{g}/1000 \text{ m}^3$ BaP) concentrations of Sawicki (50). On this basis, approximately a 100% increase in lung cancer rate is associated with a 6.2 unit (one unit of BaP = $1 \mu\text{g}/1000 \text{ m}^3$) increase in BaP or an increase of approximately 15% in deaths per unit increase in BaP. However, since the 100% increase represents the difference between the most heavily urban and the most rural environments, the pollution effect estimated from these studies should be somewhat less than 15%. Using the difference in lung cancer death rates of 13 per 100,000 of population reported between urban and rural areas in a study by Hammond and Horn (52), there is a change of about 5% in the lung cancer death rate per unit of BaP.

The committee also utilized regression analysis to separate the effects of factors that differentiate urban and rural environments, using the assumption that

Table 14. Concentration of three polynuclear hydrocarbons in the flue gas of coal-fired installations.^a

No.	Type of burner	Capacity, lb steam/hr	Load factor sampled	Benzo(a)pyrene			Benzofluoranthene			Benz(a)anthracene		
				$\mu\text{g}/1000$ m^3	$\mu\text{g}/10^6$ BTU	mg/hr	$\mu\text{g}/100$ m^3	$\mu\text{g}/10^6$ BTU	mg/hr	$\mu\text{g}/1000$ m^3	$\mu\text{g}/10^6$ BTU	mg/hr
1	Chain grate	33,000	0.61	—	—	—	250	119	3.5	—	—	—
2	Chain grate	35,000	0.45	9	4	0.1	91	42	1.0	44	20	0.4
3	Chain grate	40,000	0.47	110	75	2.8	440	300	11	—	—	—
4	Chain grate	52,000	0.41	850	500	20	530	310	12	1,400	820	32
5	Chain grate	55,000	0.81 ^b	—	—	—	—	—	—	—	—	—
6	Underfeed	160,000	0.74	240	120	13	140	72	7.7	380	200	21
7	Underfeed	25,000	0.40 ^b	53	31	1.1	590	350	12	—	—	—
8	Spreader	24,000	0.75	120	68	1.3	820	470	9.1	—	—	—
9	Pulsating grate	2,470	1.00	650	330	1.3	1,300	670	2.7	1,300	670	2.7
10	Pulverized coal	40,000	0.80	420	230	9.1	860	470	19	400	220	8.7
11	Pulverized coal	240,000	0.88	180	120	45	1,300	880	330	—	—	—
12	Pulverized coal	600,000	1.10	—	—	—	160	64	.06	—	—	—
13	Pulverized coal	830,000	1.05	66	21	31	110	34	50	—	—	—
14	Pulverized coal	1,060,000	1.00	18	6	10	380	130	220	—	—	—
15	Pulverized coal	1,250,000	1.02	80	32	59	68	27	50	—	—	—
16	Pulverized coal	2,030,000	0.78	59	20	54	130	44	120	—	—	—
17	Pulverized coal	2,100,000	0.85	56	17	28	120	37	62	—	—	—
18	Cyclone	2,200,000	0.99	40	16	49	140	55	170	—	—	—

^aData of Diehl (46).Table 15. Polynuclear hydrocarbons in the flue gas produced by different types of coal (pulsating grate stoker).^a

Coal	Firing rate, 10 ⁶ BTU/hr	Benzo(a)pyrene			Benzofluoranthene			Benz(a)anthracene		
		$\mu\text{g}/1000$ m^3	$\mu\text{g}/10^6$ BTU	mg/hr	$\mu\text{g}/1000$ m^3	$\mu\text{g}/10^6$ BTU	mg/hr	$\mu\text{g}/1000$ m^3	$\mu\text{g}/10^6$ BTU	mg/hr
Elmore No. 5	3.87	1500	840	3.2	3800	2100	8.1	5700	3200	12
Elmore No. 3	3.45	—	—	—	64	30	0.1	24	11	0.04
Elmore No. 5	4.45	540	210	1.0	1200	480	2.1	770	300	1.3
Elmore No. 5	4.29	1700	820	3.5	2600	1200	5.1	1000	450	2.1
Elmore No. 8	3.29	120	71	0.2	280	160	0.5	—	—	—
Elmore No. 8	3.52	54	25	.09	88	41	0.1	190	58	0.3
Average	—	650	330	1.3	1300	670	2.7	1300	670	2.7

^aData of Diehl (46).Table 16. Multiple regression analysis of lung cancer death rates for males in 19 countries and cigarette and solid-fuel consumption.^a

Regression coefficients r				
Age group, years	Average death rate per million persons	Constant (C_0)	Cigarettes, 1,000's per person per year (avg. = 1.76)	Solid fuel, metric tons per person per year (avg. = 1.55)
Age-adjusted	749.3	330.0	110.0	144.0
25-34	10.0	2.8	2.0	2.0
35-44	73.2	9.7	23.0	15.0
45-54	427.6	164.0	78.0	80.0
55-64	1,377.2	704.6	138.0	276.0
65-74	1,939.3	810.0	321.0	361.0

^aNAS data (47).

the lung cancer death rate is related both to cigarette consumption and to solid fuel consumption and that the effects are at least approximately additive. With this approach the regression coefficient for solid fuel consumption is approximately 20% of the average

lung cancer death rate. This suggests an increment in male lung cancer deaths of 20% per metric ton of coal burned per year per capita (Table 16).

The conclusion suggested by these results is that the products of solid-fuel combustion or of some

variables highly correlated with solid fuel may be an important etiologic factor in lung cancer. However, as discussed elsewhere in this paper, an extrapolation based on BaP levels appears to be a gross oversimplification considering the importance of adsorptive properties of soots and the synergistic capabilities of air pollutants, particularly those in tobacco smoke.

Carbon Black Manufacture

Commercial soot production has become a sizable industry and it is of interest to learn that a carcinogenic hazard has not been detected in the workers due to the presence of carbon black in the air. Although it is not clear what particle size carbon blacks were prepared in the factory under study, Ingalls could not demonstrate any cancer risk for that group (52). Similar findings were reported for workers in a French carbon black manufacturing facility (53). A plausible explanation was offered by Ingalls in the low content of acetone-extractable matter from the carbon blacks manufactured in the plant under study compared to the soots that were in contact with the British chimney sweeps' skin.

Laboratory Studies Which Support or Contradict Epidemiologic Data

A few data are given in this section to orient the reader on some background information which may be helpful in the cancer risk evaluation of increased exposure to coal dust and soot. However, none of the experiments are adequate to answer questions on human risks quantitatively.

Formation of Polynuclear Aromatics (PNA)

Ellis (54) gave an explanation for the formation of largely pericondensed aromatic hydrocarbon from organic materials on pyrolysis. At 1100°C, methane, for instance, would break down to methylene radicals and hydrogen, the free radical would dimerize to ethylene which on losing additional atoms of hydrogen would give rise to what was referred to by Groll (55) as "nascent acetylene" from which by polymerization aromatic hydrocarbons would be formed. The simpler structures would then break down losing hydrogen to give rise to carbon, hydrogen and more complex aromatic hydrocarbons. The same products were obtained by pyrolysis of natural gas, containing hydrocarbons with two and more carbons in the molecule. From these findings one can understand the observations of Kennaway that pyrolysis of organic materials might lead to carcinogenic tars (56).

Effect of Temperature on Formation of PNA

Kennaway made the important observation that on pyrolysis of isoprene polycyclic hydrocarbons were only formed at temperatures above 750°C. He identified benzene, naphthalene, anthracene, phenanthrene, and chrysene. The tar thus formed was highly carcinogenic and probably contained higher condensed systems of PNA as well (57). A critical temperature for the formation of carcinogenic polycyclic hydrocarbons was also postulated by Dickens and Weil-Malherbe who produced a non-carcinogenic soot extract from wood that had been heated to 400-450°C (58). These data support the findings on lung cancer incidence among workers employed near carbonization chambers as shown in Table 17 (59).

Table 17. Temperature range of carbonizing chambers and excess of lung cancer reported.

Carbonizing chamber	Temperature range, °C	Excess of lung cancer reported, %
Vertical retorts	400-500	27%
Horizontal retorts	900-1100	83%
Coke ovens	1200-1400	255%
Japanese gas generators	1500	800%

*Data of Kennaway (57).

Carcinogenicity of Selected PNA and Heterocycles Found in Air Pollution

Few of these compounds were studied for their ability to induce lung tumors. There are also few studies on their carcinogenicity on oral administration, but each and everyone has been tested for carcinogenicity to the skin by painting the back of mice. However, by repeated application of the solution, it is difficult to estimate the total dose required for a carcinogenic response and for that reason the subcutaneous injection route in mice is chosen here for comparison of potency. It is realized that relative potency need not be the same for other organs or tissue and for other species. It may serve the purpose of refreshing one's memory on the different constituents of soot belonging to the PNA and heterocycles.

Benzo(a)pyrene, injected in a 1:9 cholesterol:olive oil mixture, produced sarcomas in C57 mice. When the dose was 40, 4, or 0.4 µg, sarcomas were produced in 23, 5, or 1 mouse in each group of 50 (60).

Benz(a)anthracene, dissolved in triacrylin, produced sarcomas in C57 black mice on subcutaneous injection. With a single injection of 50 µg there were five sarcoma-bearing animals among 43 mice, with 200 µg 11/43, with 1000 µg 15/31, with 5,000 µg 49/145, and with 10,000 µg 5/16 (61).

Chrysene in tricaprylin at a dose of 5000 μg produced four sarcomas in 39 mice (62); in a similar experiment also on C57 black mice, of 20 mice, two developed sarcomas on subcutaneous injection of 10 doses of 1000 μg each of chrysene in arachis oil (63).

Benz(b)fluoranthene was given subcutaneously to 30 XVII nc/z mice in three injections of 600 μg each, and 18 out of 24 survivors had sarcomas (64).

Indeno(1,2,3-cd)pyrene in olive oil was injected into XVII nc/z mice and produced 10 sarcomas in 14 male and 1 sarcoma in 14 female mice on three doses of 100 μg each (64).

Dibenz(a,h)acridine, at a dose of 1000 μg in sesame oil injected subcutaneously into 19 mice, produced 8 sarcomas in 13 survivors (65) while the same dose in A strain mice with tricaprylin as solvent produced no sarcomas at the injection site but multiple lung tumors (66). Dibenz(a,j)acridine dissolved in arachis oil and injected in three doses of from 500 to 1000 μg each into strain XVII mice produced no sarcomas in the few survivors at 4.5 months (67). Other experiments with better survival also had negative results. At repeated injections of 5000 μg of the compound into 10 mice, Badger et al. observed two sarcomas (68).

There is good evidence that all the specific chemicals mentioned above are carcinogenic also when applied to the skin of mice (69). Experiments have been carried out with specific PNA to attempt the induction of cancers of the respiratory tract. The Syrian golden hamster was used for these studies and the chemicals were given by intratracheal instillation as a suspension in saline with an equal weight of iron oxide (Fe_2O_3). Without the fine suspension of the iron oxide, the carcinogen failed to induce tumors. One study gave 30 weekly doses of 2, 1, 0.5, or 0.25 mg/dose of benzo(a)pyrene and the same dose of iron oxide to 30 hamsters of each sex and observed 34, 42, 19, and 10 tumor-bearing animals, respectively, equally distributed between the sexes. The location of the tumors was mainly in the bronchi, also in the trachea but less in the lungs (70). Increasing the quantity of iron oxide administered with the benzo(a)pyrene suspension to twice and thrice the quantity of carcinogen did not alter the tumor response (71). Replacing the dust by magnesium oxide gave a similar result, although the location of tumors was different (72); choosing titanium dioxide as dust produced the same response in the hamster tracheo-bronchial tree as with iron oxide. Aluminum oxide and carbon were less effective, however. The carbon was identified only as a carbon black without details on particle size and the few tumors produced were largely benign (73).

When a number of different PNA, present in typical sooty atmospheres were compared with BaP in

the above experiments using iron oxide as particulates, it was found that 30 instillations of 0.5 mg each of benz(a)anthracene produced no respiratory tract tumors in 47 hamsters; 30 instillations of 3 mg pyrene produced one tumor in 48 animals; 0.5 mg benz(b)fluoranthene given 30 times produced one tumor in 47 animals; and 30 instillations of 0.25 mg dibenz(a,h)-anthracene produced two tumors in 46 hamsters (74).

In contrast to these largely negative results the hamsters responded to four instillations of 2 mg each of dibenz(a,i)pyrene with the production of 16 respiratory tract tumors in 34 animals and in another experiment with the same carcinogen given in 24 doses of 0.5 mg each with induction of 39 tumors in 44 animals. Here, then, is a highly potent carcinogen for that system (74).

Feron (75) also used instillation of a saline suspension of benzo(a)pyrene intratracheally in Syrian golden hamsters to study the respiratory tract lesions induced without the use of dust but with irritants like furfural. When only benzo(a)pyrene at a dose of 1 mg each was administered for 36 weeks 41 out of 62 hamsters had respiratory tumors (in contrast to the findings above), but the introduction of a 1.5% furfural solution instead of saline made only minor changes; i.e., not so much in epithelial tumor induction, but in shortening the latent period and in causing induction of peritracheal sarcomas in 20 hamsters out of 61 as compared to 2 sarcomas in the benzo(a)pyrene treated group of 62 animals (75). Similar studies using benzopyrene as the carcinogen and acrolein as cofactor did not show any cocarcinogenic activity when the hamsters were exposed to air containing 4 ppm acrolein for 7 hr/day, 5 days/week for one year (76).

Cocarcinogenicity of PNA and Compounds Related to Coal Combustion

Incomplete carcinogens were identified by Van Duuren et al. (77) in experiments in which the chemical was applied in a single dose to the skin of ICR/G1a Swiss mice and with repeated application of phorbol myristate acetate, one of the active principles of croton resin, to the skin for a year or longer. With benz(a)anthracene he observed benign tumors in 10 out of 20 animals after application of 1 mg total dose. For perylene and benz(g,h,i)perylene, the dose applied was 0.8 mg and the tumor induction was of borderline significance, but the shortened latent period definitely suggests initiating activity. In a separate study coronene at 0.5 mg total dose was found to be a weak initiator, while two other PNA not encountered in soot—namely, dibenz(a,c)an-

thracene and 6-methylanthracene, were potent initiators. Benzo(e)pyrene was inactive, as was anthracene (78).

Cocarcinogenicity was also tested by Van Duuren et al. (79) by application of a low dose of benzo(a)pyrene to mouse skin (5 μ g, three times a week) together with 15 μ g benzo(e)pyrene for one year. In different experiments 45-48 mice survived in each group and the above treatment produced 34 tumor-bearing mice with a total of 70 papillomas and 27 carcinomas. The painting of the skin with 12 μ g pyrene and 5 μ g benzo(a)pyrene produced 27 tumor-bearing animals with 40 papillomas and 19 carcinomas; and 21 μ g benzo(g,h,i)perylene with benzo(a)pyrene produced 20 tumor-bearing animals with 33 papillomas and 17 cancers. Painting benzo(a)pyrene alone produced only 13 tumor-bearing animals with 14 papillomas and 10 carcinomas. Thus the PNA on test showed a cocarcinogenic effect with benzo(a)pyrene (79).

In a different type of experiment, Horton and Christian applied some of the PNA of relevance to this report on coal combustion to the backs of mice in decalin (non-promoting) or a 50:50 mixture of decalin and dodecane (promoting). C3H male mice were treated for 80 weeks and tumor induction was monitored. A 60 μ g dose containing 0.15% chrysene was applied twice a week and yielded 13 carcinoma-bearing mice and two with papillomas-only out of 17 mice. The average latent period was 45 weeks. Pyrene, similarly tested at a 0.5% concentration, produced two carcinoma-bearing mice and two with papillomas. The latent period was 56 weeks. Fluoranthene and perylene were negative. The vehicle alone produced only two papilloma-bearing animals with a latent period of 75 weeks. All the above results were obtained with the solvent system containing the promoter dodecane. Without the promoter the equivalent studies with 100% decalin as solvent were largely negative (80).

In contrast to the cocarcinogenic effects described above another type of experimentation was used by Finzi et al. (81). A 0.3% benzene solution of benzo(a)pyrene or dibenz(a,c)anthracene (alternating every second day) was painted on the backs of 40 Swiss mice for 25 weeks. This group was compared to two other groups painted with BaP and benzene only or dibenz(a,c)anthracene and benzene every second day. The percentage of tumor-bearing animals after 25 weeks reached 90% for BaP painting compared to 45% tumor-bearing animal with the combined painting. A comparable study using perylene instead of dibenz(a,c)anthracene with a slightly different protocol produced similar results. Instead of the 90% tumor-bearing animals with benzo(a)pyrene alone, the combination of BaP and

perylene reduced the incidence of tumor-bearing animals to 33% (81).

Turning now from skin painting to subcutaneous injection into C57 black mice, anticarcinogenic effects were observed for a number of PNA introduced at a ratio of PNA to BaP as encountered in tobacco tar. The carcinogen benzo(a)pyrene was given at a dose of 400 μ g in tricaprylin. The other PNA were benzo(a)fluorene, benz(m,n,o)fluoranthene, perylene, perinaphthoxanthene, benz(a)carbazole, chrysene, benzo(k)fluoranthene, and a mixture of phenanthrene, anthracene, and pyrene. Only those mentioned above inhibited carcinogenesis by BaP significantly (82). More detail is not given because the subcutaneous route is often considered too far removed from the actual target in human cancer induction.

Experiments on Soot

Leitch (83) attempted to produce scrotal cancers in rats and rabbits by the application of soot, but after one year's time observed none. Seelig and Henigius (84) replaced the shavings in cages of 100 Buffalo strain mice with coal soot and observed 8 lung tumors compared with 1 in 50 control animals. No skin tumors were reported for these animals living in coal soot (84). Campbell (85) exposed 75 mice to a cloud of chimney soot 30 times a week for one year and got a lung tumor yield of 20%. However in his control groups he also observed lung tumor incidence as high as 20%. Feeding carbon black to mice produced no tumors in the animals and feeding methyl cholanthrene (adsorbed on carbon black) also produced no tumors in mice. When the extract of carbon black, on the other hand, was fed to mice in their diet, tumors appeared in the stomach (86).

Extracts of soot were known to be carcinogenic since the studies by Passey (87) in 1922, who painted ether extracts of household soot from bituminous coal on the skin and observed nine malignant tumors in 18 mice surviving one year. Passey and Carter-Braine fractionated the extract by distillation and obtained an active distillate above 190°C and an active residue (88).

Chimney soot extracts gave a 40% yield of sarcomas in C3H mice on subcutaneous injection (89). Also, an extract of wood soot painted on the skin of mice produced three neoplasms in 10 mice after 2 years (90). There is little doubt that carcinogenic PNA are present in those soots which goes back to very early findings of Sir Percivall Pott on the frequent occurrence of chimney sweep cancer (91).

Davis et al. recently studied intra-tracheal instillation of benzo(a)pyrene in Infusine at different dose levels with and without carbon black. The carbon black contained extractable pyrene, but no other

PNA. In these experiments on Wistar SPF rats the investigators found squamous neoplasms of the lungs in proportion to the dose of benzo(a)pyrene but observed only half as many cancers when carbon black was also present in the infusate (92).

All these experiments taken together suggest that polynuclear aromatics adsorbed on soot are not available for carcinogenic action unless a proper vehicle is available for elution from soot. Where the amount of adsorbing carbon black or soot is inadequate to remove the carcinogen from solution some cancers may develop.

In this connection it may be of interest to note that it does not require a lipid solvent to elute polycyclic hydrocarbons from soots above a certain particle size, but that plasma will suffice to extract them, although less rapidly and efficiently. The rate of elution has been studied for 48-hr exposure to saline, which eluted none of the PNA on soot, and up to 90-min exposure to plasma which eluted several PNA completely including benzo(a)pyrene and others to more than 50%. Not all of the compounds

could be accounted for 100%, so that metabolism or degradation of some of the PNA represents a possibility (75). (Fig. 4).

Projections of Carcinogenic and Cocarcinogenic Risk Due to Coal Utilization with Achievable Safeguards Due to Technological Developments

In order to assess the potential carcinogenic risk of greatly increased coal utilization for combustion, it is necessary to assume the imposition of safety measures, controls, and safeguards which can currently be formulated. Coal mining would be better and safer if it were done by surface mining, except for the enhanced destruction of agricultural land and the ecologic impact of the disturbance of the land. As a compromise will have to be worked out, the advantages and disadvantages must be compared and

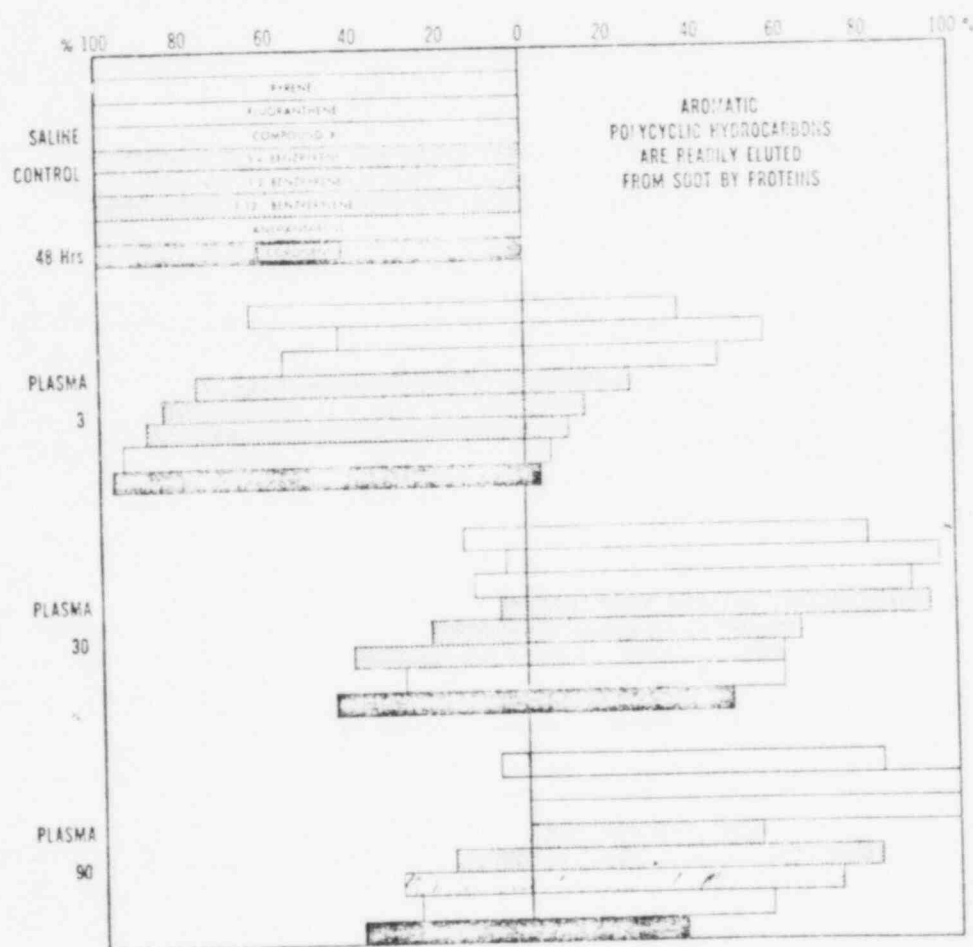


FIGURE 4. Elution of PBA from soot by plasma (75).

weighed and possible health effects must be included in the assessment. Depending on the location of the coal seams, underground mining will undoubtedly be necessary, but the new mines will have to have the benefits of technologic advances, such as high air circulation to reduce the accumulation of coal dust and gases in the air. Also the use of powerful diesel machines will carry out much of the work so that the mining population will be small.

Removal of Sulfur Dioxide

On the other side of the energy production program is the pollution from coal combustion which is already under considerable control. Removal of oxides of sulfur has been accomplished by a variety of means, some leading to usable products, others to waste materials, but all able to remove the SO_2 produced with rather high efficiency. This technology is obligatory and will be included in any new plant development. The efficiency at this stage of development in removal of SO_2 is estimated to be 90% and needs still further improvement. Other processes which would lead to the recovery of sulfur and avoid some problems of disposal of waste materials are also on the drawing boards (93). Undoubtedly under other conditions of coal utilization completely different processes will be developed, such as the extraction of inorganic sulfides (iron sulfide) from pulverized coal and removal of organic sulfur compounds by treatment with hydrogen and a catalyst. These processes will be considered under coal gasification and liquefaction when these techniques are up for health assessment.

Removal of Chlorine

The presence of chlorine in coal may be handled by the same process as described above, i.e., using lime scrubbing devices, but hydrogen chloride is quite corrosive to the equipment.

Reduction in Oxide of Nitrogen Formation

Oxides of nitrogen are formed partly by the oxidation of organic nitrogen-containing components of coal and partly by the interaction of atmospheric oxygen with nitrogen, the latter accounts for most of the oxides of nitrogen formed. Reduction of the temperature of combustion is the best way of reducing oxide of nitrogen formation from air constituents. It is not effective in preventing the oxidation of organic nitrogen-containing components of coal. However, scrubbing devices can remove some of the oxides of nitrogen and catalytic reduction or decomposition techniques can reduce NO_x emission from stationary sources (94).

Removal of Particulate Matter

Electrostatic precipitators have been employed successfully for many years for the removal of particulate matter and they can be very efficient. Removal of most trace elements as well as soot has been accomplished. One problem remains, i.e., the disposal of the waste. For the trace elements which possess carcinogenic or other toxic properties, the utilization of waste material will produce problems. Similarly the soot may carry carcinogenic PNA which may persist.

Destruction of PNA in Soil

Soil will not readily decompose many polynuclear aromatics, although specific organisms have been identified that can destroy polycyclic hydrocarbons. Most soil organisms do not seem to have that capability (95). Uptake of the PNA by plants has been documented. These studies used the hydrocarbon without soot as carrier which must change the ease of uptake considerably. It will probably be best to combust the material collected on the electrostatic precipitator to destroy the PNA that way.

Destruction of PNA in Air

If some soot passes through the electrostatic precipitator it will stay in the atmosphere for some time. Data exist on the degradation of polycyclic hydrocarbons by light and air when adsorbed or not adsorbed on soot (96, 97). The rate is different for each member of the PNA encountered in air pollution. Benzo(a)pyrene is not one of the more resistant hydrocarbons. In the free state benzo(a)pyrene is destroyed or gone to 20% in 24 hr exposure to light and air. When adsorbed on soot, it is only lost to 10% during 48 hr in light. When exposed, adsorbed on soot, to an artificial oxidant atmosphere, prepared from ozone and vaporized gasoline, twice as much is gone in 1 hr. Exposure to an oxidant atmosphere has also a far greater effect on many other polynuclear aromatics encountered on soot. Up to 75% is destroyed.

Research Needs for Resolution of Uncertainties

On the assumption that neither the miner nor the urban dweller will have to be exposed to the hazards of increased coal production or combustion and that technological improvements over today's industrial techniques will further reduce mining hazards and pollution of urban areas, it is still very desirable to understand better some of the functions of polycyclic hydrocarbons in producing their health effects.

PNA Carcinogenicity for the Lung

Data on the carcinogenicity of PNA were obtained at the beginning by skin painting on mice, subsequently by subcutaneous injection into mice. The potency of these chemicals in relationship to each other is largely based on these findings. It would be essential to get a similar comparison of activity for the tracheo-bronchial tree. Knowing the difficulties of inducing tumors in the respiratory tract compared to the skin or the connective tissue, it should be determined how the various PNA compare in carcinogenicity for the respiratory tract.

PNA Synergism with Particulate Matter

In experiments on rats and hamsters, intratracheal intubation with BaP has produced negative results which led investigators to introduce dusts, composed of various metal oxides leading to enhancement of tumor production. Replacement of the dusts by soots may make the experiments somewhat more comparable to real life and may clarify the picture of adsorption of the PNA on soot, leading to unavailability of carcinogens and thus preventing cancer induction. The particle of the general air pollution is of the size that would release the PNA after phagocytosis.

PNA Synergism with Compounds Present in Polluted Air

Some groups of chemicals have been tested for cocarcinogenic activity, mostly on mouse skin, and not very many were active. Phenol itself and catechol were two active promoters. Aldehydes were also expected to act as promoters. Furfural in conjunction with BaP was found inactive for the skin of mice but active as promoter for the lung of hamsters (75). Another important aldehyde, acrolein, was inactive as a cocarcinogen for the hamster lung in conjunction with BaP (74). It may be worthwhile to undertake a more systematic study of typical air pollutants that could act as cocarcinogens with the PNA particularly when applied to the lung of hamsters. Similarly, it would be most desirable to learn more about incomplete carcinogens, those that act only as initiators of carcinogenesis for mouse skin, but may have important properties for the lung in the presence of appropriate promoters.

Anticarcinogens

Some studies on anticarcinogenic properties of PNA have been carried out by subcutaneous injection into mice (82), others by skin painting. The results at times were quite contradictory, which was not surprising because different dose levels were

applied and different modes of administration, timing, and animal strains or species were used. A clearer picture could be obtained if a systematic study was carried out.

Genetic Susceptibility

Species that cannot activate PNA seem to suffer no ill effects from their presence. Recent studies on mice and man suggest that genetic variation in inducible mixed function oxidases may make the individual more or less susceptible to the development of lung cancer (98). It may be worthwhile to understand this relationship better and ultimately to be in a position to screen those to be exposed to PNA at their workplace for their inducible enzyme capability.

Hazards of Coal Utilization by Gasification or Liquefaction

An entirely different problem will be encountered if these processes are introduced on a large scale in the U.S. The processes and the products will represent a different degree of carcinogenic risk which should be recognized before these approaches are activated.

Epidemiological Studies

Further epidemiological studies which address the questions unresolved by the available data on associations between coal mining and cancer and air pollution and cancer are urgently needed. Specific areas which need to be explored are: the apparent excess of stomach cancer in coal miners and their wives; the possible role of tobacco consumption (smoking and chewing), air pollution, and occupational status in the etiology of stomach cancer in coal miners and their families; prospective epidemiological studies of the role of air pollution and more specifically the effluents of coal combustion, in the etiology of cancer with emphasis on more independent and quantitative assessments of the effects of cigarette consumption, air pollution (based on analytic environmental surveillance) and economic or occupational status; and a re-evaluation of migrant studies with specific regard to self-selection of the immigrants.

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Characterization of Atmospheric Pollutants from Power Plants

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Fossil-fueled power plants constitute a ubiquitous source of air pollutants in most developed countries. In the United States they have the dubious distinction of ranking third to motor vehicles and industry in total emissions and contribute approximately 25 percent of the particulates, 45 percent of the oxides of sulfur, and 25 percent of the oxides of nitrogen emitted nationwide.

At the present time approximately 80 percent of the electric power generated in the United States is derived from the combustion of fossil fuels. Of this total, coal combustion accounts for approximately 70 percent—the balance being made up by natural gas and oil. It is now apparent, however, that increased coal utilization will be the main source of the nation's electrical energy for the next several decades and that much of the coal may come from midwestern fields.

While particulates, sulfur oxides, nitrogen oxides, carbon monoxide, and a variety of aliphatic organic compounds constitute the major atmospheric emissions from fossil-fueled power plants (Table 1), significant amounts of trace metals and metalloids, acid mists, and polycyclic organic species are also produced. Most of these so-called minor pollutants are emitted in particulate form and many are highly toxic to living organisms. In discussing the characteristics of pollutant emissions, therefore, emphasis is placed not only on the amounts emitted, but also on the manner in which both major and minor pollutants attain their final form and on the physical and chemical nature of the emitted material.

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Table 1. Average Air Pollution Emissions From Power Plants According to Fuel Type (pounds per 1000 pounds of fuel)¹

Fuel	Particles ^a	CO	HC	NO _x	SO ₂ ^{**}	HCOH
Coal	85 (1-E)	0.25	0.1	10	19 S	0.002
Oil	1.7 (1-E)	0.07	0.5	17	19 S	0.1
Natural Gas	2.7 (1-E)	neg.	neg.	70	19 S	0.2

^aE is the mass collection efficiency of the control equipment.^{**}S is the percent sulfur content of the fuel by weight.

Sulfur Oxides

In the absence of controls the amount of sulfur oxides emitted from a power plant is directly related to the sulfur content of the fuel burned. The average sulfur content of U.S. coals is about 2.5 percent with about one-third of current production having less than 1 percent sulfur and thereby classifying as low sulfur coal. The sulfur is present naturally both as pyrite (metal sulfides) and as organic sulfur compounds. Residual fuel oils contain between 0.7 and 5.5 percent² of sulfur in the form of dissolved H₂S, elemental sulfur, and organic sulfur compounds. About one-quarter of the United States supply contains less than 1 percent sulfur. Natural gas used for power generation is typically very low in sulfur (which is present primarily as H₂S).³

While reducing conditions occur in parts of the fuel combustion zone of a power plant so that sulfur may initially be gasified as H₂S or S, rapid high temperature oxidation of these species to SO₂ occurs both during and immediately following combustion. In addition, the reversible reaction



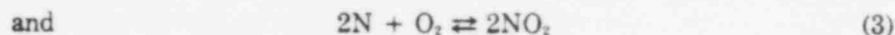
can take place, so that between 1 and 10 percent of the sulfur may be emitted as SO₃.^{4,5} The actual amount of SO₃ emitted depends upon the temperature profile in an individual plant. The reaction rates associated with Reaction 1 are fairly slow so that high temperatures promote more rapid attainment of equilibrium and thus SO₃ production. However, high temperatures also drive the equilibrium to the left (i.e., towards SO₂). The net result is that fossil-fueled power plants most commonly emit about 1 to 2 percent of the sulfur as SO₃, which rapidly reacts with water vapor to produce sulfuric acid. A small amount of the SO₂ is also chemisorbed by fly ash particles to form metallic sulfates, primarily iron.

Overall, it is estimated that approximately 95 percent of the sulfur present in fossil fuels is emitted in the form of sulfur oxides. This amounts to 19 S pounds of SO₂ per 1000 pounds of fuel where S is the weight percentage of sulfur in the fuel. The actual SO₂ concentrations

appearing at the stack exit depend, of course, on the ratio of feed air to fuel consumption as well as on the sulfur content of the fuel. Typical values lie in the range 500 to 3000 ppm with 1000 to 2000 ppm being most commonly encountered in the absence of control.

Nitrogen Oxides

By contrast with sulfur oxides, which are derived from sulfur present in the fuel, nitrogen oxides produced by fossil-fueled power plants are derived primarily from fixation (oxidation) of atmospheric nitrogen present in the combustion feed air according to the reactions:



Consequently, nitrogen oxides cannot be effectively controlled by selection or pretreatment of fuel.

The extent of nitric oxide formation depends primarily on the O_2 and N_2 contents of the feed air, the combustion temperature, and the average residence time of the oxygen and nitrogen molecules in the combustion zone.^{8,9} These dependences, which are reproduced from reference 8, are indicated in Figures 1 through 4 and are summarized by the experimental equation⁸

$$[\text{NO}]_{\text{ppm}} = 5.2 \times 10^{11} t \cdot \exp[-72,300/T] P_{\text{O}_2}^{1/2} P_{\text{N}_2} \quad (I)$$

where t is the residence time in seconds, T is the absolute temperature, and P_{O_2} and P_{N_2} are, respectively, the partial pressures of oxygen and nitrogen in the feed air.

The amount of nitrogen dioxide (NO_2) formed during combustion is generally much less than that of NO , and its rate of formation depends upon the O_2 and N_2 concentrations according to the relation

$$\frac{d[\text{NO}_2]}{dt} \text{ ppm} \propto (P_{\text{N}_2})^2 \cdot P_{\text{O}_2} \quad (II)$$

The temperature dependence of NO_2 formation by Reaction 3 is analogous to that of SO_2 formation by Reaction 1. Thus, high temperatures promote attainment of equilibrium and hence NO_2 formation, but they move the position of equilibrium in Reaction 3 to the left. In practical situations, therefore, the amount of NO_2 formed depends primarily on the amount of NO formed and thus on the combustion temperature.

Representative emission factors for NO and NO_2 combined are given in Table 1 although it should be recognized that NO_x emissions are not directly related to the amount of fuel consumed. Rather, they depend on the feed rate of air supporting combustion. Actual concentra-

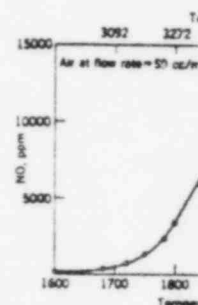


Figure 1. Net NO as a Function of Temperature

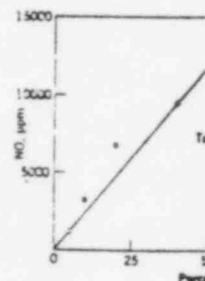


Figure 3. Effect of Pressure on NO Formation

tions of NO_x are emissions. Significant gas combustion

It is involved in many elevated pressures is essentially independent of pressure (above) have been proven even eliminated, as shown in Figure 1) due to the effect of Reaction 2.

Carbon Monoxide

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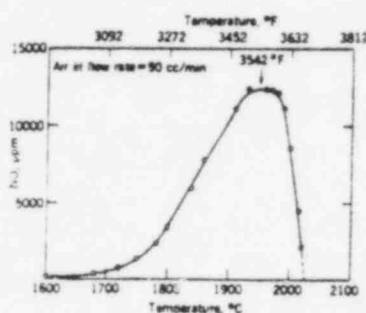


Figure 1. Net NO Production as a Function of Temperature

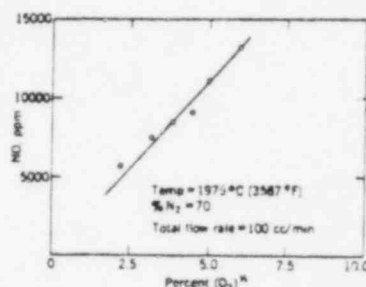


Figure 2. Effect of Oxygen Pressure on NO Formation

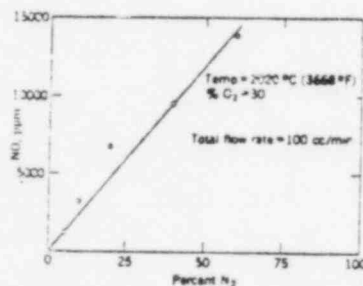


Figure 3. Effect of Nitrogen Pressure on NO Formation

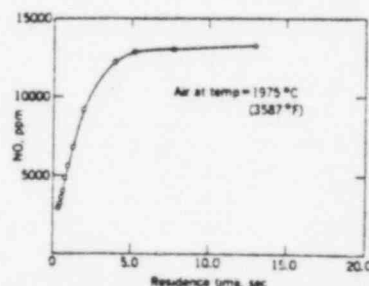


Figure 4. Effect of Residence Time at Temperature on NO Formation

tions of NO_x are normally in the range 300 to 1300 ppm in stack emissions. Significantly higher concentrations are produced during natural gas combustion than during combustion of coal or oil (Table 1).

It is interesting to note that the relatively low temperatures involved in many proposed coal gasification processes¹⁰ operating at elevated pressures will markedly reduce NO_x formation since Reaction 2 is essentially independent of pressure. On the other hand, a few gasification processes operating at extremely high temperatures (~2000°C and above) have been proposed. Here also NO_x formation may be reduced, or even eliminated, since NO production rapidly falls off above 1900°C (Figure 1) due to the onset of NO dissociation by the reverse process of Reaction 2.

Carbon Monoxide

As can be seen from the data in Table 1, carbon monoxide emissions from fossil-fueled power plants are negligible where the fuel is

natural gas. The higher emission factors given for oil and coal-fired power plants are directly related to the efficiency with which high temperature oxidation of CO takes place in the combustion region.¹¹

In general terms fossil fuel combustion can be thought of as taking place in three distinct zones. In the first, or oxidation zone, the reaction



occurs. The CO_2 is then exposed to a reduction zone where the reaction



takes place. Finally, at the periphery of the combustion region, CO is oxidized by secondary air such that



At normal combustion temperatures Reaction 4 is about ten times faster than Reaction 5 so that complete oxidation of CO is strongly dependent on the availability of oxygen at a sufficiently high temperature for Reaction 5 to take place. This requirement is achieved for gaseous fuels and, to a lesser extent, for liquid fuels, both of which are well dispersed with respect to the oxygen supply. Combustion of coal, however, takes place in a bed where the efficiency of CO oxidation depends more sensitively on the amount and configuration of the secondary air supply.

As pointed out previously, CO emissions from fossil-fueled power plants do not contribute greatly (~2 percent) to the anthropogenic CO inventory. Stack concentrations are normally in the range 200-700 ppm but can vary greatly depending on operating conditions.

Particles

Particulate emissions from coal-fired power plants constitute a major air pollution control problem. By comparison oil- and gas-fired plants emit relatively small amounts of particles (Table 1). Consequently current emphasis is on the characterization of fly ash from coal-fired power plants.

Fly ash from coal combustion constitutes a much more complex physical and chemical system than do the gaseous pollutants previously discussed. Not only do the physicochemical characteristics of the bulk particles influence their environmental impact, but these particles also contain a wide variety of more or less toxic trace constituents including metals, metalloids, and organic species. It is appropriate, therefore, to consider fly ash in terms of its bulk properties, its trace element constituents, and its organic constituents. It should be stressed,

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however, that fly ash is heterogeneous and that its composition can vary quite dramatically between different coal types and power plant operating conditions.

Bulk Properties

Particles emitted from coal combustion are primarily inorganic in nature being derived from mineral impurities present in the coal. Consequently the amount of mineral matter present in a given coal strongly influences the particle emission factor of that coal. Oil and natural gas, which contain only small amounts of inorganic impurities, have much lower particle emission factors than coal and a larger proportion of these particles are carbonaceous as compared to coal fly ash.

The major elemental constituents of coal fly ash are Si, Al, Fe, K, and Ca. Some typical composition ranges representative of both the eastern and western U.S. coal fly ashes are presented as the weight percent of the oxides in Table 2.¹² In general, western U.S. coals have a higher ash content and exhibit higher alkali and alkaline earth metal contents than eastern coals, which are typically high in sulfur.

Table 2. Typical Matrix Element Composition Ranges of Some U.S. Coal Fly Ashes Expressed as Weight Percentages of the Oxides.¹²

Major Constituents					
Al ₂ O ₃ 14-30	SiO ₂ 22-60	Fe ₂ O ₃ 3-21	K ₂ O 0.2-3.5	CaO 0.5-31.0	
Minor Constituents					
Li ₂ O 0.01-0.07	Na ₂ O 0.2-2.3	MgO 0.7-12.7	TiO ₂ 0.6-2.6	P ₂ O ₅ 0.1-1.1	SO ₄ * 0.1-2.2

*Soluble sulfate

During combustion in a power plant the major aluminosilicate impurities in coal melt forming small, mostly spherical particles. These particles exhibit no significant X-ray diffraction patterns and are, in many cases, transparent under an optical microscope. In fact the composition of fly ash is closely similar to that of silicate glass with individual particles containing widely different amounts of iron and various trace impurities.¹³ In addition some elemental carbon (soot) particles are present. It is interesting to note that much of the iron present occurs as ferromagnetic Fe₃O₄, and for some fly ashes as much as 95 percent of the mass can be separated magnetically.¹⁴ This suggests the possibility of magnetic collection of fly ash, although such collection could not be

universally applied since the proportion of ferromagnetic mass varies widely between different fly ashes.

The aerodynamic equivalent mass median diameters of coal fly ashes emitted from uncontrolled power plants typically lie in the range 8 to 30 μm ¹² and the mass is, to a reasonable approximation, log-normally distributed.^{13,14} The mass median diameters of fly ashes emitted from control devices are considerably smaller than indicated above and depend largely on the collection efficiency of the control devices. In the case of electrostatic precipitation, removal efficiencies as high as 98 percent by weight are claimed¹⁵ and mass median diameters of fly ashes emitted from these devices are typically in the range 0.5 to 2.0 μm . The efficiency of essentially all currently operating particle control devices falls off with decreasing aerodynamic particle size below about 1 to 2 μm , however, and it is these submicrometer size particles which are of primary concern since they have long atmospheric residence times, provide large specific surface areas for heterogeneous reactions, contribute greatly to visibility reduction, and are deposited mainly in the innermost (pulmonary) region of the human respiratory system when inhaled.¹⁶

The morphological characteristics of coal fly ash can be classified into four types.¹⁸ The first consists of non-spherical "clinkers" which occur mostly as very large particles and are rarely emitted to the atmosphere. The second type involves solid spheres. Essentially all fly ash particles having physical diameters less than about 5 to 10 μm are solid with densities close to 2.7 gm cm^{-3} . The third type consists of hollow spheres. These may have either quite thick or extremely thin (<1 μm) shells, and they predominate in the physical size range 20 to 60 μm . The most intriguing particles are the fourth type, which consists of hollow particles filled with large numbers (10-200) of small solid particles (Figure 5). These occur primarily in the physical size range 20 to 60 μm and preliminary studies indicate that between 20 and 40 percent of the mass of particles smaller than about 5 to 10 μm may be present as encapsulated particles in fly ashes emitted from coal-fired power plants.

The occurrence of hollow and encapsulating particles may be of considerable significance from an environmental standpoint. In the case of hollow particles the low density, and thus small aerodynamic diameter, will enhance the probability of their emission compared with solid particles having the same physical diameter. In addition, these particles tend to behave like ping pong balls on impact so that they may bounce off collection surfaces. This is particularly important in determining particle size distributions using cascade impactors.^{17,18}

The phenomenon of particle encapsulation may, however, represent a very positive factor in particle control. Thus, the aerodynamic size range of the encapsulating particles (22 to 66 μm) ensures that they will be efficiently collected by most particle control devices thus



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median diameters of coal typically lie in the range of 10 to 100 μm . In approximation, log-normally distributed, fly ashes emitted from power plants are characterized as indicated above and depend on the type of control devices. In the case of electrostatic precipitators, as high as 98 percent by weight of fly ashes emitted from these devices are greater than 10 μm . The efficiency of these control devices falls off with particle size below about 1 to 2 μm , however, particles in this size range are of primary concern because they can penetrate deep into the lungs, provide large specific surface area, and contribute greatly to visibility impairment in the most (pulmonary) region of the respiratory tract.

Coal fly ash can be classified into three categories: spherical "clinkers" which are rarely emitted to the atmosphere; large irregular particles, essentially all fly ash particles are in about 5 to 10 μm range; and a third type consists of hollow spheres which are extremely thin (<1 μm) and have a diameter in the range 20 to 60 μm . The latter type, which consists of hollow spheres, is made up of small solid particles of size range 20 to 60 μm and is composed of 20 and 40 percent of the total ash. These hollow spheres may be present as a result of the coal-fired power plants. These hollow spheres may be encapsulating particles may be of environmental standpoint. In the case of these hollow spheres, thus small aerodynamic diameter compared with the other particles. In addition, these hollow spheres have a high impact so that they are particularly important in the design of cascade impactors.^{17,18} Encapsulation may, however, be a problem for control. Thus, the aerodynamic diameter (2 to 66 μm) ensures that these control devices thus



Figure 5. A 10 μm Fly Ash Particle Showing Encapsulated Spheres

preventing emission of the small, less easily collected, particles encased inside them. In short, particle encapsulation may represent a significant natural process for the control of undesirable submicrometer size particles.¹⁹

Particulate Trace Elements

As a result of their geological origin, coal and oil contain essentially all known stable elements in trace amounts. The elements Hg, Zr, Zn, Cd, As, Pb, Mn, and Mo occur in association with inorganic material in coal—mainly in the pyritic fraction. Ge, Be, and B show marked organic association. P, Ga, Ti, Sb, and V are associated with both organic and inorganic material in coal but show a preference for organic

association whereas Co, Ni, Cr, Se, and Cu tend to be associated more with inorganic impurities.¹⁹ Trace element concentrations in oil are much lower than in coal with the notable exception of vanadium which is present as organic porphyrin complexes. During combustion these trace elements are partitioned between bottom ash and fly ash although most of the Hg, Br, and Se are emitted as elemental vapors.²⁰

The specific concentrations ($\mu\text{g/gm}$) of individual trace elements found in coal and oil fly ashes depend primarily on the trace element content of the original fuel. In general, a fly ash which contains high concentrations of one trace element will also have high concentrations of most others as well. However, the relative concentrations may differ markedly between fly ash and fuel due to the different partitioning characteristics of individual trace elements between bottom ash and fly ash. Table 3 lists some representative specific concentrations and volume concentrations ($\mu\text{g/m}^3$) of particulate trace elements emitted from coal- and oil-fired power plants. Volume concentrations will, of course, vary greatly with plant operating parameters as well as with fuel type.

One partitioning mechanism thought to be of importance in power plants involves high temperature volatilization of certain trace elements (or their compounds) followed by their condensation onto the surface of entrained fly ash particles as the temperature falls.^{16,21} This behavior would account for the observation that volatilizable trace ele-

Table 3. Specific Concentrations ($\mu\text{g/gm}$) and Volume Concentrations ($\mu\text{g/m}^3$) of Trace Elements in Coal and Oil Fly Ash^{24,25}

Element	Coal Fly Ash		Oil Fly Ash	
	$\mu\text{g/gm}$	$\mu\text{g/m}^3$	$\mu\text{g/gm}$	$\mu\text{g/m}^3$
As	10-500	60-90	30	5
Ba	100-1000	30-110	9000	1600
Be	1-10	—	—	—
Cd	10-100	—	—	—
Co	10-100	1-5	90	16
Cr	10-1000	8-20	66	12
Cu	10-1000	—	—	—
Hg	0.1-1.0	—	—	—
Mn	100-1000	12-40	45	8
Mo	10-100	—	—	—
Ni	10-1000	10-25	—	—
Pb	100-5000	10-15	—	—
Sb	1-100	1-2	5	1
Se	10-100	8-18	5	1
Sn	1-10	—	—	—
V	50-5000	5-60	100-100,000	1000-1200
Zn	1000-10,000	20-70	3500	640

and to be associated more concentrations in oil are much of vanadium which is in combustion these trace and fly ash although most vapors.²⁰

of individual trace elements primarily on the trace in a fly ash which contains also have high concentration concentrations may the different partitioning between bottom ash and fly concentrations and volume elements emitted from coal-ns will, of course, vary as with fuel type.

to be of importance in utilization of certain trace for condensation onto the temperature falls.^{18,21} This at volatilizable trace ele-

and Volume Concentration of Oil Fly Ash^{24,25}

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12	—
—	—
8	—
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1	—
—	—
100,000	1000-1200
	640

ments are preferentially enriched in fly ash as compared to bottom ash. It also accounts for the fact that some elements exhibit a noticeable increase in specific concentration with decreasing particle size (Table 4). The increase, which is a direct result of the dependence of specific surface area on particle size, is very marked when concentrations are plotted against the BET surface area of fly ash particles.^{13,22}

Table 4. Dependences of Specific Concentrations (μg/gm) of Some Trace Elements on the Aerodynamic Particle Diameter in a Representative Coal Fly Ash¹⁴

Particle diameter (μm)	As	Cd	Cr	Ni	Pb	Sb	Se	Tl	V	Zn
> 11.3	680	13	740	460	1100	17	13	29	150	8100
7.3-11.3	800	15	290	400	1200	27	11	40	240	9000
4.7- 7.3	1000	18	460	440	1500	34	16	62	420	6000
3.3- 4.7	900	22	470	540	1550	34	16	67	230	3800
2.1- 3.3	1200	26	1500	900	1500	37	19	65	310	15000
1.1- 2.1	1700	35	3300	1600	1600	53	59	76	480	13000

This dependence of trace element concentration on particle size has the net effect of decreasing the aerodynamic equivalent mass median diameters of volatilizable trace elements with respect to that of bulk fly ash.¹⁶ Therefore the following is true:

(1) Many toxic trace elements tend to be most concentrated in small, lung depositing fly ash particles which are least efficiently collected by existing particle control devices.

(2) Specific concentrations of volatilizable trace elements determined by analyzing fly ash retained in control devices are very much lower than the concentrations in particles actually emitted. Trace element emission factors cannot, therefore, be obtained by multiplying the specific concentration of an element in retained fly ash by the bulk particle emission factor.

(3) The potential toxicities of trace elements deposited on particle surfaces are enhanced since it is the particle surface which comes in direct contact with lung tissues where efficient absorption can take place.

At the present time there is little definitive information about the chemical forms of trace elements in fly ash and about the mass median diameters of emitted trace elements. It has, however, been established that selenium occurs as the element in fly ash.²³ It has also been reliably demonstrated²⁴ that the elements As, Se, Sb, and Pb are enriched at least

fivefold in emitted fly ash as compared to the coal burned, and that V, Ni, Zn, As, Pb, Se, Sb, Br, and I are enriched at least fiftyfold in emitted fly ash as compared to crustal dusts.²⁴

Particulate Polycyclic Organic Matter (POM)

The exact nature and extent of emissions of particulate organic species from fossil-fueled power plants is not well established. However the highly carcinogenic nature of polycyclic organic species (notably benzo-a-pyrene) has stimulated a number of studies of the class of organics known as POM.²⁵

Combustion of any carbonaceous fuel, whether it be pure methane or coal, leads to the formation of a large number of species containing two or more aromatic rings. The actual mechanism of POM formation is not fully understood although the available evidence²⁶ suggests that high temperature vapor phase formation of carbon-carbon bonds takes place, probably via a free radical mechanism. In any event, essentially the same several hundred compounds are formed in similar relative amounts irrespective of the type of fuel.²⁶

POM emission factors for fossil-fueled power plants are generally small,²⁷ but they show a remarkable apparent dependence on the efficiency of furnace operation (Table 5). Total annual emission estimates for residential heating and power generation in the U.S. amount to 500 tons expressed as benzo-a-pyrene.²⁸ It is generally held that the very low POM emissions from power plants result from their efficient breakdown to carbon dioxide and water at the high temperatures involved. However, the extraordinary differences observed between emissions from power plant furnaces and less efficient combustion operations leads one to suspect the validity of the numbers. In this regard it should be noted that emission factors are generally based on analyses of fly ash retained in control devices and it is by no means clear that this material has similar POM content to emitted fly ash.

Table 5. POM Emission Factors for Coal Fired Furnaces* in (pounds/ton of coal) X 10⁴

Species	Pulverized Firing	Chain Grate Stoker	Hand Fired
Benzo-a-pyrene	0.2-0.52	0.3	3520
Pyrene	0.8-1.6	3.5	5260
Benzo-a-pyrene	0-2.3	1.1	880
Perylene	0-0.6	—	526
Fluoranthene	—	6.0	8800

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The way in which POM vapors become associated with fly ash particles is not well understood.²⁷ It has been suggested²⁷ that essentially pure POM particles may form by self-nucleation followed by agglomeration. POM may also adsorb onto the surface of entrained fly ash particles. Both mechanisms would lead to the predominance of POM in extremely small particles ($\sim 0.1 \mu\text{m}$). Consideration of the vapor pressures of representative polycyclic aromatic species at the temperatures encountered in a power plant shows that neither self-nucleation nor condensation would be likely to occur. POM would, therefore, be expected to exist in the vapor phase at all points within the plant. Consequently it is appropriate to think in terms of an adsorption mechanism.

The equilibrium for the process



is strongly dependent on temperature T , and is given by an equation of the form²⁸

$$\frac{\text{POM}_{\text{ads}}}{\text{POM}_{\text{vap}}} = (\text{Const}) (N_p) (\sigma_p^2) \left[\frac{\pi}{2 MRT} \right] \exp (\Delta E / RT) \quad (\text{III})$$

where N_p is the number of fly ash particles per unit volume, σ_p is the mean particle diameter, M is the molecular weight of the adsorbing species and ΔE is the difference between the activation energies for adsorption and desorption.

Evaluation of Equation III for adsorption of POM onto glass-like fly ash spheres of the size distribution encountered in a power plant shows (Figure 6) that POM would be expected to adsorb quantitatively onto fly ash at, or close to, the stack exit. Preliminary field experiments substantiate this prediction.²⁸

The consequences of this adsorption mechanism are of considerable importance since they suggest that POM emissions from fossil-fueled power plants may be very much greater than hitherto supposed. They further show that particle control devices would be ineffective in removing POM which is present as vapor at precipitator operating temperatures, and that after adsorption, POM would predominate in very small particles. This prediction is in accord with the observation of small mass median diameters for POM in the atmosphere.¹⁶ Finally the mechanism would account for the large emission factors observed for small furnaces from which fly ash is collected for analysis after it is emitted and Reaction III has approached equilibrium.

In view of the disquieting correlations which have been reported between atmospheric POM levels and the incidence of lung cancer,²⁸ it is of considerable importance to reevaluate the actual emissions of POM from fossil-fueled power plants. In this regard it is also important to establish whether POM is decomposed within the plant, as

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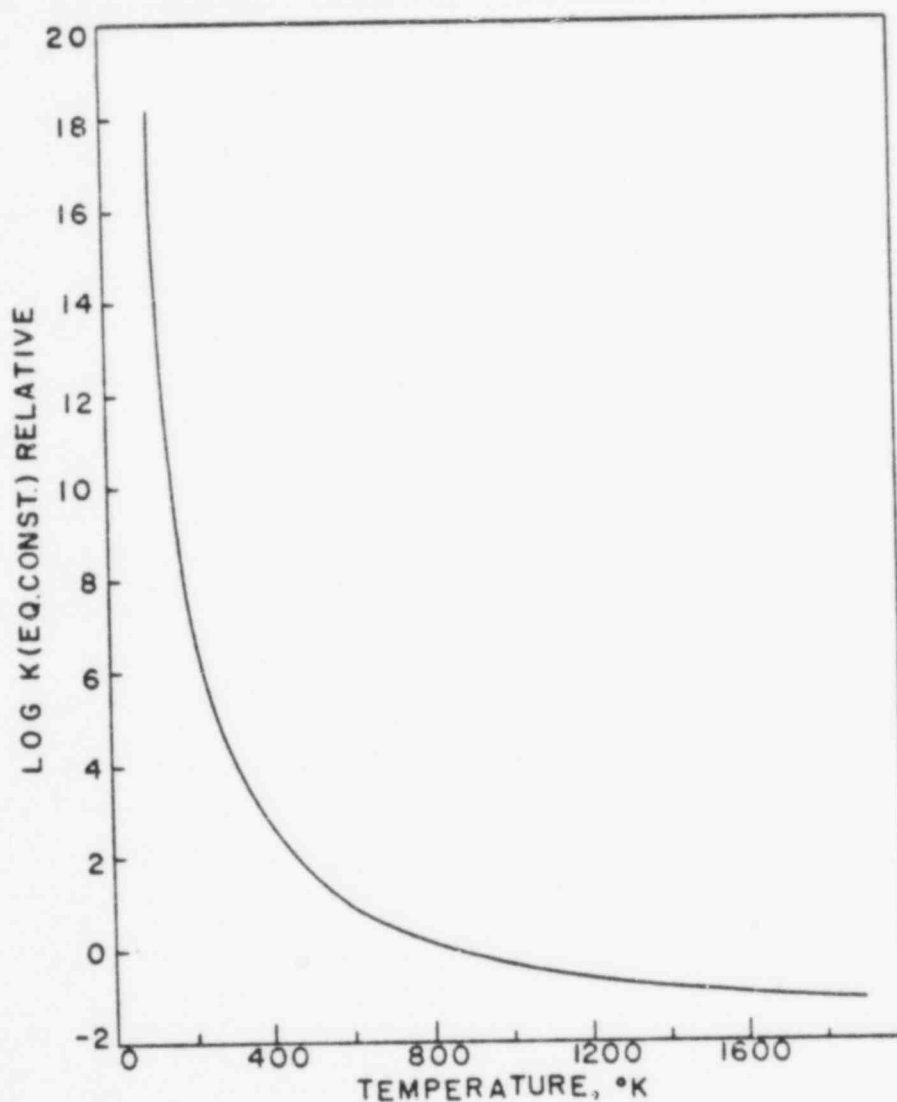


Figure 6. Theoretical Ratio of POM Adsorbed on Fly Ash to that in the Vapor Phase as a Function of Temperature. Particle diameters of $2\mu\text{m}$ and an activation energy [ΔE in Equation III] of 8 kcal are assumed.

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References

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Other Emissions

In addition to the pollutants already discussed, fossil-fueled power plants emit a very wide variety of pollutants in more or less minor amounts. Foremost among these are gaseous hydrocarbons, aldehydes, and sulfuric and hydrochloric acid mists.

The nature of the various hydrocarbons, aldehydes, and other gaseous organics is not well known as these compounds are generally determined by nonspecific techniques. The actual emission factors are low (Table 1). While mechanisms of formation similar to those proposed for POM² can be invoked to explain the formation of certain hydrocarbons, mechanistic pathways are, for the most part, unknown.

Sulfuric and sulfurous acid mists are formed in small amounts near the exit to power plant stacks where the temperature is sufficiently low to allow formation of liquid water droplets which absorb SO₂ and SO₃. Some metal-catalyzed oxidation of sulphite to sulphate almost certainly takes place in these droplets, which are extremely acidic and corrosive. Indeed, sampling equipment is often rapidly corroded near a stack exit due to the presence of sulfuric and, to a lesser extent, hydrochloric acid mists. Quantitative information on emissions is apparently not available, so the relative importance of acid mist emissions from power plants is unknown.

Conclusions

In overview, it appears that the most important pollutant emissions from fossil-fueled power plants have been identified and that approximate emission factors are known. An important exception may involve POM for which currently accepted emission factors may be spuriously low.

The basic processes giving rise to each major pollutant species are known in outline, although there is need for much more detailed investigation of mechanisms. In particular, control of the oxides of nitrogen, of particles, and of POM may be facilitated by modification of combustion and post-combustion conditions based on a detailed understanding of formation mechanisms.

References

1. R. F. Sawyer, in *Combustion Generated Air Pollution*, ed., E. S. Starkman, Plenum Press, New York, p. 275, 1971.

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Potential Health and Environmental Effects of Trace Elements and Radionuclides from Increased Coal Utilization

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This report addresses the effects of coal-derived trace and radioactive elements. A summary of our current understanding of health and environmental effects of trace and radioactive elements released during coal mining, cleaning, combustion, and ash disposal is presented. Physical and biological transport phenomena which are important in determining organism exposure are also discussed. Biological concentration and transformation as well as synergistic and antagonistic actions among trace contaminants are discussed in terms of their importance in mobility, persistence, availability, and ultimate toxicity. The consequences of implementing the President's National Energy Plan are considered in terms of the impact of the NEP in 1985 and 2000 on the potential effects of trace and radioactive elements from the coal fuel cycle. Areas of needed research are identified in specific recommendations.

Introduction

Combustion of coal for the production of electrical and thermal energy is not without attendant health and environmental effects. Numerous reports have been prepared in recent years concerning these effects relative to our current pattern of coal utilization of approximately 650 million tons per year. Most studies have dealt with specific parameters of coal utilization such as health effects of coal combustion (1), toxicity of coal-derived trace elements (2), effects of coal-derived trace elements on water quality (3), and effects of coal-derived radionuclides (4). Recently several reports have appeared addressing an integrated assessment of coal utilization (5-8) and these reports have been utilized extensively in developing the following materials. Specifically, EPA 77-64 "Effects of Trace Contaminants From Coal Combustion" (5) has been used as a basis for the present analysis and sections of that report have been repeated verbatim with new information inserted in appropriate locations.

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The President's National Energy Plan (NEP) contains assumptions which bear directly on questions about health and environmental impacts of trace elements and radionuclides from increased coal utilization. The most important assumptions are that annual coal production will grow from 650 million tons (15.3 quads) in 1975 through 1,200 million tons (28.2 quads) in 1985 to 1,910 million tons (44.9 quads) in 2000, and that by 1985, all emission sources will be in full compliance with environmental regulations promulgated by the U.S. Environmental Protection Agency (EPA) and by individual states. The NEP is based on application of the Best Available Control Technology (BACT) being applied to all new or expanded utility and industrial boilers. As outlined in Public Law 95-95, the 1977 amendments to the Clean Air Act of 1970, BACT is to replace the New Source Performance Standards (NSPS). Although not directly addressed in the NEP, fly ash and scrubber sludge may be defined as hazardous substances under the Resource Conservation and Recovery Act of 1976. This will have a significant impact on allowable release rates from landfills and settling ponds used in fly ash disposal. The Surface Mining and Reclamation Act of 1977 will play a major

role in determining coal availability by placing more stringent regulations on levels of mine drainage and on reclamation practices for both existing and new mines. The NEP assumes no advanced coal combustion or coal liquefaction before 2000. Coal gasification is assumed to contribute 1.2 quads by 1985 and 3.8 quads by 2000 with attendant solid waste and water use problems.

The objective of the present paper is to discuss the current status of our understanding of health and environmental effects of trace elements and radionuclides from coal utilization and to estimate the probable impacts of increasing coal utilization as envisioned in the NEP. A discussion of environmental and biological transport is included because transport and transformations of hazardous elements determine organism exposure and ultimate toxicity. It should be pointed out early that accurate, inexpensive analytical techniques for determining amounts and chemical forms of trace contaminants are essential to understanding and evaluating transport and effects of these materials. With the exception of transportation, which is covered elsewhere, the complete coal fuel cycle is addressed in this study.

Summary

Trace elements and radionuclides potentially hazardous to human health and ecosystems are present in coal. Trace elements of concern include, among others, As, Be, Cd, Cr, F, Hg, Ni, and Pb. Concentrations of these elements vary considerably among coal types. Radioactive elements of concern in coal include ^{235}U , ^{238}U , ^{232}Th , and associated daughter products. Concentrations of radionuclides in coal are generally less variable than those of trace elements, values of 1 ppm for U and 2 ppm for Th being reasonable national averages.

Trace and radioactive elements can enter the environment prior to coal combustion through runoff from mining, cleaning, and storage operations; during combustion in atmospheric emissions of respirable particulates and volatile elements; and following combustion through runoff and leachate infiltration into ground water from bottom ash, fly ash, and scrubber sludge deposited in settling ponds and landfills. Trace contaminants released to the environment from the coal fuel cycle may result in exposure of organisms at considerable distances due to atmospheric transport of particulate and gaseous forms, or contaminants from solid wastes (ash) may reach drinking water supplies through hydrologic transport in ground and surface waters.

At nearly every point along physical transport

pathways in aquatic and terrestrial environments, opportunities exist for interactions of trace elements with life forms. Organisms, especially microorganisms in aquatic environments, can absorb, concentrate, and transform trace and radioactive elements into more concentrated forms or more toxic compounds. Biotransformation of trace and radioactive elements is particularly important in determining effects on man and other organisms, since it is the molecular form of these contaminants that determines their persistence, availability, bioaccumulation, and toxicity. Bioaccumulation is of particular concern for elements such as Cd, Hg, and Pb because current intake levels for these substances are near tolerable human health limits.

Ecological effects of trace and radioactive elements from the coal fuel cycle are presently or will be associated primarily with mining, cleaning, and solid waste (ash, sludge) disposal. The acidic nature of mine drainage from eastern coal fields tends to hold metal ions in solution and promotes their transport to surface and ground waters. Acid mine drainage from inactive mines in the eastern United States is the greatest single source of drainage and transport to aquatic environments, and is very difficult to control. Western coal generally lacks acid-forming substances, although increased salinity of surface and ground waters in western coal regions could become a problem due to soluble salts in mine spoils. During overburden removal for strip mining, ground water aquifers are commonly intercepted; hazardous elements may enter these disturbed aquifers. Impacts associated with elements in runoff: (a) leachate from coal cleaning and storage are similar to but of lesser magnitude than those associated with coal mining.

Concentrations of trace contaminants in atmospheric emissions from coal-fired power plants do not appear to be a significant ecological hazard. Trace element concentrations in soils fall rapidly with distance from power plants and tend to be at background levels at distances ≥ 3 km from the plant. With installation of efficient electrostatic precipitators, atmospheric emissions of trace elements should not be acutely harmful to vegetation and other biota, especially beyond a 3 km radius. Only fluorine appears to deserve special watching. Likewise, the potential for chronic toxicity to ecosystems is relatively low, except in local areas already enriched with a particular element. However, sublethal, chronic or synergistic effects of trace elements on ecosystems have received little attention.

About 92% of particulate materials produced in utility boilers is removed by electrostatic precipitators. Fly ash, bottom ash and scrubber sludge

all contain trace and radioactive elements. These are generally released to ground water at low concentrations, with attenuation occurring very close to the disposal site. Very little information is available on the chemical form, bioavailability and toxicity of these contaminants. By 1985, 60 to 100 million tons of fly ash with elevated levels of trace elements will be annually discharged into settling basins or landfills situated in close proximity to coal-fired power plants. Elements such as As, Cd, Co, Hg, Ni, Pb, Se, U, and Zn all exhibit mobilization rates from these deposits that are larger than 10% of the natural weathering rates. Cadmium, Hg, and U appear to be mobilized through coal combustion at rates comparable to their natural weathering rates. These elements have a definite potential for runoff to surface waters and leachate intrusion into ground water and their concentrations should be monitored closely.

There is reasonable concurrence that some trace contaminants in coal may constitute human health problems from either direct toxicity or risk of cancer. Among those most toxic to man are Cd, Hg, and Pb, intake levels of which are already near tolerable health limits. Three elements — As (III), Cr (VI), and Ni (carbonyl) — are accepted as having high carcinogenic importance to man. Of these, As (III) and Cr (VI) probably occur in fly ash leachate, but at unknown concentrations, while Ni (carbonyl) does not occur. There is little or no teratogenic potential from Cd, Hg, or Se compounds at concentrations found in atmospheric emissions or fly ash leachate. The potential for contamination of drinking water supplies by trace elements in leachates from settling ponds or landfills is very real and needs to be evaluated. As previously noted, ash disposal sites will increase in both size and number, amounting to 60 to 100 million tons of wastes annually by 1985.

Estimated annual release rates for radionuclides from a 1000 MW(e) coal-fired power plant amount to 0.04 to 0.35 mrem/yr whole body dose, as a maximal annual dose commitment per individual. To compare the magnitude of radiation from coal combustion emissions, it is useful to use dose equivalent rates for natural background and coal emissions. The dose equivalent rate for the whole body from all natural radiation sources is 80 ± 40 mrem/yr. The corresponding coal combustion radiation rate is 0.007 mrem/yr. On this basis, atmospheric releases of radionuclides from increased coal combustion do not represent a significant public health problem unless coal containing > 5 ppm U come into general use. Radionuclide releases from ash disposal sites have not been evaluated, and depending upon ash leaching rates, could become a significant human health consideration.

There are several areas of uncertainty which should be pointed out. These areas are listed below; recommendations for needed research are listed at the conclusion of this report.

(1) The chemical form of trace elements is very important as a determinant of transport through the environment and of toxic effects on health and ecosystems. Most studies of coal emissions and leachates focus on simple elemental analysis. Lack of knowledge of chemical species of trace elements precludes making a confident and adequate assessment of the potential health and ecological effects of trace elements from coal utilization.

(2) Potential contamination of drinking water supplies by several toxic or radioactive elements in leachates from waste disposal presents a real public health problem. The chemical form of each element may be significantly altered by microorganisms in the physical transport process, and these chemical forms will determine the rate of environmental transport, the bioaccumulation and toxicity of these elements. Too little is known about these processes.

(3) Given that several trace elements in leachates exhibit mobilization rates that are larger than 10% of natural weathering rates, do these elements effectively remain in settling basins or are they injected into waterways and into food chains? Unquestionably, the movement of trace elements from coal combustion disposal sites should be regarded as a potentially significant health problem and bears intensive monitoring in some sites.

(4) While the ambient atmospheric loading of trace elements does not appear to be as great a potential problem as intrusion into waterways from leachates, there is a need to monitor atmospheric concentrations at selected sites. Few data exist on trace element ambient concentrations, fallout and re-entrainment from disposal sites. Atmospheric and environmental levels of cadmium, fluorine, mercury, lead, arsenic (III), and possibly Cr (VI) should be particularly monitored at these selected sites.

Current Status

Sources of Hazardous Elements in the Coal Fuel Cycle

Extraction, cleaning, transportation, storage, combustion or conversion, and ash disposal are the sources of trace elements and radionuclides in the coal fuel cycle (6). These contaminants may enter the atmosphere, landscape, and hydrosphere and, depending upon physical, chemical, and biological factors, enter food chains leading to man. Contaminants introduced into the atmosphere may reach man

Table 1. Average trace element concentration in coal by state^a

	Trace element concn, ppm												
	Northern Appalachian		Southern Appalachian				Eastern Interior			Powder River Region		Four Corners	
	W. Va.	Penn.	Eastern Ky.	Ala.	Va.	Tenn.	Ill.	Western Ky.	Ind.	Mont.	Wyo.	New Mexico	Ariz.
As	9	16	6	13	10	9	6	7	7	<6	1	2	2
Ba	77	70	79	110	99	120	49	44	31	380	170	270	39
Be	1.2	0.8	1.5	0.74	1.1	0.58	1.3	1.4	1.7	1.5	2.4	0.94	0.97
B	20	15	19	30	13	24	81	70	85	60	36	43	49
Cd	—	—	—	—	—	—	2.9	—	—	<0.1	0.46	<2.6	<0.54
Cr	19	24	19	19	20	19	29	18	19	3	5.8	11	9.7
Co	17	18	15	18	14	13	15	16	24	7.7	5.2	15	—
Cu	11	13	11	14	13	11	8.3	8.8	9.7	3.2	4.4	5.9	4.9
F	70	90	30	90	50	120	59	—	50	70	160	160	70
Pb	4.9	5.2	4	3.7	6.1	4.9	33	6.4	7.2	4.8	0.61	4.7	3.9
Li	44	64	78	75	34	36	45	16	24	27	19	16	19
Mn	21	21	26	19	42	23	73	19	26	57	14	19	9.7
Hg	0.12	0.20	—	—	—	—	0.18	—	0.08	0.07	0.05	0.08	0.05
Mo	6.2	9.8	5.2	11	8.3	7.8	8.8	7.4	5.2	4.8	2.2	2.0	0.97
Ni	18	20	16	17	22	16	25	16	33	3.3	4.1	8.1	4.9
Se	3.4	3.7	3.1	5.1	4.4	4.9	2	3.1	4	3	0.8	2.0	2.1
Te	—	—	—	—	—	—	—	—	—	—	0.025	0.03	<0.02
Tl	—	—	—	—	—	—	—	—	—	—	0.4	0.24	<0.2
Sn	1.5	1.1	4.6	2.2	2.3	1.8	2.6	2.5	0.74	1.1	1.4	1.9	0.97
V	30	33	29	31	33	34	35	32	35	12	15	25	9.7
Zn	17	22	15	22	23	23	140	48	73	42	37	19	9.7
Zr	63	68	60	56	44	45	88	77	100	77	39	110	39
U	(range, not avg.)	<10-30	20-190	10	—	<10	—	<10-80	—	10	10-340	10-1000	10-6200

^aSource: Dvorak (6).

and other animals through inhalation and plants through fumigation while those entering the aquatic and terrestrial environments reach plants and animals through root uptake and ingestion. Trace elements and radionuclides in U.S. coals have been widely studied (4, 7, 8). Concentrations of trace elements in coal are sometimes difficult to determine accurately and tend to vary considerably among different coal types (Table 1). Thus, it is not appropriate to compute a national average for each trace element in coal (9). Radioactive elements in coal, ²³⁵U, ²³⁸U, ²³²Th, and associated daughter products, are also variable (Table 2), but values of 1 ppm U and 2 ppm Th have been assumed to be reasonable national averages (7, 10).

Coal extraction, both surface and subsurface, produces solid wastes and acid or alkaline mine drainage which contain trace elements and radionuclides that are transported to aquatic environments (6). Acid mine drainage from inactive underground mines is difficult to control and is the greatest single source of drainage in the eastern United States (11). The acidic nature of acid mine drainage tends to hold metal ions in solution and

promotes transport to surface and ground waters. Trace elements of concern include Al, As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, and Zn (12). In western coal provinces acid formation is almost nonexistent, but transport of alkaline drainage containing soluble salts from mine spoils to receiving waters is one of the most significant water quality problems in those regions (13).

Coal processing or cleaning produces coal fines and rock material. The refuse is separated into gob (course-boulder to pebble-size rock) and slurry (clay-sized particles of coal fines). Problems associated with coal cleaning refuse are generally limited to the coal regions of central interior and eastern provinces (6). Acid drainage or runoff of refuse piles are sources of trace elements to terrestrial and aquatic environments.

Large coal-fired electricity-generating stations [≥ 1000 MW(e)] require coal storage in order to maintain a continuous supply between shipments. Permanent coal stockpiles for a typical 1000 MW (e) plant may vary from 500 to 900 thousand short tons and require from 1 to 2.5 hectares (6). Suspension of coal dusts and infiltration and runoff waters are

Table 2. Range of uranium and thorium concentrations and geometric means (expected values) for coal samples taken from various regions of the United States.^a

Region	Coal	Number of samples	Uranium concentration (ppm) ^b		Thorium concentration (ppm) ^b	
			Range	Geometric mean	Range	Geometric mean
Pennsylvania	Anthracite	53	0.3-25.2	1.2	2.8-14.4	4.7
Appalachia	Bituminous	331	<0.2-10.5	1.0	2.2-47.8	2.8
Interior	Bituminous	143	0.2-43	1.4	<3-79	1.6
Northern Great Plains	Subbituminous, lignite	93	<0.2-2.9	0.7	<2.0-8.0	2.4
Gulf	Lignite	34	0.5-16.7	2.4	<3.0-28.4	3.0
Rocky Mountain	Bituminous, subbituminous	134	<0.2-23.8	0.8	<3.0-34.8	2.0
Alaska	Subbituminous	18	0.4-5.2	1.0	<3.0-18	3.1

^aSource: McBride, (4).

^bThe arithmetic average concentrations of thorium and uranium for all coal samples and various ranks of coal for the whole United States are given in Table 3.

Table 3. Arithmetic averaged concentrations of uranium and thorium in coal for the whole U.S.

Coal rank	Samples	Thorium, ppm	Uranium ppm
All coal	799	4.7	1.8
Anthracite	53	5.4	1.5
Bituminous	509	5.0	1.9
Subbituminous	183	3.3	1.3
Lignite	54	6.3	2.5

major trace element and radionuclide sources to the environment. Terrestrial effects are generally negligible except on areas immediately below and adjacent to the piles. Ground sealing prior to establishing the coal pile can reduce infiltration into ground water (14). Contamination of aquatic environments from runoff from coal piles is similar to but of lesser magnitude than that from acid mine drainage.

Coal combustion produces fly ash and slag or bottom ash as solid waste products. Slag is that portion of total ash which melts to a viscous fluid at combustion temperatures, and bottom ash is the remainder that does not melt and is too heavy to be entrained in flue gas. The amount of slag and bottom ash produced in combustion is a function of coal type and boiler design. Bottom ash is generally mixed with fly ash and pumped in a slurry to settling ponds or dewatered and transported to landfills. Settling ponds are sometimes lined with clay to reduce leachate movement into ground water (14). In the absence of liners, trace elements and radionuclides in leachates can move into underlying soil and ground water (15) and are subject to a variety of chemical, physical, and biological factors that govern their mobility and availability in the environment.

Trace elements in coal tend to partition or concentrate in certain phases during combustion. Klein et al. (16) categorized trace elements into three classes: (1) elements that are not volatilized in the combustion zone, but instead form a melt that becomes both fly ash and slag (Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rh, Sc, Sm, Sr, Ta, Th, Ti); (2) elements that are volatilized on combustion, and condense or adsorb on the fly ash as the flue gas cools, leading to depletion from slag and concentration in the fly ash (As, Cd, Cu, Ga, Pb, Sb, Se, Zn); and (3) elements that remain almost completely in the gas phase (Hg, Se, Cl, Br). The elements Cr, Cs, Na, Ni, U, and V were intermediate in behavior and were placed between classes one and two. Following combustion, trace elements released to the atmosphere in association with particulates may be selectively adsorbed in different particle size ranges (17) and may be enriched on fly ash particle surfaces relative to the interior of the particle (18).

Coal gasification appears to be the only coal conversion technology that will be on-line by the year 2000 (19). Trace elements and radionuclides may be released to the environment from gasification primarily from noncombustible solid wastes that will be disposed of in landfills or slurry ponds. Atmospheric releases of volatile or hydride-forming species is a potential but undefined source of trace elements from gasification.

Environmental Transport

Before the effects of coal-derived trace contaminants on man and ecosystems can be evaluated, it is necessary to estimate the transport, transformation and bioaccumulation of these contaminants as they move from the power plant to the receptor. In addition,

tion to determining routes of transport and transformation, rates for these processes also must be determined before we can predict environmental fate and levels of exposure. Information on the physical and chemical characteristics (e.g., particle size, solubility, and valence state) of materials released to the environment is a vital prerequisite to study of transport processes. The following discussions of environmental transport are based in part on an analysis by Crawford et al. (20).

Atmospheric Transport and Dispersion. Seasonal and annual pollutant concentration fields in the atmosphere can be calculated with reasonable accuracy (within a factor of 2 to 3) at distances of up to 10 km from the effluent source if attention is restricted to simple terrain types and typical daytime atmospheric stability categories (21, 22). Probability distributions of hourly concentrations from seasonal and annual data can also be calculated with similar accuracy. At longer distances, models can be formulated to account for transport and, to a lesser extent, dispersion. The data required for distances > 10 km are not readily available however, and the models have not been thoroughly validated.

Wet Deposition. Precipitation scavenging of particles and gases has been measured in the neighborhood of coal-fired power plants, and the experimental results are fairly well modelled theoretically, at least for estimates of total mass scavenged. Details of the removal as a function of particle size, however, remain in a primitive state.

To estimate precipitation scavenging on a total-mass basis, two approaches are available. In one, a scavenging rate coefficient which accounts for the particle size of the trace contaminant is used (23). Estimates of the removal rate for snow scavenging are also available (24). In the second approach, a wet deposition velocity is derived using washout ratio data (23, 25). These washout ratios show relatively little variation for the trace contaminants and using them, one can define a convenient wet deposition velocity for typical annual rainfall amounts in the northeastern United States (~100 cm/yr) as approximately 1 cm/sec for trace metals of interest. It is appropriate to use the washout ratio for long-term-average estimates; the scavenging rate approach should be used for short-term estimates. Methods for including precipitation scavenging in diffusion calculations are available (26).

Dry Deposition and Resuspension. Dry deposition of particles to smooth surfaces as a function of particle size and turbulence intensity is fairly well known from wind tunnel studies, and theoretical analyses demonstrate a fair understanding of the processes involved. Dry deposition of submicron

particles to real surfaces (e.g., grass, shrubs, trees, lakes, etc.) is an unknown. Best available "guesstimates" suggest using a dry deposition velocity for all particles to all real surfaces: $v_d = 1$ cm/sec. However, different values are obtained for different atmospheric conditions and surface roughnesses.

Resuspension of particles has only recently become of interest in the atmospheric sciences, although much useful information is available in the soil and agricultural science literature. However, in these fields, the emphasis has been more on wind erosion than on the resuspension of submicron particles which is of dominant interest for evaluation of inhalation health effects. In this regard, attention must be paid to bounce-off during the deposition process (27), resuspension by rain splashing (28), and freeing of submicron particles from supermicron particles during dissolution in water (29) and by bombardment of larger particles (30).

Water and Solutes Transport in Soils. For sites downwind from a coal-burning power plant where trace elements or their complexes reach the soil surface by wet or dry deposition from the atmosphere, the most important determinants of their environmental fate are likely to be sorption and desorption on soil particles at the soil surface and the subsequent mobility of these trace elements as a result of soil erosion caused by both wind and water.

The transport of coal-derived trace elements and radionuclides within the soil depends on water movement and chemical reactions within the soil profile. The use of available techniques for predicting and monitoring movements of soil water in the vicinity of a coal-burning power plant depends upon accurate field determinations of the horizontal gradients in the water table head and hydraulic conductivity at the site in question.

When the movement of water through the soil has been characterized, information about chemical and physical reactions which occur simultaneously with the soil water behavior is required in order to predict the retention and transport of trace elements in the soil. Processes of sorption and desorption between the organic and inorganic solid phases of the soil are usually strong and can prevent rapid leaching of these elements into surface and ground waters. On the other hand, some chemical forms of trace substances are repelled from the solid phases and may leach readily with the water. Many reactions in the soil are Eh- and pH-dependent. Some contaminants present in coal waste material may interact with the soil exchange complex and may be far more soluble than one would expect from a simple water extract; others, although highly soluble in water extracts, may precipitate with materials present in the soil.

Processes of erosion and sedimentation represent large portions of the mass flow and should be included in conceptual models and measurements of hydrologic transport (31).

When the kinds of information described above are available, estimates of the migration of trace elements from land disposal sites that receive slag, scrubber effluent, fly ash, and bottom ash can be made. Vertical and horizontal movements in both the water-saturated and unsaturated zones of the soil can be estimated from the disposal site to the receiving waters.

Transport in Aquatic Environments. Trace contaminants that enter the aquatic environment are usually rapidly taken up through adsorption by components having the highest surface-to-volume ratios, primarily the small suspended solids and sediments, and absorption by similar sized microbiota. The largest reservoir of trace contaminants is the bottom sediment. Here a complex association of inorganic and organic components similar to those found in soil form a system which governs the availability of contaminants to the rest of the ecosystem. The physical factors pH, Eh, pore space, and chemical transformations influence the retention/mobility of contaminants in aquatic systems. Similarly, biological transformations play a key role in aquatic transport and distribution. In streams, contaminants may be transported downstream in dissolved form or in association with suspended sediments, ultimately to be deposited into lake sediments or taken up in food chains and cycled among various biological components.

Biological Transport and Transformation

At nearly every point along the physical transport pathways in both aquatic and terrestrial environments, opportunities exist for interactions with the biotic components. Organisms can absorb hazardous elements from their physical environment and dilute, concentrate, transform, and immobilize these materials which may or may not affect ultimate contaminant toxicity. Biological transport plays a major role in determining exposure of organisms to contaminants, but only a minor role in material transport through the environment with little or no effect on contaminant inventory.

Food Chains. Primary producers generally serve as the base of food chains and may accumulate elements through roots (plant uptake), leaves (foliar absorption), absorption through cell walls in aquatic plants, and adsorption on external surfaces. Elements physiologically fixed in plant tissues as opposed to those on plant surfaces or in intracellular

water streams may have different properties and behave differently when ingested by consumers (32). Elements may return to the physical environment through death and leaching, or they may enter food chains through ingestion by consumers. Following ingestion, elements may pass straight through the digestive tract or they may be assimilated. Assimilation rates may vary from $< 1\%$ per day for certain elements up to 100% per day for others depending upon both animal and element species in question (33). Following assimilation, elements are distributed in various tissues at various rates in the consumer's body. Cadmium, for example, tends to accumulate in renal tissues and methylmercury in the central nervous system. Other elements, particularly heavy metals and transuranics tend to be bone seekers. Elimination of elements from various tissues proceeds at various rates and results in release of the chemical into the digestive tract to be eliminated from the consumer through egestion. Consumers may die or they may be consumed by subsequent steps in a food chain. Compounding this simplified picture of a food chain are the biotransformations that may occur, changing the structure and biological activity of chemicals, and the question of direct uptake from surrounding air (inhalation) and water (gill and epidermal absorption).

Soils tend to be the sink for most chemical contaminants released to terrestrial environments. In addition to water relations and soil sorption-desorption phenomena, microbial interactions and root uptake play major roles in transport and distribution of chemicals in terrestrial systems. Microbes can operate in both aerobic and anaerobic environments and have profound effects on element mobility. From the soil-soil-water continuum plants may accumulate elements through root uptake, a process of both active and passive nature. Plant roots show preferential uptake of particular elements and can exclude others at membrane boundaries. Heavy metals entering plant roots are believed to be chelated prior to their movement in xylem and phloem streams (34).

Typically, aquatic food webs are more complex than those found in terrestrial systems. Adsorption-desorption of elements on suspended sediments and direct absorption by organisms from water are added parameters in aquatic systems. Chemical contaminants generally reach aquatic environments by direct deposition (disposal), runoff from land surfaces, and leachates in ground water. Chemical and physical reactions among sediments, interstitial water, the water column, and decomposers can affect the routes and rates of transfer as well as the chemical and biological properties of contaminants. Aquatic

plants obtain elements from the water column through absorption although surface adsorption is important because of high surface-to-volume ratios found in algae and other phytoplankton. Decomposers may act upon organic matter in anaerobic sediments resulting in release of heavy metals to interstitial waters and their subsequent diffusion into the overlying water mass. Because of the chemical and biological activity present, sediments may act as sources and sinks of chemical contaminants in the aquatic environments.

Biological Concentration. The ability of animals and plants to accumulate chemical contaminants to levels above those of their food source or substrate is a common biological phenomenon. Trace elements, including heavy metals and radionuclides, are accumulated to varying degrees (35-37). In aquatic systems, water is typically the reference point, while soil serves a similar role in terrestrial systems. Biological concentration of elements is governed by the amount of element present in the diet or surrounding environment, the chemical and physical forms of the element which determine its biological availability, the quantity of food consumed containing the element, the degree of assimilation of the element through cellular barriers (i.e., cuticle, lung, digestive tract, gills, etc.), and the extent of retention in the organism's tissues. Biological concentration occurs with natural elements for cellular maintenance and growth. It can also occur with hazardous elements when there is a strong chemical or physical resemblance to a common element or molecule which is necessary for everyday life processes (38).

Due to the variations that exist in the factors governing biological concentration among different environments and species as well as within one species in a particular environment, it is not true that because biomagnification occurs at one step in a food chain, it will also occur in subsequent steps.

Biological concentration factors for hazardous elements (Table 4) may vary over many orders of magnitude (10^2 to 10^5) in aquatic and terrestrial environments (36, 37, 39). Typically, biomagnification is greatest in aquatic environments where surface-to-volume ratios are greatest and where adsorption may overshadow absorption in relative importance. Bioconcentration factors for trace elements in terrestrial environments are generally less than unity with some exceptions.

Biological Transformations. Trace elements and radionuclides introduced into the environment are subject to biochemical interactions typically with microorganisms in soils and sediments although there are some biochemical transformation of hazardous chemicals in higher organisms. Microor-

ganisms are very versatile in their ability to chemically interact with natural and synthetic chemicals (41, 42).

The biochemical process of methylation of heavy metals and metalloids has received considerable attention in recent years although the reaction was first observed with arsenic in the late 1930's (43). Methylation is believed to be a detoxification mechanism for converting toxic ions to a more volatile form that will be released to the atmosphere (44). Several microbial species are capable of performing this transformation in soils and sediments under both aerobic and anaerobic conditions. Methylated forms of trace metals are frequently more toxic and are more readily absorbed by higher organisms than are inorganic forms. Methylation of mercury by microbes in marine and freshwater sediments is the best documented case of this type of biological transformation (35). Arsenic, selenium, lead, and tin are examples of other toxic elements that undergo methylation (45).

Higher organisms, including man, are capable of affecting biotransformations of hazardous chemicals. Reactions of Cd and metallothioneine in retention of this element in renal tissues are well documented by Friberg et al. (46).

Biotransformations of hazardous chemicals in the environment are particularly important in determining effects on man and other organisms because the molecular form and biochemistry of these transformed chemicals determine their availability, persistence, bioaccumulation, and toxicity.

Synergism and Antagonism. The combined action of two different chemicals may be greater than or less than the sum of the independent actions of each material. If chemical effects are simply additive, the increase is a simple algebraic addition. If the effect is greater than a simple algebraic addition, then synergism or potentiation has occurred. If the effect is less, antagonism exists. In the case of additive effects, the two compounds have the same points of attack. In potentiation, one compound usually acts on the metabolism of the second compound. The concept of synergism or potentiation covers both increases in usual effects of toxic compounds and production of lesions not observed by the action of either toxic compound alone (47). Synergisms and antagonisms are important in systems receiving multiple inputs of trace contaminants (i.e., aquatic ecosystems and ground water).

Ecological Effects

Ecological effects of hazardous elements have received increasing attention in recent years (6, 48, 49).

Table 4. Biological concentration factors for selected trace elements in aquatic and terrestrial environments.^a

	Biological concentration factor ^b				
	As	Cd	Hg	Pb	Zn
Aquatic					
Water	1	1	1	1	1
Plants	170	1000	1000	200	1000
Invertebrates	330	2000	100,000	100	10,000
Fish	330	200	1000	300	1000
Terrestrial					
Soil	1	1	1	1	1
Plants	0.01	0.3	0.4	0.07	0.4
Invertebrates	0.01	17		0.02	8
Mammals	0.001	0.008	5	0.001	0.6
Birds	0.001		50	0.001	

^aSource: Van Hook (40).^bRatio of concentration in organism to concentration in substrate.

although most of this attention is focused on atmospheric releases of particulates and associated trace elements. Only recently have the problems associated with ground water contamination from ash disposal come to light (3, 15) although there has been considerable work with acid mine drainage and the hazardous elements contained therein (6). Similarly, coal-derived radionuclide impacts have been addressed from the human health point of view (4, 50), but insufficient data exist to evaluate the potential impact in natural ecosystems. The following discussions are based primarily on the work of Jones et al. (49) with supplemental information added where appropriate.

Coal Extraction, Cleaning, and Storage. Effects of hazardous elements from extraction on aquatic ecosystems will result primarily from acid mine drainage and erosion-induced siltation (51). Historically, these effects have been severe throughout eastern coal regions. The recently passed Surface Mining and Reclamation Act of 1977 should definitely improve this situation. Effects include decreased productivity and diversity, temporally and spatially altered species composition, altered species composition, and, in heavily polluted systems, absence of life. Factors which influence the effects of acid mine drainage and associated hazardous elements include degree of effluent dilution in receiving waters, the presence of other pollutants including sewage and industrial wastes, chemical states of metals in natural waters, pH, temperature, organic matter content, and synergisms (52). Western coals generally lack acid-forming substances (i.e., pyrites) which, along with the alkaline nature of western soils and overburden, suggests that acid mine drainage should be minimal in western coal regions. Increased salinity of surface and ground

waters in western coal regions appears to be due to soluble salts in mine spoils (53). Surface coal extraction can also affect ground water resources. Ground water aquifers are commonly intercepted during overburden removal with subsequent effects on ground water flow and quality. Hazardous elements may enter these disturbed aquifers and be mobilized and leached into surface waters.

Ecological effects of coal cleaning and storage are similar in nature but lesser in magnitude to those associated with acid mine drainage from coal extraction. Acid drainage or runoff from refuse piles may affect terrestrial and aquatic systems by lowering pH. Soils surrounding the refuse piles may accumulate potentially toxic levels of trace elements or radionuclides leached from the refuse by acid water. Aquatic environments adjacent to refuse piles can be severely impacted through sedimentation of fines and associated elements (6). The major long-term impact to terrestrial systems will probably be that the disposal area can only be returned to limited land uses (i.e., wildlife cover, recreation).

Coal pile runoff and leachates contain coal fines, hazardous elements, and humic acids and may be acidic. Terrestrial effects are limited to land under and immediately adjacent to coal piles while aquatic effects including elevated element concentrations and suspended solids will be more widespread. In arid environments, or during dry spells in other areas, fugitive dusts from coal and refuse piles may be suspended in the atmosphere and are subject to deposition on vegetation surfaces and inhalation by animals.

Coal Combustion — Solid Wastes. Combustion of coal results in solid wastes including precipitated fly ash, bottom ash, slag, and SO₂ scrubber sludges which require onsite disposal, and gaseous and par-

ticulate emissions that pass through emission control devices and are released through stacks to the atmosphere. Currently, about 92% of the particulate material produced in utility boilers is removed with electrostatic precipitators (54). Fly ash, bottom ash, and slag all contain trace and radioactive elements, but the exact composition can vary widely depending on coal geology and boiler operating conditions. Elements tend to partition themselves into different ash components as has been discussed earlier. Studies of migration of trace elements from ash pond leachates through soils have produced variable results depending on coal type, operating conditions, and ash disposal sites. One study suggests no migration into ground water (55), whereas other investigators (15) indicate that trace metals are released to ground water at generally low concentrations, with attenuation occurring very close to the disposal site. While this may tend to minimize ground water contamination, it does not prevent uptake by plants whose roots penetrate the new water table created by the presence of the ash pond. Water and solutes will move upward and laterally through the soil from the new water table when soil surface evaporation and plant transpiration exceed rainfall infiltration. Accumulated hazardous elements may be toxic to the vegetation, or they may simply be stored and then become toxic to animals which consume the vegetation.

Aquatic environments receive trace elements and radionuclides from ash disposal through ground water (minimal) and direct runoff from settling basins. Direct runoff may contain dissolved and suspended materials which may or may not be available chemically to the biota. EPA guidelines call for application of BACT (best available control technology) to waste water effluents by 1983. Currently, best practicable control technology is applied at varying levels of success. At least 30 trace elements have been identified in measurable quantities in coal ash and a number of these are toxic to aquatic organisms at either the initial concentration or following biological transformation and/or concentration (56). Concentrations of radium, thorium, and uranium have been reported in fly ash (50), but there are insufficient data to assess the effects of these radionuclides or their daughter products on aquatic or terrestrial ecosystems from ash disposal sites. These data are particularly important considering that about 92% of the ash produced in coal combustion is placed in settling ponds and landfills. There are few data on the effects of trace elements on surface waters, but a study by Holland et al. (55) demonstrated concentrations of B, Ba, Cr, Hg, and Se in ash leachates exceeding federal surface water

standards for these elements. Results from this study varied from sample to sample and care must be exercised in generalizing to new situations.

To understand the effects of coal-fired steam-plant-derived elements on the aquatic system, it is necessary to quantify discharge of these elements. Calculations reported by Vaughan et al. (48) and Dvornak et al. (6) indicate that the atmospheric deposition of elements derived from coal combustion should exert a minimal influence on the chemical composition of lakes and rivers. The only elements that could be elevated were Hg, Cu, Sn, and Mo. This conclusion was reached despite the use of maximum transfer rates of fly ash deposited on soil and its migration to the drainage streams in the hypothetical watershed. An important additional consideration, however, is the impact of slag and fly ash discharges into the aqueous environment. The basis for this concern is that approximately 32×10^6 tons of fly ash with elevated levels of toxic elements is annually discharged into settling basins situated in close proximity to many coal-fired steam plants (57). Because it is known that many elements are leached from the fly ash (15), it is important to determine the mobilization potential of toxic metals from fly ash settling basins to the nation's surface and subsurface waters.

To obtain a better understanding of this mobilization potential, Klein et al. (58) calculated the quantity of elements that were annually discharged prior to 1975 in slag and fly ash to settling ponds and compared these values with data on natural weathering. Results of these comparisons indicate that except for Br, which is almost exclusively emitted as a vapor, the discharge into ash settling basins accounts for more than 1% of the elements mobilized by weathering. Elements such as As, Cd, Co, Cu, Fe, Mo, Ni, Pb, Se, U, and Zn all exhibit mobilization rates that are larger than 10% of the weathering rate, while rates for Mo, Se, and U are comparable to natural rates. Application of this analysis to more recent information (6, 7, 19) on coal combustion (6.8×10^6 t/yr) and on Cd and Hg concentrations in coal (0.5 and 0.2 $\mu\text{g/g}$, respectively), in soil (0.2 and 0.03 $\mu\text{g/g}$, respectively), and in water (0.1 and 0.07 $\mu\text{g/l}$, respectively), indicates that these elements are currently mobilized in coal combustion at rates equivalent to their natural weathering rates. Cadmium releases are predominantly associated with precipitated fly ash in settling ponds and landfills whereas the majority of the Hg exists in the plant stack with only about 10% going into solid waste disposal sites. Due to these considerations, it would be appropriate to investigate the regional effects of these fly ash-derived elements; that is, do the ele-

ments effectively remain in the settling basins or are they injected into the nation's waterways. Until such evaluations have been made, it will be impossible to predict, in a quantitative manner, whether coal-fired steam plants will exert any modification on the chemical composition of the nation's waterways.

The very high pH encountered in ash settling basins may influence the behavior of trace elements if this pH influence extends beyond the confines of the ash settling basin (i.e., into subsurface and surface waters). This high pH results from the hydrolysis of alkali and alkaline earths and may often exceed 11. In most ash settling basins it appears that atmospheric CO₂ diffusion into the water is not rapid enough to lower the pH. One would predict that many metals would precipitate either as hydroxides or by coprecipitation (e.g., calcium carbonate). If settling is not complete, however, particulate matter containing elevated levels of metal carbonates, hydroxides, or sulfates could reach the discharge waters. Upon reaching lower pH discharge waters, these particulates might redissolve, thus producing an increase in available metals to aquatic plants and organisms. Alternatively, high pH effluent waters might produce a beneficial effect, in terms of metal removal, on lakes and rivers with low buffering capacity. The change in pH, however, might also affect the plants and organisms in the receiving waters. These implications should be considered before the impact of coal-fired steam plants on the aquatic ecosystem can be evaluated.

Coal Combustion — Atmospheric Emissions. Coal combustion emissions released through stacks to the atmosphere can be transported over considerable distances (see Environmental Transport section). The ecological effect of hazardous elements associated with these emissions will vary as a function of chemical and physical form of the element, the site of deposition, and the amount of material deposited. As pointed out earlier, volatile elements in coal include As, Be, Cd, F, Hg, Se, Sb, Br, Cl, Cu, Ga, I, Ir, Mo, Pb, and Zn (16, 58, 59). All pose some degree of potential hazard to man and might adversely impact the environment at some threshold concentration. The amounts and forms of these elements that exit the stack of a coal-fired power plant are largely unknown and probably vary between plants, depending on the coal source and pollution control technology. The effect of electrostatic precipitators in reducing these emissions is likewise unclear, although some consider a high percentage of these elements should be found in the particulate of the precipitators. Natusch et al. (17) reported that As, Sb, Cd, Pb, Se, and Tl preferentially concentrated on particulates in the respirable range, a large part of which is not

removed by existing high-efficiency precipitators.

Cannon and Swanson (60) found that concentrations of trace elements in soils (i.e., Hg, As, Se, Te, Cd, Be, and Pb) dropped rapidly with distance from the Four Corners Power Plant, and concentrations were lower than those for average soils at distances beyond 3 km. Vegetation within 3 km of the plant had not, within the time span of their study, accumulated significant quantities of these potentially toxic trace elements. The authors concluded that with the installation of more efficient precipitators, the atmospheric trace element emissions from this plant would not be considered harmful to the biota. Horton et al. (61) measured the concentrations of 29 trace elements in soils and vegetation within approximately 11 km of a coal-fired power plant in South Carolina that had been operating since 1952. With the possible exception of Se (in soils) and Mn (in ground water), none of the trace elements released to the atmosphere from the plant contributed significantly to the concentrations of the elements in the immediate environment. No enrichment or depletion of trace elements was detected in soils in the vicinity of Allen Steam Plant near Memphis, Tennessee, but the soil was under the influence of agricultural practices (62). Klein and Russell (63), however, reported that sandy soils on the eastern shore of Lake Michigan near a power plant were found to be enriched in Ag, Cd, Cs, Cr, Cu, Fe, Hg, Ni, Ti, and Zn. Vegetation was enriched in Cd, Fe, Ni, and Zn.

Vaughan et al. (48) modeled the cumulative impacts of trace element emissions over a 40-year period from a hypothetical 1400-MW(e) power plant in the western United States burning representative western coal. Their model predicted that four trace elements, Cd, Mo, Cu, and W, might accumulate (by at least a factor of two) in growing plants. However, they did not have sufficient data to make predictions for a number of trace elements such as Ga, Ce, Ra, Te, Th, Tl, and V. In a similar analysis on a hypothetical 1000-MW(e) power plant, Dvorak et al. (6) concluded that even when the atmospheric particulate emission rate is at the maximum allowed by NSPS (0.1 lb/10⁶ BTU), the impacts to vegetation are expected to be minimal. These authors point out Cd and Se as having the greatest potential for adversely affecting animals.

A number of the trace elements (i.e., Fe, Cl, B, Mn, Zn, Cu, Mo, Co, Se, I, Cr, Sn, V, F, Si, and Ni) are essential at low concentrations for either plant or animal life but are toxic at higher concentrations (64). Some of the nonessential trace elements, such as Cd and Hg and essential Zn and Cu in marine environments, are toxic to sensitive species in con-

Table 5. Potential toxicity of trace elements in coal.^a

Element	Terrestrial			Comments
	Plant	Animal	Aquatic	
As	Low	Low	Low	Know enough on toxicity for terrestrial ecosystems, in some instances may be beneficial
B	High	Medium	Low ^b	
Be	Medium	High	High ^b	
Bi	Medium	Low	Low ^b	Speciation important
Cd	High	High	High	
Co	High	Medium	High	Cr ³⁺ very toxic — need to know speciation
Cr	High	Medium	Medium	
Cu	High	Medium	High	
F	High	High	Low	Complexion in soil reduces toxicity, in some instances may be beneficial
Hg	Medium	High ^b	High	
Mn	Low	Low	Low	
Mo	Low	Medium	Low	Enriched in plants, toxicity in food cycle
Ni	High	High	Medium	
Pb	Low	Medium	Medium	
Sb	Medium	High ^b	Low ^b	Potential for net beneficial effects
Se	Medium	High	Low ^b	
Sn	Low	Low	Low	
Ti	Low	Low ^b	Medium ^b	High enrichment in plants — beneficial or adverse effects
Tl	High	High	Medium ^b	
V	High	Low ^b	Medium ^b	
W	Medium	Medium ^b	Low ^b	Very mobile in plants
Zn	Low	Medium	Medium	

^aSource: Jones et al. (49).^bUncertain.

concentrations only slightly above those occurring naturally (65). Biotic dose-response relationships for trace elements are at best poorly defined, and almost nonexistent for those species comprising natural ecosystems. The effect of high concentrations of trace elements is ultimately a function of the tolerance of individual plants or animals.

Jones et al. (49) have classified the potential toxicity of various trace elements in coal into three main categories — high, medium, and low — for terrestrial and aquatic life (Table 5). The authors consider this information to be a "best estimate" based on their collective experience, knowledge, and intuition. It should be pointed out that the impact on the overall soil-water-plant system is also a function of the chemical state of the trace element which impacted the system and its interaction with the local environment. This interaction will determine the trace element availability and, therefore, the fraction of the total trace element concentration that can affect growth.

Soils represent the principal repository of trace contaminants from fossil-fuel combustion over geologic time. Therefore, the soil is the principal medium for long-term exposure of coal effluents to terrestrial plants and animals. The effects of trace

metals on important soil microbial processes and the role of soil microorganisms in influencing the long-term availability of trace metals to plants are largely unknown. Inhibition of microbial processes may have important secondary effects on the ecosystem. Furthermore, microorganisms exist predominately in the immediate vicinity of the soil particle where trace metal concentrations are highest. Microorganisms thus have the potential for alteration of the form of the metal through interaction with normal metabolites or by direct conversion processes.

Trace elements have long been known to affect plants. In the case of the essential trace nutrients (Fe, Cl, B, Mn, Zn, Cu, and Mo), a broad range of possible responses exists, ranging from deficiency to toxicity. In the case of the nonessential trace elements, only the no-effect (tolerant) and toxic portions of the dose-response curve are expressed. Under natural conditions, there are examples of plants growing under both deficient and toxic conditions. Whether the trace element emissions from coal-fired power plants can enhance or inhibit plant growth depends on whether these elements will have a significant effect on naturally occurring concentrations. There is no reason to expect acute effects on plants from atmospheric trace element emissions

from coal combustion systems and little reason to expect acute effects to aquatic systems. The potential for chronic toxicity is relatively low except for particularly toxic elements such as F (66) or in local areas already enriched with a particular element.

Some trace elements combine the properties of high toxicity, a potential for bioaccumulation in food webs, and persistence in the environment. Many of these substances are toxic in sensitive animal species at concentrations that are only slightly above naturally occurring levels (64, 65). Higher trophic levels, as a result of bioaccumulation, may be affected at "ambient" concentrations that would not be expected to affect plants. Even with these reservations, it is probable that trace elements in emissions have little or no discernible effect on animals. Effects would seem possible only if the emissions that are currently accepted are in error by an order of magnitude. Sublethal, chronic, or synergistic effects of trace contaminants that may be of significance in natural terrestrial animal populations have received little attention (6). However, because some of the trace elements have been reported to adversely affect soil/litter communities (67) and possibly alter primary productivity (67, 68), and, in turn, secondary productivity, potential long-term impacts on ecosystems could occur if trace elements emitted from coal combustion persist or accumulate in ecosystems to toxic levels.

Health Effects

Any assessment of possible health effects from coal combustion contaminants requires, *inter alia*, definition and quantitation of source and transport terms. Given information on "what" and "how much" can be breathed and ingested, an evaluation of the human exposure and intake estimations can proceed utilizing background, dietary, occupational, experimental, and environmental information, provided these data exist. A number of reports have been published on health aspects of trace contaminants from coal combustion (1, 4, 6, 48, 69-71). These reports have been utilized in developing the following discussion.

Physiological and pathological responses of a population to radionuclides and trace elements from coal will reflect the individual's ability to respond and the duration of exposure. Short-term adverse effects will be manifest in those subgroups more sensitive to the pollutant (i.e., children, aged, infirm) as an increased incidence of respiratory diseases, aggravation of preexisting chronic cardiopulmonary diseases, and premature death. Chronic exposure on the other hand may result in an increased incidence of respiratory diseases and cancer in the total popu-

lation. The major health effects of concern relative to coal combustion products include physiological irritation, direct toxicity, carcinogenesis, and physical synergisms. The following discussions center primarily around atmospheric emissions from coal combustion with much less emphasis on solid wastes (ash and slag). This is due to a virtual absence of information about the contribution of coal-ash-derived hazardous elements to the ambient levels in man's environment or their subsequent contamination of food or drinking water.

Electrostatic precipitators are typically more efficient for larger diameter particles in flue gas. Particulates existing the power plant stack are generally in the respirable size class. The toxic effect produced by respirable particles depends on the chemical species they contain. Smaller particles tend to be more toxic than larger ones due to size and selective adsorption of heavy metals (17). Submicron fly ash particles represent a double threat to human health (6); they reach the pulmonary region and remain there for extended time periods, and they can deliver a given concentration of hazardous element to a very localized area thereby magnifying the effect.

Coal Extraction, Cleaning, and Storage. Human health effects of hazardous elements associated with coal extraction, cleaning, and storage include inhalation of coal dusts which may contribute to development of black lung (coal worker's pneumoconiosis) (72), and ingestion of trace elements and radionuclides from drinking water contaminated by acid mine drainage. Acid mine drainage impacts are generally more widespread, and in communities without alternate sources of water, or undeveloped water sources, these impacts can represent a severe problem (6). Runoff from coal piles and coal-cleaning wastes contribute to water quality degradation but on a much smaller scale than acid mine drainage. Atmospheric loading of coal particulates arises through resuspension of coal fines from storage piles and from accidental ignition of both coal piles and coal-cleaning waste piles.

Coal Combustion. The radiological impact of coal-fired power plants appears to be adequately evaluated for atmospheric releases (4, 73). McBride et al. (4) estimated annual release rates for a 1000-MW(e) power plant burning coal at a rate of approximately 100 tons/hr, containing 1 ppm of uranium and 2 ppm of thorium (both assumed to be in secular equilibrium), and releasing 1% of its fly ash to the atmosphere (the average ash release for 1972 was 8%). Under these conditions, ^{228}Th , ^{232}Th , ^{223}Ra , and ^{212}Pb each contribute approximately 5×10^{-3} Ci/yr; ^{238}U , ^{234}U , ^{230}Th , ^{234}Th , ^{226}Ra , ^{210}Pb , ^{210}Po , ^{210}Bi each contribute approximately 8×10^{-4} Ci/yr;

and ^{222}Rn and ^{222}Rn together account for approximately 1.2 Ci/yr. These release rates were then applied to a population of ~ 3.5 million persons living within a 90-km radius of the power plant. The dose calculations took into account doses from immersion, contaminated ground surface, inhalation, and ingestion, wherein all doses from food and water were derived from within the 90-km radius of the plant (74, 75).

The following population dose commitments were determined: 10 to 25 man-rem/yr whole body dose and approximately 100 to 240 man-rem/yr bone dose. The corresponding average individual dose commitments were 0.003 to 0.007 mrem/yr and 0.03 to 0.07 mrem/yr, respectively, where the ranges pertain to emission patterns from different stack heights (300-50 m). The maximum individual dose commitment at 500 m from the stack was 1.9 mrem/yr and was independent of stack height. The dose commitment is based largely on ^{226}Ra ingestion and essentially doubles if the U content of the coal is doubled. If bituminous coals are used, the U concentration is often as high as 20 parts per million, so this could increase both the release and dose commitment figures by an order of magnitude, assuming all other factors remain constant.

Of relevance are the data of Martin et al. (50), who measured downwind levels of U from a 1400-MW(e) coal-fired power plant and found fCi/m³ concentrations, implying daily intakes by humans would be of the order of a few femtocuries. Ambient air levels of approximately 400 aCi/m³ of U have been reported, indicating a concentration of about 2 pCi/g for atmospheric dust or approximately 2 ppm by weight, which is not greatly different from the U concentration in fly ash from an average anthracite coal.

To compare the magnitude of the radiation dose from coal combustion emissions to that from natural background (76), it is useful to use dose-equivalent rates. On this basis, NCRP (76) indicates that the dose equivalent rate for ^{226}Ra from natural background is about 7 mrem/yr for bone and less than 1 mrem/yr for the whole body. The dose equivalent rate for the whole body from all natural radiation sources is 80 ± 40 mrem/yr; the corresponding coal combustion figure would be 7×10^{-3} mrem/yr. Radiation protection limits for whole body irradiation of individuals within a population are set at 500 mrem/yr with an average genetic dose limited to 170 mrem/yr (5 rem in 30 years). A proposed guideline would limit the whole body dose to members of the critical population to 5 mrem/yr from atmospheric releases.

The new EPA Primary Drinking Water Regulation for Radioactivity (40 CFR 141, 1975) limits the ^{226}Ra

and ^{228}Ra combined activity to 5 pCi/L, gross α activity to 15 pCi/L, and any combination of β - α whose concentrations produce a dose equivalent of 4 mrem/yr to the whole body. Whether any of these regulations might be exceeded in the immediate environs of a coal-fired power plant is uncertain. This uncertainty is due to a lack of information concerning the release of radionuclides from solid waste disposal sites which receive in addition to bottom ash and slag, the 92% of the fly ash from combustion that is removed from flue gas by electrostatic precipitators.

Morrow et al. (69) have made estimates of chemical toxicity of nonradioactive trace elements using maximal expected airborne levels 1 m above the ground associated with 0 to 15- μm diameter particles within a 20-km radius of a 1400-MW(e) coal-fired power plant with a plume height of 300 m [see Table 23 of Vaughan et al. (48)]. The predicted air concentrations resulting from their calculations, and presumably good to a factor of 3, were compared to ambient air concentrations, atmospheric standards for population exposures, reference man data for inhalation intakes, and occupational Threshold Limit Values (TLV). By this approach, generally accepted, safe ranges of atmospheric concentrations were established.

Results of their analysis revealed several uncertainties. Three elements [As (III), Cr (VI insol), and Ni carbonyl] are generally accepted as having potential carcinogenic importance, so the general approach used in this tabulation may be inappropriate. For Ni, As, and Cr, a critical question concerns the occurrence and magnitude of the carcinogenic forms of these elements, namely, As (III), Cr (VI insol), and nickel carbonyl, oxide, sulfide, and carbonate in coal combustion effluents. On the basis of the currently available information, Cr (VI) probably occurs; the nature of the nickel compounds is unknown, but the highly volatile carbonyl is assuredly absent from fly ash. For As, the expectation is good for both the III and V oxidation states, but no quantitative findings exist — only the indication that fly ash leachates contain both forms.

The reported teratogenic properties of certain Cd, Se, and Hg compounds, the mutagenic potential of certain Pb and Hg compounds, and the carcinogenic properties of Be and Se (77) are, in general, only demonstrable at high doses or under uncommon circumstances. Consequently they warrant no species concern at this time.

Information on the metallo-organic forms of Hg is lacking, as it is for other elements, but there is little likelihood that they occur in the emissions from coal combustion associated with particulate matter. Even if alkyl mercury were the singular form of Hg emit-

ted, its acceptable air concentration indicates that it probably would be unimportant toxicologically.

Because of the uncertainties in the assumptions and models used, the variability in the trace element composition of coal and in the naturally occurring levels at specific power plant sites, Be and F may constitute potential health problems in the immediate environment of coal power plants. Otherwise, the majority of the elemental concentrations calculated by Morrow et al. (69) appear to be one or more orders of magnitude below the "acceptable air concentrations."

Berry and Wallace (2) sampled the plants and soil around a coal-fired electric plant at Moapa, Nevada, burning approximately 100 tons of high ash coal per hour, and concluded that forage and milk from the area could become seriously contaminated if high arsenic coals (> 500 ppm) were used for several decades. Excessive Cd contamination of forage and dairy products also could be envisioned and some concern was expressed regarding F contamination. In other studies of coal power plants, some enrichment of trace elements (e.g., Hg, Se, and Pb) in soil and plant life has been reported (60, 61). In the Four Corners study (60), Pb was found enriched in soils, but no toxic trace metals were found in excess of average soil values at a 3-km distance from the plant.

Comparisons of data from Vaughan et al. (48), Pinkerton et al. (78) and Bolton et al. (62) indicate that the soil build-up of trace metal contaminants will be slow, and allowing order-of-magnitude perturbations in depositions and soil conditions, one would not expect excessive bioaccumulation to occur in plants unless the bioavailability of exogenous fractions is orders of magnitude greater than that of typical soil. There is evidence that exogenous elements are more water soluble, implying greater bioavailability on the one hand and shorter soil retention times on the other. A potentially more important source of water and biotic contamination relates to slag and fly ash disposal. Ponding, ground burial, and other disposal techniques will lead to consequences of greatly different magnitude, and as pointed out earlier, very few data are available in this area. Thus, one of the greatest uncertainties in this health effects evaluation relates to the potential intake of heavy metal contaminants from water and food exposed to ash disposal effluents.

The first Food and Drug Administration Market Basket Survey (79) indicated that for some metals (e.g., Cd) the dietary intake levels are already approaching tolerable limits. The initial survey estimated the daily intake of five selected metals in $\mu\text{g/day}$ for a U.S. adolescent male as follows: As, 10.1; Cd, 51.2; Hg, 2.9; Pb, 60.4; and Se, 149. On the basis of the provisional WHO/FAO tolerated intake

limits for heavy metals by adults, the Market Basket Survey estimates for total Hg, Pb, and Cd intake are about 7, 14, and 75%, respectively, of the WHO/FAO limits. Cadmium has an unusually wide distribution in foodstuffs so that soil levels will be reflected generally in water, fruit, vegetables, meats, and dairy products. In addition, current mobilization of Cd and Hg through coal combustion is near the natural weathering rates for these elements and can be expected to increase with increased coal use.

Trace elements and radionuclides do not exist in isolation in the environment; they are released in association with major coal combustion contaminants (i.e., SO_2 , NO_x , particulates) and may undergo chemical and physical transformations following discharge from power plant stacks. It is probably that such secondary chemical and physical interactions of the major and trace emissions, together with their physiologic interactions with tissues of exposed persons, may represent a most important aspect of the toxicology associated with combustion of coal. The two following examples illustrate the potential importance of such interactions.

Gaseous pollutants, including SO_2 , NO_x , and O_3 , that increase the rate of cell proliferation of the tracheal-bronchial epithelium are highly suspect as important promoters or cofactors in the pathogenesis of lung cancer. In a survey of smelter workers exposed to As_2O_3 , the greatest excess of lung cancer was found in instances where there were accompanying exposures to high to moderate levels of SO_2 .

Oxidation of SO_2 to SO_4 does not always occur at perceptible rates in the atmosphere. Such oxidation appears to depend on the simultaneous presence of other factors — possibly hydrocarbons from automotive exhaust, or trace metals which may act catalytically. Adverse health effects in sensitive members of the population now appear to be better related to concentrations of sulfate aerosols than to SO_2 . Acidic sulfate aerosols have, theoretically, the potential to combine with heavy metal cations with unknown consequences. Thus a variety of synergistic actions from pollutant mixtures can be anticipated which will cause and/or exacerbate pulmonary dysfunction and chronic cardiopulmonary diseases.

Conclusions

Current Situation

Ultimately, trace elements from coal return to the soil or sediment systems whence they originally came. The trace elements and radionuclides in coal naturally occur in soils. Consequently, anthropogenic contributions of these elements in soils

are hard to distinguish from the large natural variability at distances of more than a few kilometers from a particular power plant. The chemical forms of trace contaminants are important determinants of transport and effects, yet most studies have focused on total elemental amounts or concentrations.

Basic concepts and models exist to describe the various pathways of environmental and biological transport. The rates of transport, however, are not well known, nor are input data on climatology, hydrology, and environmental chemistry available for most sites. It is important to obtain improved data on transport and transformation rates, particularly in relevant chemical and biological areas. These data will be essential in determining organism exposure to coal-derived hazardous elements.

Coal Extraction, Cleaning, and Storage. Acid mine drainage, particulate loading of the atmosphere from coal and refuse piles, and ground water contamination continue to be major problems associated with mining, processing, and storing coal. These problems are expected to improve as the new Surface Mining and Reclamation Act is implemented. Acid mine drainage from both surface and deep mines is prevalent in the Eastern and Interior Coal Provinces of the United States while alkaline mine drainage presents problems in the western provinces. Abandoned mines represent the major source of acid mine drainage in the eastern United States. Particulate loading of the atmosphere from the extraction-processing end of the coal fuel cycle occurs from suspension of coal fines and coal ash dusts from stable and burning coal and waste ash piles. Effects from these dusts and coal fines will presumably be confined to the immediate surroundings. Coal and refuse piles also serve as sources of hazardous elements in runoff and leachates which may enter the soil system and in some cases contaminate ground water. Generally, ground water contamination from these sources is minimal because of attenuation in soils. Effects of trace elements and radionuclides from coal extraction, cleaning, and storage are generally subtle when compared to the acid nature of drainage and runoff. Acute effects will be very difficult to sort out. Chronic effects may occur as a function of biological concentration and transformations that may render elements more hazardous because of amount, form, or location of accumulation.

Coal Combustion — Solid Wastes. Solid wastes from coal combustion consist of slag, bottom ash, precipitated fly ash, and scrubber sludge (if SO_2 scrubbers are used). These wastes are typically stored wet in settling ponds or are dewatered and deposited in landfills. Settling ponds may also be mined following drying with the dry ash then moved

to landfills. Some coal ash is used for commercial purposes (e.g., cement additive). Leachate infiltration into ground waters immediately below and adjacent to ash disposal sites is not well studied. Data are lacking on chemical species present; chemical form governs mobility, availability, and toxicity. Likewise, there are few data available on the contribution of settling pond outfalls to the hazardous element burden of surface waters. Direct input of dissolved and suspended trace elements and radionuclides into these waters can have a direct effect on water quality and aquatic life depending on waste water treatment. An understanding of the problems associated with coal waste leachate and runoff containing hazardous elements is essential when we consider that currently 92% of the ash in coal is trapped by precipitators and disposed of on the plant site. Preliminary estimates of trace element releases from coal combustion to ash disposal sites indicate that 12 trace elements, including As, Cd, Hg, Ni, Pb, and U, are released at rates that are > 10% of natural weathering rates, meaning that coal extraction and use is short-circuiting the geochemical cycle for trace elements.

Coal Combustion — Atmospheric Emissions. Evaluation of the ecological effects of trace elements and radionuclides from coal combustion requires information about the kinds and amounts emitted during the combustion process, their transport and deposition in the environment, and their availability, accumulation, and toxicity in ecosystems. Based on an incomplete data set concerning the items described above, it appears that atmospheric releases of trace and radioactive elements are not likely to have significant, detectable effects on the chemical composition of soil, vegetation, and water in the near term. There are, however, certain areas of the country where detectable effects may occur (e.g., areas of sandy soils and low fertility or areas with sizable ambient concentrations of trace contaminants). In these areas, several trace elements bear watching. These include: F, Cd, Ni, Tl, Cu, V, Zn, Co, Mo, W, and Hg in terrestrial ecosystems; and As, Cd, Co, Hg, Cu, Pb, and Sn in aquatic environments. Fluoride may warrant special attention because of its reactivity and high toxicity in terrestrial systems.

In dealing with soil-plant relationships, emphasis should be placed on hazardous elements that enter soil in the highest concentration (e.g., Hg, W, Cd, and V); are soluble and thus more available to plants (e.g., Cu, Hg, and Ni); are mobile in the plant and transported to edible tissues (e.g., Ni, Tl, and W); and are most toxic to plant and/or animals and man (e.g., Cd, Ni, F, Tl, V, U, and Hg). Furthermore, recognition should be given to the potential benefi-

cial effects of Mo, Zn, Cu, and C in terrestrial systems and to the stimulating effects, particularly in respect to eutrophication, of some of the trace elements in aquatic systems. The major pollutants in stack emissions from coal-fired power plants (SO_2 , NO_2 , and their transformation products) are of importance in terms of their interactions (synergisms/antagonisms) with trace elements and radionuclides as well as in terms of their direct effects.

There is an inadequate data base for determining the health effects, present or potential, of the trace elements from coal combustion or conversion plants. There is, however, highly suggestive evidence that some contaminants [e.g., Ni, Cd, Cr (VI), As (III), and F] may constitute potential health problems from either direct toxicity or carcinogenesis. Mercury, Pb, and Cd should be followed closely because current intake levels are near the tolerable intake limits. Radioactive emissions from coal combustion currently contribute < 1% to background radiation dose from all natural sources. However, they could become a health consideration if bituminous coals with high U content (> 5 ppm) are utilized. Important synergistic effects between certain coal-derived metals and other inorganic and organic substances in the environment can be anticipated, and these may prove important in health effect assessments. In the domain of food and water intake, particularly as affected by ash settling ponds and landfills, no toxicological assessment of trace elements or radionuclides is feasible at this time. However, this should be regarded as a potentially significant health problem area which justifies monitoring of these sites.

National Energy Plan Implications

Implementation of the NEP will result in a doubling of coal extraction and use by 1985 and a tripling by 2000. Industrial boilers currently using gas and oil will switch to coal, and electric utilities will add considerably to their generating capacity through coal combustion. Gasification may become a significant coal consumer before 2000. The NEP calls for application of the Best Available Control Technology (BACT) to new boilers. It is assumed that this application will result in a 1% release of ash from combustion to the atmosphere. Assuming U.S. coals average 5% ash, BACT application in 1985 will result in 0.6 million tons of fly ash released to the atmosphere and 59.4 million tons of solid wastes requiring disposal in settling ponds or landfills. Conversion of industrial boilers to coal will serve to disperse sources of particulates to air and will require additional ash disposal areas. Regional air and water quality may change under this dispersed concept.

Trace element and radionuclide effects on health and the environment must be looked at from the point of view of the impact of the NEP on the coal fuel cycle and the relative contribution of hazardous elements from coal contrasted with other sources of regional and local environmental burdens.

Coal Extraction, Cleaning, and Storage. The NEP will have a direct impact on coal extraction, cleaning, and storage. Doubling and tripling coal production in the next 25 years will result in increases in acid mine drainage. The amount of the increase will depend upon enforcement of current regulations and those promulgated under the Surface Mining and Reclamation Act. With BACT being applied, western coals are less attractive in the east because of high transportation cost and low BTU content even though they are low sulfur coals. Eastern coal (high sulfur) will be used in plants equipped with SO_2 scrubbers. This leads to a considerable increase in eastern coal mining with attendant acid mine drainage problems. Hazardous elements in mine drainage may reach ground and surface waters with subsequent ingestion by man and other animals. Western coal production will also increase with attendant alkaline mine drainage problems. Coal cleaning, typically restricted to the east and central regions, will increase with leachate and runoff containing hazardous elements moving into ground water. Storage piles will be more widespread with more opportunities for runoff to reach surface waters and perhaps ground waters. Additional mining and cleaning of coal will lead to increased spoils and cleaning wastes. Coal fines from these wastes along with dusts from coal storage areas will serve as fugitive sources of particulates containing hazardous elements to the atmosphere. Depending on local environmental conditions, these particulates may constitute a health hazard. From the point of view of trace elements and radionuclides, the greatest impact of increased coal mining, cleaning, and storage is the additional burden of these elements to air, soil, and water in environments that are already stressed by ambient levels of these and other pollutants. The degree of synergisms occurring among these contaminants is not well known. Potential hazards from elements released in mining and cleaning will be restricted to particular regions, whereas potential hazards from coal storage may exist nationwide.

Coal Combustion — Solid Waste. Application of BACT coupled with a proposed tripling of coal utilization by 2000 will result annually in some 95 million tons of ash requiring disposal. Scrubber sludges for SO_2 control will add to this solid waste disposal problem. Unless new engineering designs are developed for settling ponds and landfills, direct runoff

to surface waters and leachate intrusion into ground water will certainly occur on a larger scale than at present. Trace elements and radionuclides entering surface waters will add to existing burdens and result in degradation of water quality and potential toxic effects on aquatic species. Contamination of drinking water supplies presents a real human hazard for elements such as Cd and Hg which are already near tolerable intake limits, and causes an economic burden in the form of advanced water treatment plants. Although present studies indicate minimal ground water contamination from coal-ash landfills because of attenuation in soils, the national impact of an additional 60 million tons of ash by 2000 will add significantly to the trace element and radionuclide burden in soils and in some cases exceed their buffering capacities, which will lead to accelerated ground water contamination. Further, this additional coal-ash waste will be much more widely distributed across the country as a result of industrial boilers switching to coal added to the new coal-fired boilers put into service. Mobilization of elements through coal combustion already exceeds 10% of natural weathering for several trace toxic elements and can only be expected to increase with increased coal use.

Coal Combustion — Atmospheric Emissions. Particulate emissions from coal combustion and conversion by 2000 are estimated to reach one million tons annually. These emissions will be predominantly in the respirable range and will contribute both trace element and radionuclide insults to plants and animals. Volatile forms of hazardous elements will accompany stack gas emissions. It is difficult to assess the direct health and environmental effects of coal-combustion-derived hazardous elements. Their accelerated release from increased coal use will add, perhaps significantly, to the ambient atmospheric loading from all other sources. Synergistic actions with coal-derived and other organic and inorganic chemicals in the atmosphere will become more important in determining organism response to increased ambient levels. Thus, a major determinant in potential coal-derived hazardous element effects will be the ambient air quality of the region (i.e., industrial vs. rural) receiving the additional burden. The general public health of the U.S. population will be a factor in determining hazardous element effects from the point of view of irritants, co-factors, and physical synergists.

It is unlikely that atmospheric emissions of hazardous elements will have a measurable effect on concentrations in soil, vegetation, and water. In local situations, however, certain trace elements (F) and radionuclides (Rn) may reach levels causing concern because of both increasing coal use and

switching to coals containing higher concentrations of these elements or their parents. Because of the ubiquitous nature of Cd and Hg (and perhaps Pb) and the fact that their daily intake already approaches tolerable levels, these elements may become real health hazards from coal utilization.

Recommendations

The ability to assess the health and environmental impacts of trace elements and radionuclides derived from current and future coal utilization depends on a basic understanding of (a) the chemistry and physics of elements in coal and ash in the natural environment (mining), in settling ponds and landfills (solid wastes), and in fly ash (atmospheric emissions); (b) the physical and biological transport through air, soil, water, and organisms; (c) the interactions among emissions and ambient pollutants, water, and other natural environmental chemicals; and (d) the ecological and human health effects of coal-derived emissions both singly and in the presence of other environmental stresses. Once this information is available, it will be possible to determine reasonable trace and radioactive element release rates as functions of both environmental tolerance and costs associated with effluent controls. Until this information is on hand, certain activities should be pursued.

(1) Characterization of concentrations and physicochemical states of specific trace elements and radionuclides in both atmospheric emissions and aqueous effluents from coal combustion and conversion should be performed. These monitoring activities should be carried out even though hazardous elements are not considered criteria pollutants and their release rates are not regulated. Special attention should be given to characterization of elements, including As, Cd, Cu, Hg, Ni, Pb, and Zn, in leachates from ash disposal systems, to the oxidation states and chemical forms of Ni, As, and Cr, to the nature and occurrence of organometallic compounds, and to the levels of Cd, Be, and fluorides in terrestrial environments within 40 km of coal-fired power plants.

(2) An assessment of the contribution of trace and radioactive elements from the coal fuel cycle relative to all other sources should be made to put coal-derived hazardous elements in proper perspective.

(3) Rapid, reliable methods should be developed to ascertain the movement of water and solutes in the vicinity of coal ash disposal sites.

(4) Watershed-scale mass flow budgets for trace elements from coal mining and processing operations are needed and should be based on both measurement and model simulations.

(5) Models should be developed that accurately track and predict atmospheric transport and diffusion of coal-derived emissions over rugged terrain, during very stable conditions, and over long distances. Special emphasis should be applied to dry deposition on natural surfaces.

(6) Information about chemical and physical behavior of specific hazardous elements in soils and water is needed. Data requirements include rates of solubilization and transformation, phase distributions, chemical form, and availability. The rate and extent of solubilization on a regional basis is also needed.

(7) The role of the coal-derived hazardous elements As, Cd, Cr, Cu, Hg, Ni, and Pb in drinking water should be evaluated in terms of toxicological and carcinogenic potential.

(8) Compliance testing of environmental control technologies for atmospheric emissions should be vigorously pursued with emphasis on improving removal efficiencies for particulates in the respirable size range.

(9) Methods of removing hazardous elements, including As, Cd, Cr, Cu, Hg, Pb, and Zn, from waste streams (i.e., acid mine drainage, coal pile runoff, settling pond outfalls) need to be developed to reduce the environmental contribution from coal utilization.

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Cytotoxicity to Alveolar Macrophages of Trace Metals
Adsorbed on Fly Ash¹CATHERINE ARANYI,* FREDERICK J. MILLER,† SANDRA ANDRES*
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Fly ash fractionated into <2-, 2- to 5-, and 5- to 8- μ m size ranges and coated on the surface with PbO, NiO, or MnO₂ was used to examine the cytotoxic effects *in vitro* of particle concentration and size to alveolar macrophages (AM). For the various fly-ash samples, statistically significant decreases were demonstrated in viability, total protein, and lactate dehydrogenase activity with increasing concentration and decreasing particle size. The toxic effect was not due to solubilization of the test metals in the media since no toxicity could be demonstrated using particle-free leaches. The percentage of metal adsorbed on the fly ash varied within a narrow range and therefore at a given concentration the AM were exposed to fairly constant amounts of the test elements irrespective of particle size. Thus cytotoxicity is particle size as well as dose dependent and the greater toxicity of the smaller particles appears to be due to their larger surface area.

INTRODUCTION

Alveolar macrophages (AM) play an important role in the detoxification and protection of the lungs from inhaled particles and infectious agents. There is evidence that certain trace-metal-containing particulates released into the environment as stationary or mobile source emission byproducts can adversely affect the phagocytic, bacteriolytic, and metabolic functions of AM. Since the health hazards associated with potentially toxic metals or metal compounds entering the body as respirable-size particulates have been recognized, their effects on the pulmonary cellular defense system has been increasingly investigated. (Bingham *et al.*, 1968, and 1972; Graham *et al.*, 1975a,b and 1978; Graham and Gardner, 1977; Gardner *et al.*, 1976; Adkins and Gardner, 1976). These cells have also been used for the *in vitro* screening and toxicologic ranking of various pure compounds that may represent inhalation hazards (Waters *et al.*, 1974 and 1975, Aranyi *et al.*, 1977).

The objective of these studies was to evaluate whether physical characteristics such as size and surface area of fly-ash particles alone as well as those coated with various trace metals are contributing factors to their cytotoxicity to AM. Fly-ash particles are formed during burning of coal in power plants, when at temperatures exceeding 1100°C the mineral residues fuse and are carried into the effluent stream by the gases and the volatile coal fractions. It is known that in the fugitive emissions

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The test suspensions were incubated for 21 hr at 37°C in a humidified 4% CO₂ atmosphere in wells of disposable plastic cluster dishes that were placed on a rocker platform for agitation. After incubation the suspensions were transferred into siliconized centrifuge tubes and the AM attached to the cluster dishes were removed with rubber policemen and combined with the corresponding suspensions in the centrifuge tubes.

Viability was determined by microscopic counting of 400 to 500 AM. The percentage of AM that had phagocytized the test particles was determined from the same slides. For monitoring cell lysis via loss of cellular protein, the test suspensions were subsequently washed and centrifuged three times in HBSS and the pellets were resuspended in 2.0 ml of HBSS to remove serum and other interfering media supplements before determination of total protein levels.

For determination of enzyme activity the washed cell pellet was resuspended in distilled water for osmotic shock, the volume adjusted to 2.0 ml, and the suspension placed in ice was sonicated with the microtip of an ultrasonic generator. The cell suspension was divided into two portions: one portion was used for enzyme assays after centrifugation at 63g to remove the fly-ash particles and the other portion was treated with 1% sodium deoxycholate (Schwarz/Mann, Orangeburg, N.Y.), the resulting lysate centrifuged at 10,000g, and the supernatant used for protein assay.

Enzyme activity was determined using commercial assay kits (acid phosphatase, lactate dehydrogenase (LDH): Boehringer-Mannheim Corp.; β -glucuronidase: Sigma Chemical Co.). Acid phosphatase activity was determined by using the enzyme to hydrolyze *p*-nitrophenylphosphate at 37°C and measuring the liberated *p*-nitrophenol colorimetrically at 405 nm. LDH activity was analyzed by measuring the rate of oxidation of NADH at 366 nm. This oxidation is proportional to the conversion by the enzyme of pyruvate to lactate. Total protein content was analyzed by the Lowry method (Lowry *et al.*, 1951) with the use of bovine serum albumin standard (ICN Inc. Irvine, Calif.).

Experimental Design and Data Analysis

Three to six replicate experiments were conducted for each test sample using AM obtained from one to three rabbits. Within one experiment a minimum of five exposure concentrations selected to produce a viability response over a wide range was tested in triplicate cultures using three wells of a cluster dish and three replicate assay determinations within each well for every parameter examined.

Specific enzyme activities were calculated as mU/mg cellular protein. Except where stated, changes in enzyme activity and of total cellular protein content were expressed as percentages of the corresponding controls. Since viability of the control AM was not affected by the 21-hr incubation, the viability values were reported directly as percentages of total AM in each culture.

For statistical analysis, linear regression and inverse prediction were used to determine the EC₅₀ values, i.e., the concentrations of fly-ash particles which reduced the responses of the various parameters studied to 50% of the control levels. Williams' test (Williams, 1971 and 1972) was used to determine the lowest effective concentration (LEC) among the dose levels tested, for which at this and all higher doses there is evidence of an effect on a given parameter. The error

estimates needed to perform Williams' test were obtained from analyses of variance wherein the control responses were included as separate determinations and the variability in overall response from experiment to experiment was eliminated via a blocking factor. Duncan's multiple range test (Duncan, 1955) was used to elucidate significant differences in the phagocytic response of AM for the various particle types.

RESULTS

Characterization of Fly-Ash Particles

The percentage of adsorbed lead, nickel, or manganese on the treated fly-ash particles showed only small variations among the different size fractions of the same treatment groups. The overall change ranged from 2.63 to 3.85% with the untreated fly-ash sample containing less than 0.03% of the test metals (Table 1).

In order to demonstrate that no cytotoxicity was contributed by solubilization of the test elements or other compounds from the fly ash, the metal oxide-treated fly-ash particles per se were preincubated in the maintenance medium for 21 hr at 37°C at the highest concentration used for exposure of the cells. When the filtered culture media from these tests were subsequently incubated for 21 hr at 37°C with AM, the viability of the cells did not differ from the unexposed control AM.

Cytotoxicity of Fly-Ash Particles

The toxicity of fly-ash particles was first evaluated by measuring their effect on AM viability. When cells were incubated in the presence of various concentrations of PbO₂, NiO₂, or MnO₂ treated, or untreated fly-ash particles in the <2-, 2- to 5-, and 5- to 8-μm size ranges, highly significant ($P < 0.0001$) negative linear dose-response relationships between particle concentration and viability of the AM were found for all treatment groups and for all size ranges. Figure 1 shows the least-squares lines resulting from the linear regression analyses as well as the mean of the viability observed for each concentration tested.

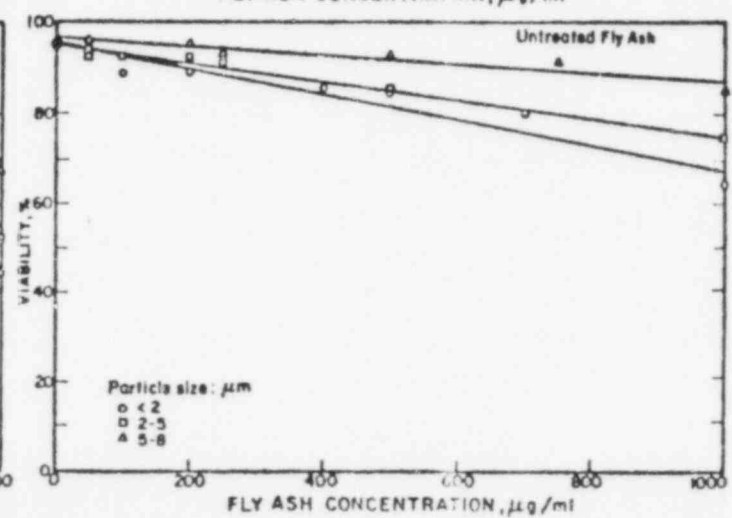
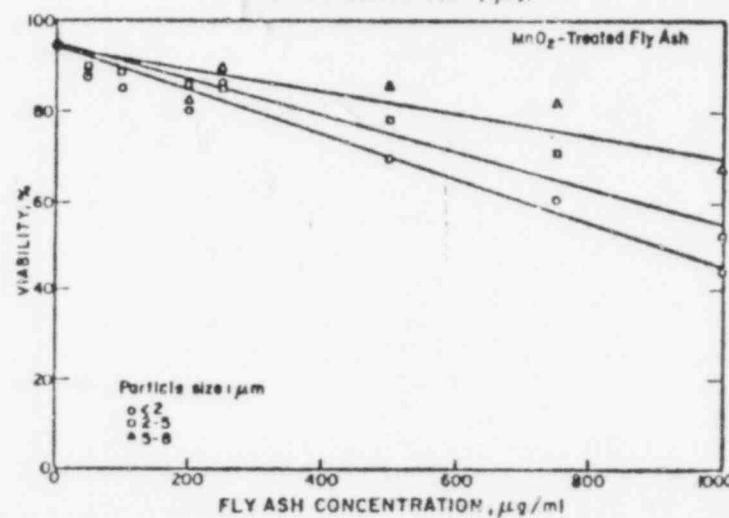
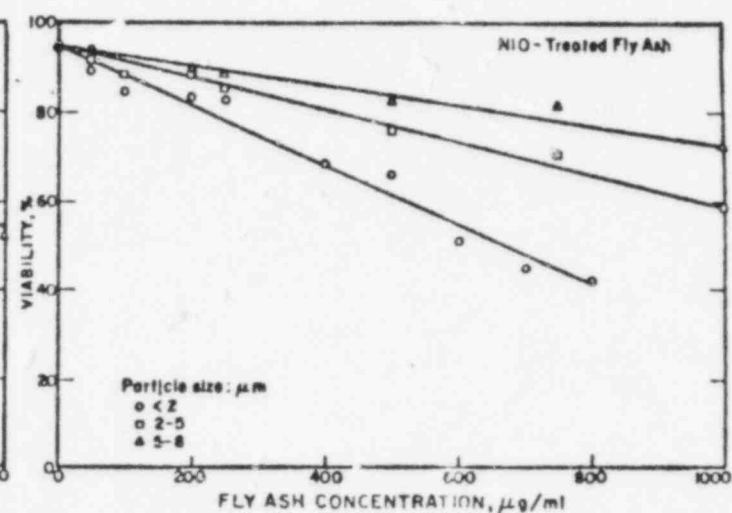
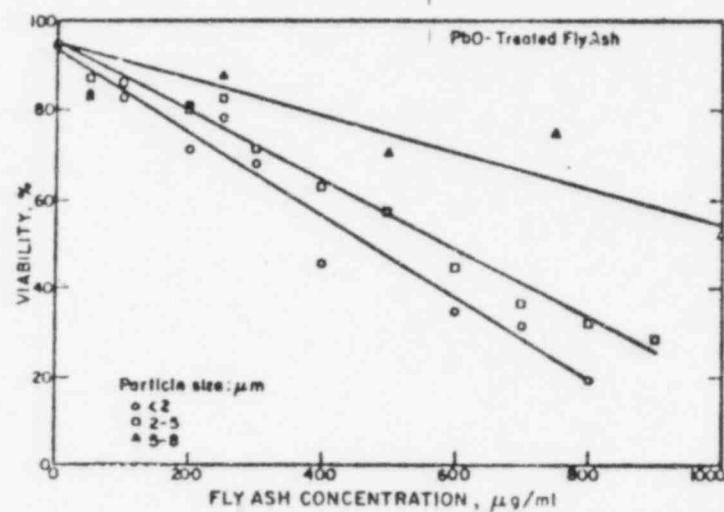
The results indicate that for each particle size, PbO₂-treated fly ash was most toxic, NiO₂- and MnO₂-treated particles had intermediate effects, and the untreated fly ash was least toxic, as it reduced viability at markedly higher concentrations than the treated particles. The data also show, that within the same treatment group, as particle size increases a significantly greater concentration is required to reduce viability to the same level.

The PbO₂- and NiO₂-treated fly-ash particles in those size ranges that can be retained in the alveolar region (<2 and 2 to 5 μm) were subsequently used in

TABLE I
ANALYSIS OF METAL TEST ELEMENTS ADSORBED ON FLY-ASH PARTICLES*

Test element	Weight percentage of metal adsorbed on particles sized:		
	<2 μm	2-5 μm	5-8 μm
Pb	3.85	3.84	3.15
Ni	2.63	2.91	2.77
Mn	3.22	3.67	2.91

* Uncoated fly ash contained <0.03% Pb and Ni and <0.01% Mn.



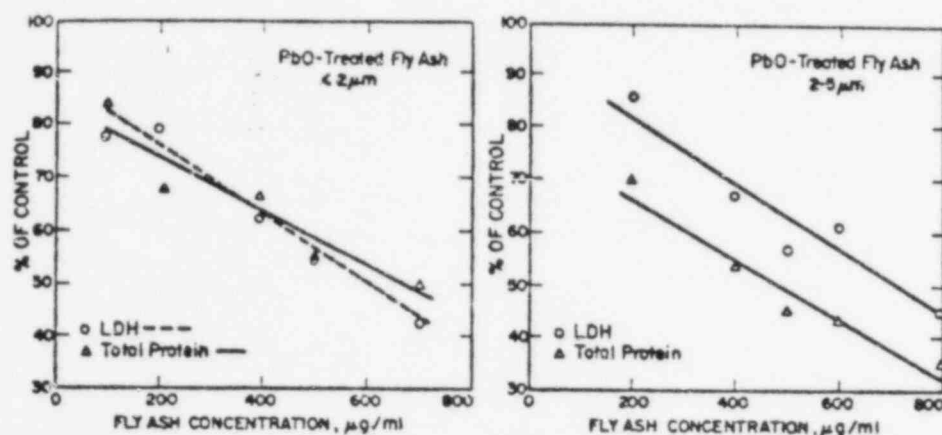


FIG. 2. Effect of particle concentration and size of PbO-treated fly ash on total protein content and LDH specific activity in macrophages. Results are expressed as percentages of the control responses. Each point represents the mean from three replicate experiments with triplicate assay determinations for each parameter. All regressions were significant at the 0.03 level.

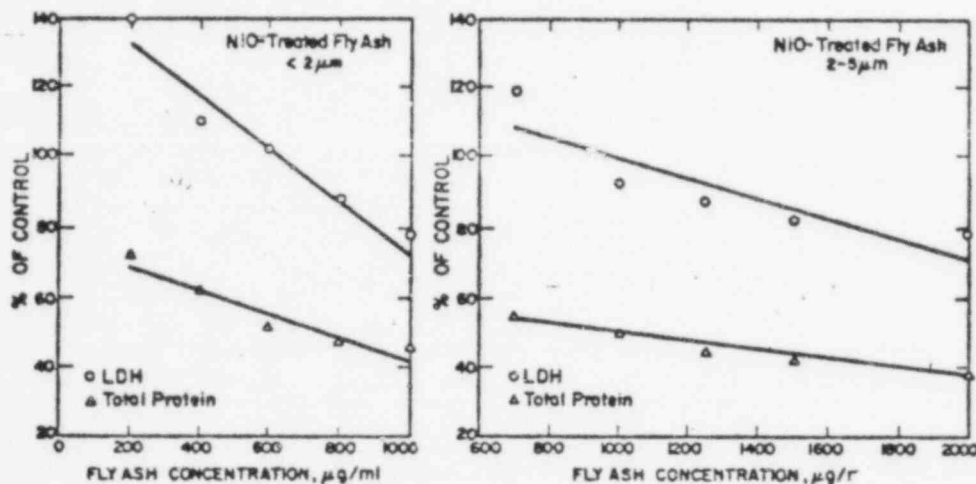


FIG. 3. Effect of particle concentration and size of NiO-treated fly ash on total protein content and LDH specific activity in macrophages. Results are expressed as percentages of the control responses. Each point represents the mean from three replicate experiments with triplicate assay determinations for each parameter. All regressions were significant at the 0.03 level.

studies conducted to determine if similar dose-responses for total cellular protein levels and specific activity of LDH, acid phosphatase, and β -glucuronidase could be established. The MnO_2 -treated samples were omitted, since their effect on viability was somewhat similar to that of the NiO-treated particles.

When AM were assayed after incubation with the test particles at concentrations chosen to produce cell viabilities ranging from 30 to 80%, total cellular protein levels and LDH specific activity for the PbO-treated fly ash (Fig. 2) and

FIG. 1. Effect of concentration and size of fly ash on viability of macrophages. The mean viability observed at each concentration is plotted, although the regressions were calculated using the individual data points. Each regression for the 5-8 μm particles was based upon 50 data points, while the sample size for the other regression lines varied between 56 and 81 points. The "zero dose" data points ($n = 28$) shown as a solid circle were used in each regression and all regressions were significant at the 0.0001 level.

TABLE 2
CONCENTRATION OF FLY-ASH PARTICLES REQUIRED TO REDUCE MACROPHAGE VIABILITY,
TOTAL PROTEIN CONTENT, AND LDH SPECIFIC ACTIVITY TO 50% (EC₅₀)

Particle treatment/size (μm)	EC ₅₀ (μg/ml)					
	Viability		Total protein		LDH activity	
	<2	2-5	<2	2-5	<2	2-5
PbO	470	584	681	488	586	707
NiO	670	1250	749	1007	1325 ^a (1000) ^b	2779 ^a (2000) ^b

^a Extrapolated above the tested concentration range.

^b Highest concentration tested.

NiO-treated fly ash (Fig. 3) generally followed the decreases observed for viability. However, this was not the case for the two lysosomal enzymes examined. The specific activity of acid phosphatase showed a moderately decreasing trend that was not entirely consistent and no change in the specific activity of β -glucuronidase was observed.

Regression analyses demonstrated significant ($P < 0.03$) negative linear relationships with particle concentration for LDH specific activity and total cellular protein levels. The estimated concentrations of particles that reduced these parameters and viability to 50% (EC₅₀) are summarized in Table 2. For LDH specific activity of NiO-treated AM, the EC₅₀ values had to be extrapolated beyond the tested exposure range.

Based on the EC₅₀ values a toxic ranking can be established for the particles with respect to treatment as well as to particle size. As noted earlier, the results for viability indicate that PbO-treated fly ash was more toxic than NiO-treated fly ash and within the same treatment group, higher concentrations were required to reduce viability with increasing particle size. The estimated EC₅₀ concentrations of the particles for total protein content, representing cell lysis, and LDH specific activity generally confirmed the toxic ranking determined in the viability-dose-response experiments, with the exception of total protein values found for the PbO-treated fly-ash particles in the 2- to 5-μm size.

Although it is of interest to establish the relative toxicity between these particles, more meaningful information to the environmental toxicologist is represented by the lowest concentration of the particles that results in deleterious effects. Thus Williams' test was used to estimate the lowest effective concentrations (LEC) required to reduce a given experimental parameter significantly, relative to the corresponding control level. The results summarized in Table 3 demonstrate that from the LEC values the same general observations as noted earlier can be made, namely, toxicity is more pronounced in PbO- than NiO-treated fly ash and smaller particles cause greater damage. It can also be seen from the data that in contrast to the estimated EC₅₀ values there is no inconsistency in the toxic ranking based on total protein determinations. As expected, the LEC levels are substantially lower than the EC₅₀ concentrations for all of the metal treatment-particle size categories. In addition, whereas no EC₅₀ estimates could be obtained for acid phosphatase and β -glucuronidase by linear regression analysis, LECs for acid phosphatase could be determined for PbO-treated fly-ash particles using Williams' test.

TABLE 3
LOWEST EFFECTIVE CONCENTRATION (LEC) OF FLY-ASH PARTICLES REQUIRED TO PRODUCE A
SIGNIFICANT EFFECT RELATIVE TO CONTROL RESPONSES*

Particle treatment/size (μm)	LEC ($\mu\text{g/ml}$)							
	Viability		Total protein		LDH		Acid phosphatase	
	<2	2-5	<2	2-5	<2	2-5	<2	2-5
PbO	50	200	100	200	100	200	400	400
NiO	200	250	200	750	1000	<i>b</i>	<i>b</i>	<i>b</i>

* Determined by Williams' test.

* Among the concentrations tested, none was found significantly ($P < 0.05$) different from control.

The effects of fly-ash treatment, particle size, and exposure concentration on phagocytic activity were determined using analysis of variance. The analysis of the significant interaction between particle size and concentration is given in Table 4. In the presence of <2- μm particles, approximately 93% of the AM phagocytized at the lowest concentration (250 $\mu\text{g/ml}$), while almost all of the cells had engulfed particles at the next highest concentration (500 $\mu\text{g/ml}$). This represented a significant difference between the percentage of AM that had phagocytized at 250 $\mu\text{g/ml}$ relative to all other exposure concentrations. In the presence of the 2- to 5- μm particles, only 82% of the AM phagocytized at 250 $\mu\text{g/ml}$, the process was more concentration dependent, and more of the differences between increasing concentration levels were significant.

DISCUSSION

Comparison of the toxicity of test substances on the basis of EC_{50} concentrations is often advocated. Unless the slopes of the dose-response curves are parallel, the toxic ranking may be different if comparisons are made at lower dose ranges. The environmental toxicologist is greatly interested in determining the lowest dose at which there is evidence of a response. However, there are seldom enough dose levels studied such that there are sufficient data for determining the true regression model and often there is disagreement about what magnitude of

TABLE 4
EFFECT OF PARTICLE SIZE AND CONCENTRATION ON PHAGOCYTOSIS

Particle concentration ($\mu\text{g/ml}$)	Percentage of macrophages that had phagocytized sized particles*	
	<2 μm	2-5 μm
250	92.9	81.7
500	96.6	91.7
750	96.7	93.0
1000	97.7	95.1

* Means connected by vertical line do not differ significantly ($P < 0.05$) from each other, as determined by Duncan's multiple range test.

difference between the fitted regression and the background response level is biologically significant.

Williams' test provides an alternative in that the analysis is based only on the assumption that the responses to the toxicant are monotonically ordered. Thus, the experimenter assumes *a priori* that if there is a response it will be in a known direction and will, if anything, increase in magnitude with increasing dose. There is also a nonparametric equivalent of Williams' test which can be used if the requirement of normally distributed data with equal group variances is not satisfied (Shirley, 1977). While in the current study the ranking between PbO- and NiO-treated fly-ash particles did not differ using Williams' test from the ranking obtained on the basis of EC₅₀ values (except for the total protein values of the PbO-treated samples) such would likely be the case if another EC level would be chosen for comparison. Furthermore, the LEC is of considerably more interest from an environmental perspective than is the dose causing a 50% decrement relative to the control response.

The effects of the various fly-ash particle preparations on viability, total protein content, representing cell lysis, and LDH specific activity in AM showed significant dose responses with particle exposure concentration. The results demonstrated that for a given treatment and a given concentration of fly ash, toxic effects increased with decreasing particle size. The percentage of adsorbed metal varied within a limited range for all test particles, and within a given metal treatment category the variability was even smaller. Therefore, since the AM were exposed to the particles on a weight concentration per cell number basis and, the percentage of metal was approximately the same for the various size ranges within a given treatment group, the AM were exposed to fairly constant concentrations of the test metals irrespective of particle size.

It also has been established that cytotoxicity was not due to any solubilized compounds released from the particles into the incubation medium. Thus, the increase in toxicity observed with decreasing particle size suggests that the toxic effect is due to surface interaction between particles and AM as well as to particle concentration. This is in agreement with the observation that for a given concentration, the percentage of phagocytizing AM increases with decreasing particle size. Moreover, since the smaller particles can be phagocytized in larger numbers, they provide more surface area for interaction with the intracellular milieu. Large particles do not affect AM as readily, because they cannot be engulfed in similar numbers, and, after engulfment, a smaller surface area is exposed in the phagolysosomes.

Thus, these studies provide experimental evidence that the size of the carrier particles affects the cytotoxicity to AM of a substance adsorbed on their surface and thereby demonstrate that for evaluation of inhalation hazards the size of the particle delivered to the AM as well as the size range that permits penetration into the alveolar region is extremely relevant.

ACKNOWLEDGMENTS

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A group of asthmatics reported daily symptoms for over seven months while air pollution and weather parameters were monitored. Significant correlations were found between attack rate and pollution levels commonly found in large cities.

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Asthma and Air Pollution from a Coal-Fueled Power Plant

Introduction

Earlier studies of the relationship between air pollution and acute asthmatic episodes have generally been of three types. In the first type, specific allergenic pollutants (e.g., castor bean dust or grain dust) were clearly established as asthmagenic on the basis of patients' history, skin tests, and re-exposure to the pollutant under control conditions.¹⁻³ In the second, associations were found between air pollution in general and asthma symptoms recorded in diaries, in emergency room, clinic or physicians' records, or during interviews.⁴⁻⁹ In the third type, the clustering of asthma episodes and their association with low wind speed indicated that an airborne substance was involved, but standard pollution measurements showed no correlation with attack rates.¹⁰⁻¹²

In none of the studies involving the usual ubiquitous pollutants could researchers specify the harmful agent or agents, or find those levels of pollution at which health effects first become marked. Nor could they generally disentangle the effects of air pollution and weather.

The present study was designed to obtain such information. For 7 months daily symptom reports were kept by a panel of asthmatics who were intermittently exposed to high levels of pollution because their homes were within 1/2 mile of a coal-fueled power plant. At the time of the study, the plant had low stacks, no abatement devices, and used high-ash, high-sulfur coal as fuel, and therefore emitted substantial quantities of particulates, sulfur dioxide and oxides of nitrogen. Our purpose was to quantitate the relationship between short-term relatively high-dose pollution exposure and frequency of asthma episodes.

Methods

Population Selection

New Cumberland, West Virginia was chosen for the present study because air quality measurements showed wide day-to-day fluctuation of pollution levels, and because its small area (1 mile by 1/2 mile) made intensive monitoring of pollution levels relatively simple. Subjects were located by telephone survey of all households in the small town (population 2,100). All residents claiming respiratory symptoms were screened by a staff physician (A.C.). Criteria for inclusion in the study were two:

1. History of intermittent episodes of respiratory distress, generally unaccompanied by fever or increased sputum production, in which wheezing was the predominant symptom.
2. Experience of three or more such episodes in the preceding 12 months.

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M.A.; and Carl M. Shy, M.D.

Most subjects had been told by their physician that they had "asthma," "allergic asthma," or "asthmatic bronchitis." Each subject was asked if he knew of neighbors with respiratory symptoms; this enabled us to find several subjects among the few local families without telephones.

Forty-three suitable subjects were identified. Of these, 14 were lost to the study, because of refusal to be interviewed (1), protracted hospitalization or travel (2), or repeated failure to return diary forms (11). Of the remaining 29 subjects, 9 reported no attacks or one attack during the study. All analyses presented are for the data of the 20 subjects who reported more than one attack.

A questionnaire administered to the 42 initial subjects inquired into age, sex, race, education, rent paid, duration and severity of asthma, medicine usually taken, symptoms during and between attacks and history of smoking and allergy. The distribution of these characteristics among the 14 study dropouts was not significantly different from that of the final participants. The group of subjects excluded because their attacks were too infrequent was younger, had fewer smokers, was slightly better educated and paid slightly more rent than the final study group.

Monitoring of Pollution and Weather

Three pollution monitoring stations were established at sites picked to give a representative sampling of population exposure. At each station, continuous measurements made included total suspended particulates (High Volume Sampler -24 hour samples),¹³ sulfur dioxide (Coulometric method),¹⁴ soiling index (AISI tape sampler-2 hour tape samples),¹⁵ suspended sulfates (24-hour samples,¹⁶) and suspended nitrates (24-hour samples¹⁷).

At one weather station in the center of town, and one on a nearby ridge, meteorologists took continuous hourly measurements of temperature, wind speed and direction, humidity and barometric pressure.

Diary Reports

Each subject received a diary form (Figure 7) and return envelope weekly. The diary form asked day of week

time of day, duration, severity, and place of onset for each episode. Three to five days after the end of each weekly reporting period, nonrespondents were phoned and reminded to submit the missing report. Each week approximately 15 per cent of the study population had to be telephoned.

Physician Visits

A staff physician made several week-long visits to New Cumberland. During these visits, subjects were asked to contact the physician each time they had an attack. The doctor then visited each one to confirm the occurrence of an asthma episode.

Analysis of Data

Methods of analysis included a stepwise multiple regression procedure with an analysis of the correlation coefficients, for log-transformed as well as for untransformed data. The association between attack rate and each pollutant was examined within three temperature ranges, as was the association of temperature with attack rate within three pollution ranges. Regressions were also calculated for each pollutant on the temperature-adjusted attack rate. Best-fit lines were plotted for each pollutant against attack rate and against temperature adjusted attack rate.

Results

The Population

Table 1 gives the population's age, sex, duration and severity of asthma, allergy and smoking history, and educational level. The final study group contained primarily adults (80 per cent), with at least a high school education. About half the group were male, half were smokers, half had a history of allergy, and all were Caucasian.

Table 1—Characteristics of the Study Population

Variable	Category	
Age	16 or less	Over 16
	4	16
Sex	Male	Female
	9	11
Duration of Asthma	10 years or less	More than 10 years
	9	11
Frequency of Episodes	12/year or less	More than 12/year
	0	20
(Non-asthmatic)	Positive	Negative
Allergic History	10	10
Smoking History	Smoker	Non-smoker
	11	9
Educational Level	Did not graduate HS	HS or more
	7	13

Association of Attack Rates with Pollution or Weather Parameters: Two-Variable Analysis

Averages.—Correlation coefficients were calculated between daily averages of each measured pollution or weather parameter and reported daily attack rate, and then between pollution and weather parameters. As the first column of Table 2 reveals, all pollutants as well as temperature correlated significantly with attack rate, although temperature, sulfur dioxide, and soiling index showed the greatest correlations. Figure 1 shows scattergrams for attack rate versus each variable that was significantly associated with attack rate. "Best-fit" linear regression lines are superimposed on the scattergrams. We attempted to fit threshold functions, i.e., S-shaped curves to the data. For each variable, however, the best fit S shaped curve did not explain more attack rate variation than the best-fit linear-regression line.

Lags.—The data were re-analyzed assuming 6, 12, 18 or 24 hour lags between pollution or temperature levels and occurrence of asthma episodes. Temperature and soiling index remained significantly correlated with attack rate with

Figure 1A—Scattergrams With Best-Fit Lines for Attack Rate versus Significant Variables

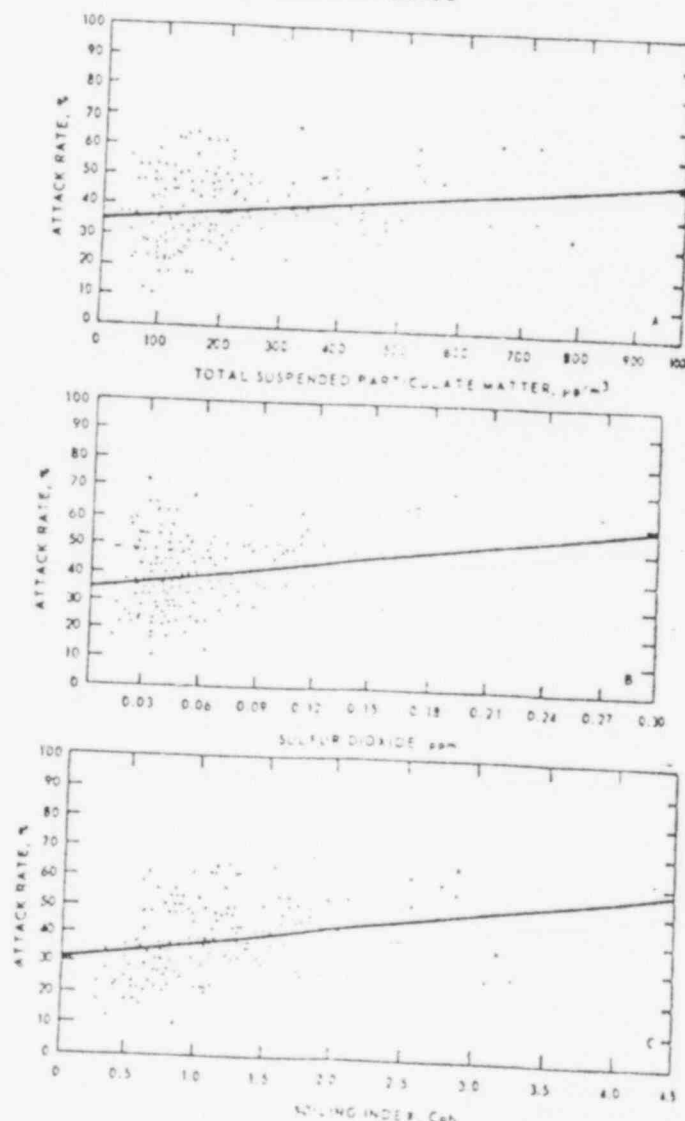
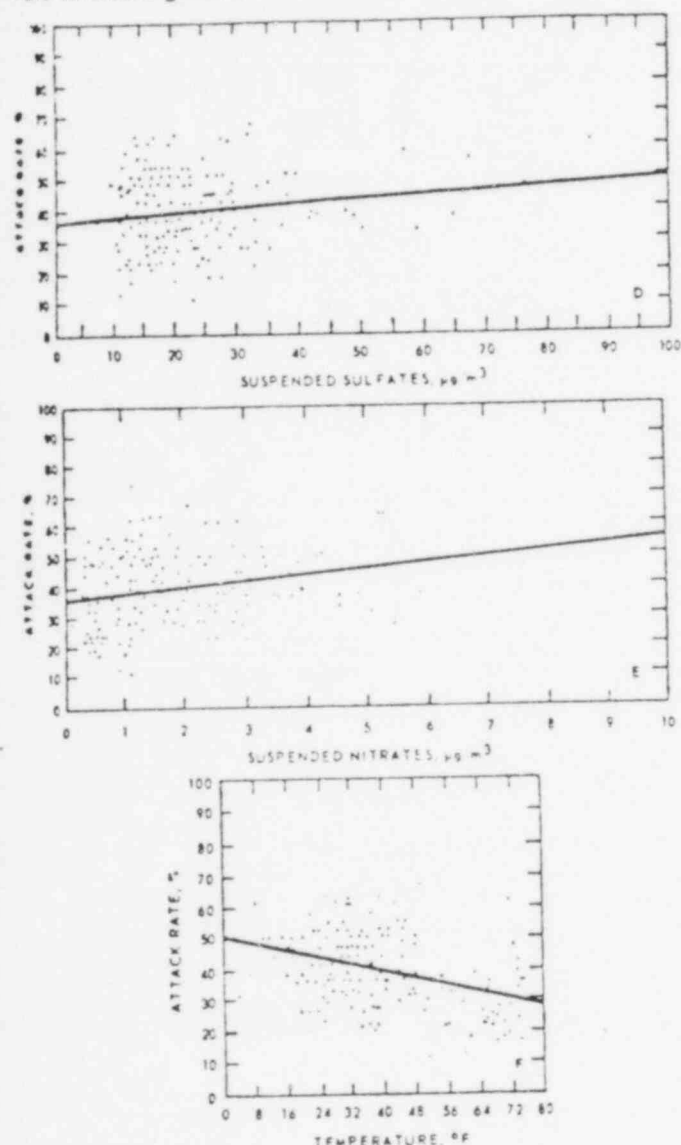


Figure 1B—Scattergrams With Best-Fit Lines for Attack Rate versus Significant variables



any of these lags. The correlation between attack rate and sulfur dioxide level decreased with increasing lag, becoming insignificant at lags of 18 hours or more.

Peaks—Analyses were repeated for all variables characterizing 6-hour temperature rather than by 24-hour averages. Correlations were virtually identical with those found for daily averages.

Too few days occurred with a low 24-hour pollution average but a high 6-hour peak, or with a high 24-hour average temperature but a low 6-hour minimum for us to make a meaningful analysis. The present study therefore could not distinguish the effects of short term (6-hour) high pollution exposure from those of longer term (24-hour), lower dose exposure.

Lags—Analysis of averages, lags and peaks of log-transformed data produced results no different from those described above.

High-low Analysis—Table 3 gives attack rates for high- and for low-pollution days and for days of high and low temperature, humidity, barometric pressure and windspeed. Cut off points demarcating "high" from "low" variable days were arbitrarily chosen so as to roughly equalize the number of days in each category and because these were points at which relatively large increases of attack rate occurred. In addition the table shows relative risks of high pollution, high humidity, and low windspeed, low temperature and low barometric pressure. Relative risk of high pollution varied from 1.03 for suspended sulfates and suspended nitrates to 1.24 for soiling index. The relative risk of low temperature was 1.29. Significant High-low differences in attack rate were found for suspended particulate, soiling index, sulfur dioxide, temperature, humidity and windspeed.

General Temporal Patterns—Temperature, sulfur dioxide and soiling index, the three variables showing highest correlations with attack rate, were tabulated with attack rate by quarter of day, day of week, and month of year.

Pollution levels and attack rate both peaked during the second quarter of the day; over half of all attacks were reported to have begun during this interval. Temperature was lowest between midnight and 6 a.m.

Figures 2 and 3 show average values of temperature, sulfur dioxide, soiling index and attack rate as functions of

Table 2—Correlation Coefficients for Pollution and Weather Parameters, and Attack Rate

	Attack rate	Sulfur dioxide	Soiling index	Temperature	Total Suspended particulates	Suspended nitrates	Suspended sulfates
Attack rate							
Sulfur dioxide	+ .320†						
Soiling index	+ .387†	- .525†					
Temperature	- .427†	- .205†	- .466*				
Total suspended particulates	+ .241†	+ .537†	+ .419†	- .021			
Suspended nitrates	- .169*	+ .316†	+ .488*	- .084	+ .543†		
Suspended sulfates	- .199†	+ .349†	+ .480†	- .197*	+ .567†	+ .361†	
Barometric pressure	- .038	- .055	- .122	- .043	- .156*	+ .165*	+ .107
Windspeed	- .050	- .072	- .290†	- .124	- .033	- .023	+ .267†
Humidity	- .112	- .112	- .223	- .162*	- .168*	- .186*	- .089

* P < .05

† P < .01

day of week and month of year. Figure 2 shows a "middle of the week" trend for attack rate and pollution, but no trend for temperature. Figure 3 shows average monthly attack rates varying directly with average monthly pollution levels and inversely with temperature; these relationships obtained in each season studied. Identical tabulations of the other pollution variables, though not presented here, showed similar characteristics.

As these figures and Table 2 show, each variable significantly correlated with attack rate was correlated with several other variables as well. These simple analyses thus failed to distinguish between primary and secondary associations.

Figure 2—Attack Rate, Temperature, Sulfur Dioxide Concentration, and Soiling Index as Functions of Day of Week

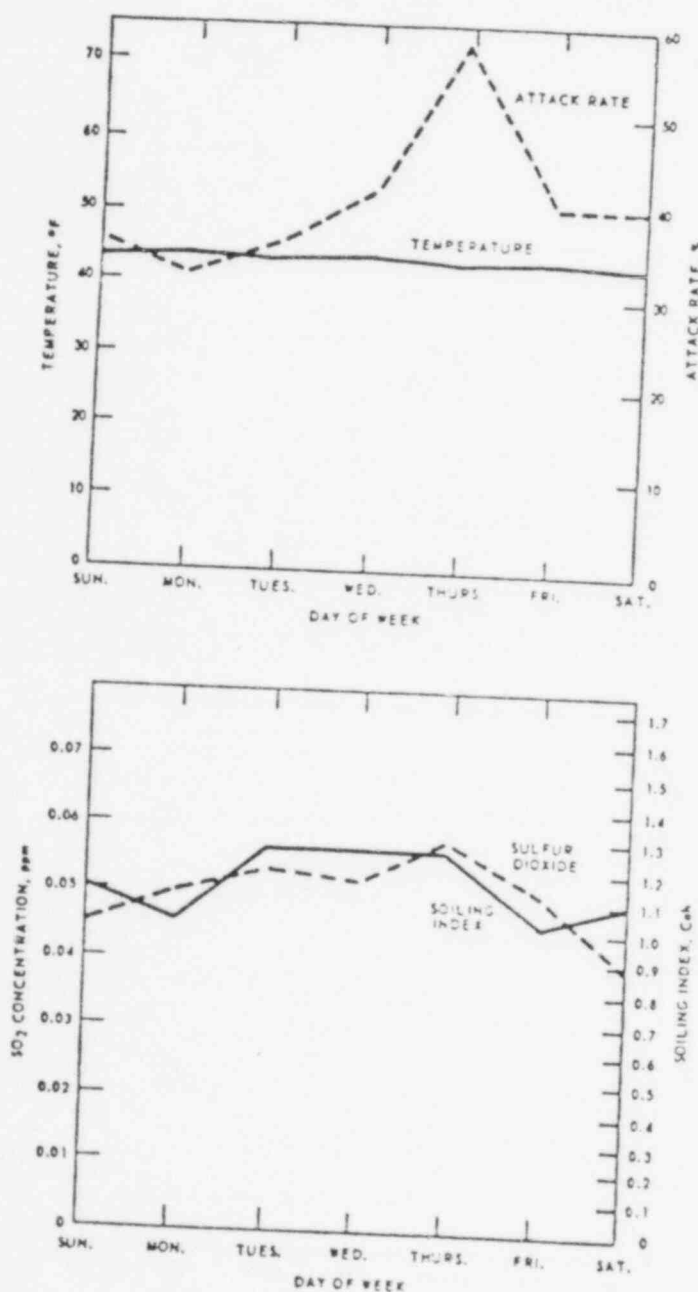
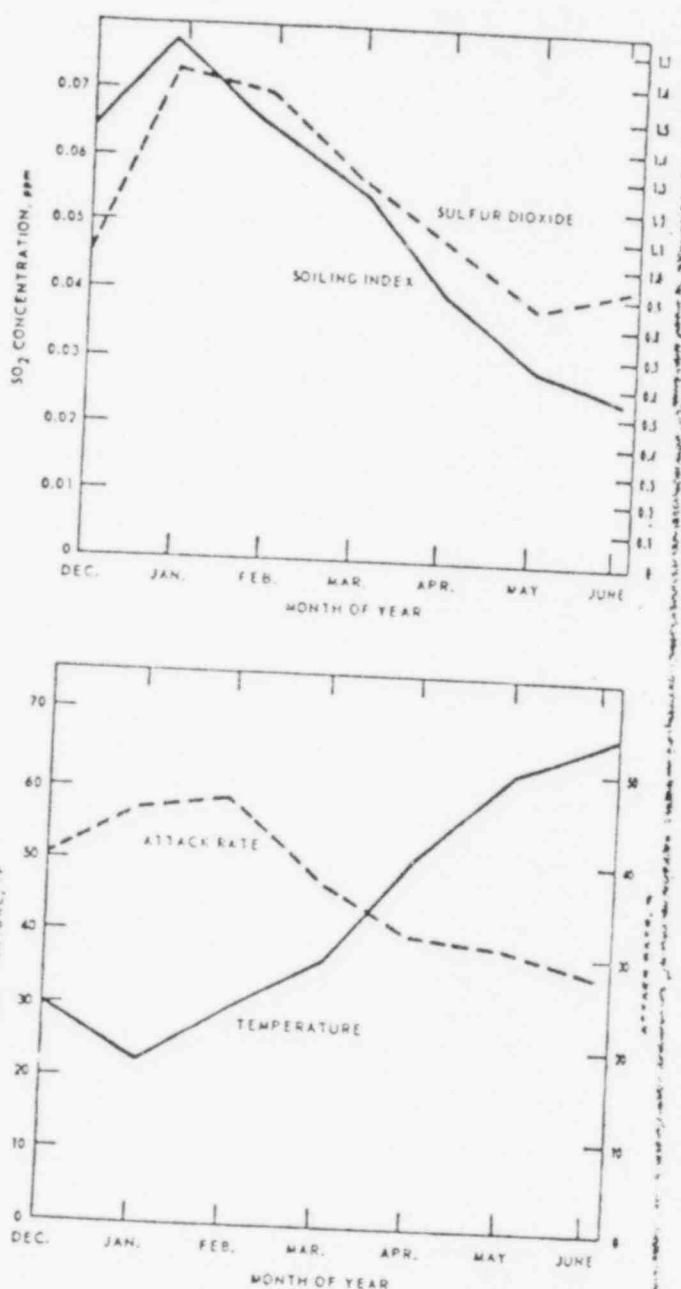


Figure 3—Attack Rate, Temperature, Sulfur Dioxide Concentration, and Soiling Index as Functions of Month of Year



Separation of the Effects of Weather and Pollution Parameters: Multivariate Analysis

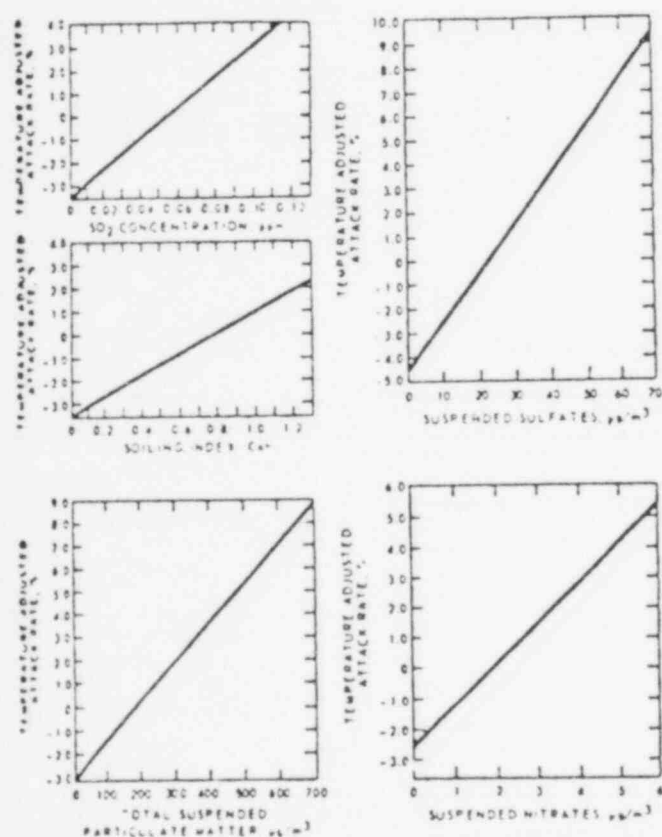
Since temperature showed by far the strongest association with attack rate, each variable was examined separately after the effects of temperature were removed in a multiple-regression analysis. Sulfur dioxide, soiling index, total suspended particulates, suspended sulfates and suspended nitrates were each found to explain a significant amount of residual variation in attack rate (Table 4). After temperature and any one of these five variables had been taken into account, none of the other four variables explained a significant amount of attack rate variation. These results are confirmed in Figure 4, which shows best-fit lines for

Table 3—Asthma Attack Rate and Pollution and Weather Variables: High-Low Analysis

Variable	Attack rate on "low" variable days (A)	Point demarcating "high" and "low" days	Attack rate on "high" variable days (B)	Relative risk of "high" variable days (B/A) or low Temperature (A/B)	Significance of differences in mean attack rates
Soiling index	0.342	1.0 Coh	0.422	1.24	P<.01
Sulfur dioxide	0.364	.07 ppm	0.448	1.23	P<.01
Total suspended particulate	0.349	150 $\mu\text{g}/\text{m}^3$	0.412	1.19	P<.01
Suspended nitrates	0.374	2 $\mu\text{g}/\text{m}^3$	0.388	1.03	NS
Suspended sulfates	0.378	20 $\mu\text{g}/\text{m}^3$	0.382	1.03	NS
Temperature	0.441	32 F	0.346	1.29	P<.01
Barometric pressure	0.380	29.4 inches Hg	0.374	0.98	NS
Windspeed	0.367	4 mph	0.391	1.06	P<.05
Humidity	0.362	80%	0.393	1.09	P<.05

"temperature-adjusted attack rate" against each pollution variable. On these graphs the difference between observed attack rate and attack rate predicted from temperature data is plotted against pollution level. The best-fit lines are all of significant slope and explain a significant proportion of residual attack rate variation. This series of analyses thus showed independent effects of temperature and of air pollution on attack rate, but could not specify which pollutants were most important.

Figure 4—Temperature-Adjusted Attack Rate versus Pollution Levels: Best-Fit Lines



tion on attack rate, but could not specify which pollutants were most important.

Figure 5 shows best-fit lines for attack rate versus each pollution variable as a function of temperature range. These graphs show that air pollution's effect on asthma is greater at moderate temperatures than at temperatures below 30°F, but that asthma attack rate is greatest at low temperatures.

Figure 6 shows best-fit lines for temperature versus attack rate for three pollution levels and two indicator pollutants, sulfur dioxide and soiling index. These reveal that temperature variation has a greater effect on attack rate at low pollution levels than at high pollution levels.

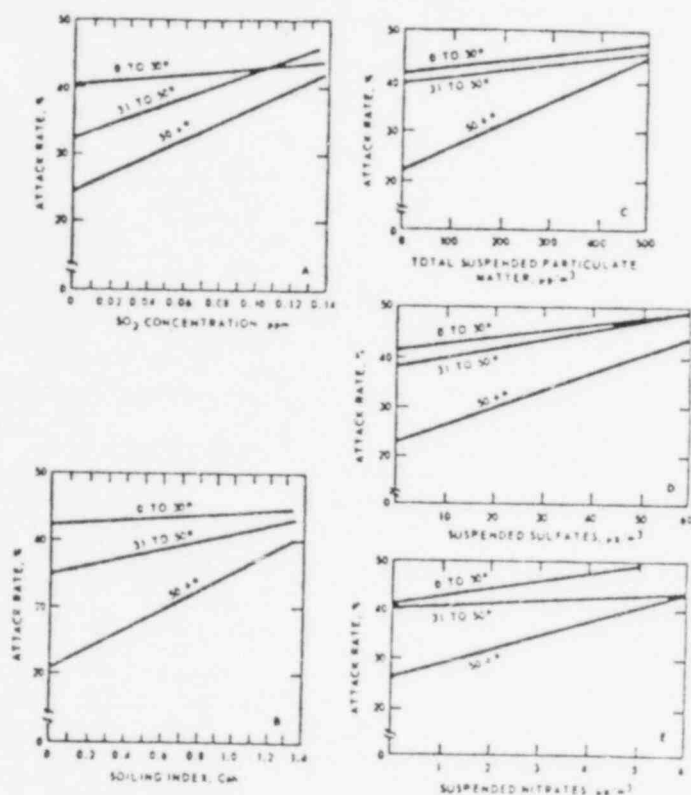
Physician Visits

The attack rate reported during the several physician visits was not significantly lower than that reported for other weeks matched for season and general pollution level.

Table 4—Residual Variation in Attack Rate Explained by Each Variable After Effects of Temperature are Removed

Factor	Degrees of freedom	Sum of squares	% of sum of squares	F-value	P
Total		2.5363	100		
Temp (alone)	1	0.5151	20.31	38.7395	.00005
Temperature with:					
AISI	1	0.0996	3.92	7.8268	.00585
SO ₂	1	0.1002	3.95	7.8772	.00570
TSP	1	0.0979	3.86	7.6875	.00630
Nitrates	1	0.0601	2.36	4.6265	.03315
Sulfates	1	0.1391	5.48	11.1641	.00106
Barometric Pressure	1	0.00003	0.00	0.0022	.9627
Windspeed	1	0.0044	0.17	0.3271	.5695
Humidity	1	0.0047	0.18	0.3544	.5526

Figure 5—Attack Rate versus Pollution Levels Within Three Temperature Ranges: Best-Fit Lines



Discussion

We had feared that New Cumberland residents, in their discontent with the local power company, would over-report illness on days when pollution levels were visibly elevated. However, since attack rates reported during the 3 weeks in which a doctor confirmed the presence of each asthma episode were not lower than those reported for preceding or following control weeks, it is unlikely that this was a significant bias.

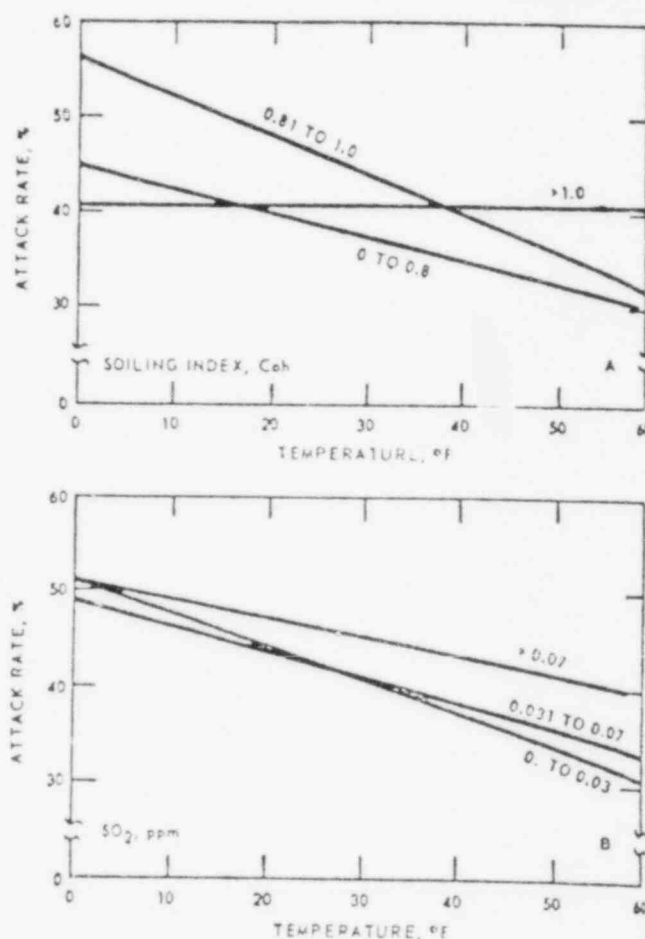
We attempted to judge severity of attack by inquiry into duration of attack, restriction of activities, dose of medicine taken, and whether or not a doctor visit was made. These proved to be of little value for this population, because little within-person, between-attack variation, occurred. Most subjects rarely saw a doctor, rarely stayed home from work or school because of an attack, took one dose of medicine, and had symptoms for less than 2 hours.

Several aspects of the data deserve further comment. First, pollution levels and attack rates were associated *within* each season. The months of peak attack rate were January and February. These months also had the highest pollution levels and lowest temperature levels, and are characteristically the time when acute respiratory infections are most frequent.

Second, the diurnal pattern for reported attack rate in this study showed the peak rate of symptom onset occurring between 6 a.m. and noon, rather than between midnight and 6 a.m., as reported elsewhere.⁶ The reason for this is unclear.

Third, suspended sulfate levels showed the strongest association with attack rate after the effects of temperature

Figure 6—Temperature versus Attack Rate for Each of Three Pollutant Concentration Ranges: Best-Fit Lines



were removed. This finding may reflect only the unusual *positive* correlation of suspended sulfates and temperature (all other pollutant variables show negative or insignificant correlations), or may reflect the irritative properties of sulfuric acid mist. Previous studies have shown that sulfuric acid mist is capable of increasing pulmonary resistance in healthy adults,²¹ and have shown associations of mortality with suspended sulfate levels.²²

A single pollutant cannot, on the basis of this data, be singled out as the prime cause of asthma episodes. It is clear, however, that although temperature is strongly associated with attack rate, air pollution concentrations are significantly associated with attack rate, too, even after the effects of temperature have been removed.

Increases in air pollution concentrations were found to have a greater effect on asthmatics when temperatures were moderate than when they were below freezing (Figure 5), although the reported attack rate on days of low temperature was usually high regardless of air pollution concentrations. Similarly, decreases in temperature had a greater effect on attack rate on low pollution days than on high pollution days. On high pollution days attack rates were unusually high, and were not significantly affected by temperature variation. These data seem to imply that there is an upper limit to the ability of environmental factors to bring on asthma episodes, at least in the temperature and pollution ranges studied. Once this limit has been reached, by virtue of low

Figure 7—New Cumberland Asthma Diary

NEW CUMBERLAND ASTHMA DIARY

Date _____ No. _____ Your Name _____

		Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
Did you have an asthma or wheezing attack today?	No							
	Yes: 1 attack							
	Yes: more than 1							
At what time did the attack begin?	Midnight to 5 AM							
	5:01 AM to Noon							
	Noon to 5 PM							
Were you in New Cumberland when the attack began?	6:01 PM to midnight							
	No							
How many doses of medicine did you take?	Yes							
	None							
	1 dose							
Was the attack bad enough to make you see a doctor?	2 doses							
	more than 2 doses							
Was the attack severe enough to keep you from school or work, or from your usual activities?	No							
	Yes							
What do you think brought on the attack?	No							
	Yes							
How long did the attack last?	Less than 1/2 hour							
	1/2 to 2 hours							
	2 to 4 hours							
	More than 4 hours							

temperature or high pollution levels, further variation in other environmental factors has no effect.

The temperature-independent pollution effects occurred at pollution levels commonly found in our major cities. In New York City, for example, for the months June through November 1969, 14 of 38 representative monitoring stations reported sulfur dioxide averages greater than .07 ppm, and 33 of 38 reported average soiling indices greater than 1.0 Coh.²³ The city-wide average sulfur dioxide level for Chicago exceeded .065 ppm in 1966 and 0.07 ppm in 1967, with correspondingly high particulate concentrations.²⁴ Furthermore, as the need for electric power increases, expansion of existing coal-fueled power plants and the construction of new plants appear inevitable. The present data should emphasize the desirability of expanding facilities in sites relatively distant from population centers.

Previous attempts to relate air pollution to asthma have been blocked by several problems. Pollution monitoring has been inadequate because of unsophisticated instrumentation or the impossibility of continuous monitoring.^{1,2,7,9,10,16} Procedures for quantifying morbidity have been inaccurate or insensitive.^{4,8,9,16} Terminology has been unclear.^{8,9} It has not been possible to separate the effects of air pollution from those of temperature, season, barometric pressure or windspeed, or to reasonably estimate dose response relationships between air pollution and health effects.^{4,15}

In the present study, weather and pollution were inten-

sively and continuously monitored, a fairly sensitive device was used to measure attack rate, checks on biases were made, and a clear, generally acceptable definition of asthma was used. With these precautions, significant effects of pollution have been found independent of, or in addition to, those of weather. In this study, too, certain desirable information could not be obtained. The effects of the several pollutants could not be separated, since they came from the same source and accumulated under the same inversion conditions. For both pollution and temperature, it was not possible to tell whether 6-hour averages or 24-hour averages were of greater predictive value for asthmatics. The effects of sharply falling barometric pressure could not be evaluated, since no such drops occurred. Finally, since there were no nearby communities without significant pollution exposure, there were no area controls. The conclusions of the present study would be strengthened by finding that a group of asthmatics in a nearby but minimally polluted area did not always show symptoms increases on the same days as the New Cumberland asthmatics.

It is clear that similar studies in other areas and with more subjects would be desirable.

Summary

Twenty asthmatics gave daily symptom reports for over 7 months, while local air pollution and weather param-

eters were intensively monitored. Significant correlations were found between reported attack rate and temperature and between attack rate and pollution levels after the effects of temperature had been removed from the analysis. These temperature-independent air pollution effects occurred at levels of pollution commonly found in large cities, and appeared greater at moderate than at low temperatures.

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The authors of this paper were, at the time of submission, in the Community Research Branch, Division of Effects Research, Air Pollution Control Office, Environmental Protection Agency, Dr. Cohen, then Medical Officer, is now a resident in medicine at Pen Bent Brigham Hospital, Boston. The other authors continue with EPA. Address reprint requests to Carl M. Shy, M.D., Deputy Director, Division of Health Effects Research, NERL, EPA, Research Triangle Park, North Carolina 27711. This paper was submitted for publication in May 1971.

Mutagenicity of Filtrates from Respirable Coal Fly Ash

Abstract. Incubation of histidine-requiring auxotrophs of the bacterium *Salmonella typhimurium* with cyclohexane-, saline-, and serum-soluble surface components of respirable fly ash particles produced an increased number of revertants in two frameshift tester strains. The results are consistent with the hypothesis that both organic and inorganic mutagens are present in coal fly ash.

Coal combustion for electric power generation is predicted to increase dramatically throughout the remainder of this century. It can be estimated that in 1974 a total of 2.4×10^6 metric tons of fly ash was released to the atmosphere from all coal-burning facilities in the United States (1). As part of our studies of the potential health impacts of electrical energy-producing coal combustion technologies, we evaluated the mutagenicity of soluble components of respirable coal fly ash. Recent studies have shown a high positive correlation between carcinogenicity of substances for animals or man and mutagenic activity in a bacterial test system (2).

Kilogram quantities of size-fractionated fly ash were collected downstream of the electrostatic precipitator from the smokestack breaching of a large modern power plant burning pulverized low sulfur, high ash coal (3). Of the four sized fractions obtained, the finest fraction, with a mass median diameter (MMD) of $2.2 \mu\text{m}$ and geometric standard deviation (σ_g) of 1.8, is the most biologically important since particles of this size have the longest atmospheric residence time, are most efficiently deposited in deep lung, and are least efficiently removed (4). Five strains of histidine-requiring (*his*⁻) auxotrophs of the bacterium *Salmonella typhimurium* (supplied by B. N. Ames) were used. The testing methods and mutations involved have been described (2). Briefly, strains TA100 and TA1538 have been used to detect base-pair substitution mutagens; TA1537, TA1538, and TA98 are strains that are susceptible to frameshift mutagens. Strains TA98 and TA100 have an ampicillin-resistant R factor not present in the other strains. Sufficient histidine was added to agar plates to allow the histidine-requiring bacteria to replicate several times in the presence of the test substance. After incubation, the histidine-synthesizing (*his*⁺ revertant) bacteria colonies were counted.

Two media were selected for mutagenicity studies with fly ash. Dulbecco's phosphate-buffered saline was used because it has the pH and tonicity of physiological fluids, and horse serum was used because serum has a chemical composition similar to lung alveolar fluid

carcinogenic heavy metals (5). Fly ash samples were incubated separately with each of these media for 2 weeks at 37°C. After incubation, the fly ash mixtures were centrifuged at 35,000g, and the supernatants were passed through a 0.45- μm membrane filter to remove particulate matter. Media controls of serum or saline were treated in the same fashion as the fly ash mixtures. Filtrates were added to filter paper disks in the standard spot test and also added to soft, top agar pour plates. No mutagenic activity was found with the spot test, but revertants were seen with the plate technique. This was evidence that the mutagen or mutagens did not diffuse into the media from the paper disks. Of the five strains tested, TA98 and TA1538 showed *his*⁺ revertants, whereas TA1535, TA1537, and TA100 did not. Because strain TA1538 showed two to three times the number of revertants as TA98, TA1538 was used in subsequent tests with varying concentrations of fly ash. Serum filtrate had approximately tenfold greater activity than the saline filtrate (Fig. 1). Solubility of substances responsible for mutagenic activity in saline, a polar solvent, suggested the presence of polar organic or inorganic mutagens. Although these tests confirmed the presence of direct mutagens, many mutagens require metabolic conversion by cellular microsomal enzymes to active mutagens (2). In further experiments, addition of optimal concentrations of rat liver homogenates from rats treated with polychlorinated biphenyl (Arochlor 1254) (2) did not significantly increase the number of revert-

ants in either the saline or serum filtrate (Table 1).

Further work was designed to evaluate the chemical nature of the active fly ash components. Fly ash was extracted directly with cyclohexane, a nonpolar, nonmutagenic organic solvent. The extract was evaporated to dryness and reconstituted with dimethyl sulfoxide, and this mixture was tested for mutagenicity. About 40 percent of the mutagenic activity of the serum filtrate was present, and metabolic activation increased the number of revertants 2.2-fold (Table 1). At least a portion of the activity thus can probably be attributed to mutagenic nonpolar organic compounds. In contrast, after extraction of the saline filtrate with cyclohexane, mutagenic activity was found only in the aqueous fraction. This confirmed the polar nature of the activity of the saline-soluble fraction and suggested the presence of at least two mutagenic compounds.

To further assess the chemical specification of the mutagenic activity in the serum filtrate, 2 mM disodium ethylenediaminetetraacetic acid (EDTA), a metal chelator, was added to serum filtrate. The number of *his*⁺ revertants was increased by about 60 percent compared to the untreated filtrate (Table 2). In order to test the hypothesis that EDTA had chelated mutagenic metals complexed with serum proteins, EDTA-treated and untreated serum filtrates were fractionated on a Sephadex PD-10 column with a cutoff at 25,000 daltons. EDTA (2 mM) was added to one portion of serum filtrate and stirred overnight at 4°C before elution on the column. A second portion was prepared in the same manner without prior treatment with EDTA. Each of these two filtrates was eluted with three void volumes of double-distilled water. The first fraction contained more than 95 percent of the total serum protein. The second had the remaining protein and a

Table 1. Number of TA1538 *His*⁺ revertants per plate with and without metabolic activation. The concentration of fly ash incubated with serum and saline before filtration was 78 mg/ml; the cyclohexane extract was evaporated under nitrogen and reconstituted with dimethyl sulfoxide to the equivalent of 78 mg/ml. All controls were treated in a manner analogous to the test materials. Spot tests were positive with 4-nitro-quinoline-N-oxide without S-9 (the supernatant fraction of rat liver homogenate, centrifuged at 9000g) and with 2-aminofluorene and S-9 added. Mean values \pm the standard error of the mean (S.E.M.) were for three replicate determinations. The number of spontaneous revertants per plate was 7 ± 1 . The number of revertants with addition of S-9 alone was 20 ± 1 .

Test media	S-9 not added		S-9 added	
	Fly ash	Control	Fly ash	Control
Serum filtrate*	154 \pm 32	10 \pm 2	202 \pm 18	12 \pm 5
Saline filtrate*	17 \pm 3	4 \pm 1	40 \pm 9	16 \pm 2
Cyclohexane extract	62 \pm 2	5 \pm 2	151 \pm 8	27 \pm 5

small amount of low-molecular-weight compounds, while the third fraction contained only low-molecular-weight components. Each of the three fractions was lyophilized and reconstituted with double-distilled water before testing. Regardless of prior treatment with EDTA, the total mutagenic activity in the fractions was lower than that in the original filtrate (Table 2). Of the total net activity after subtraction of background revertants (5.0 ± 1.0 percent), 79, 18, and 3 percent were present in the first, second, and third untreated fractions, respectively. Of the total net activity after subtraction of appropriate control values (Table 2) 83, 0, and 17 percent were found in the three EDTA-treated fractions, respectively. The significant increase ($P < .001$) in the activity of the low-molecular-weight fraction of the EDTA-treated serum filtrate lends credence to the hypothesis that EDTA acted by chelating mutagenic metals from serum proteins. The mutagenic activity was predominantly associated with the fraction of higher molecular weight, with or without EDTA treatment. This activity may be due to organic compounds postulated, as a result of the cyclohexane extraction studies, to be present on fly ash surfaces. Mutagenic organic compounds—for example, polynuclear aromatic hydrocarbons—have been shown to bind to proteins (6). Additional explanations for the relative enhancement of the mutagenicity of the serum filtrates compared to the saline filtrates include the possible presence of (i) enzymes in serum capable of converting promutagens to mutagens or (ii) protein-mutagen complexes that are more available to the bacterial cells.

We have studied the trace element composition of the fractionated fly ash. The respirable fly ash fraction, relative to the other sized fractions, has the highest concentration of many elements (7) that in some chemical forms have been reported to be mutagenic (8-13) or carcinogenic (14). In order of decreasing concentration enhancement, relative to the coarsest fraction (MMD = $20 \mu\text{m}$; $\sigma_g = 1.9$), the following elemental concentrations (micrograms per gram) for some mutagenic or carcinogenic metals analyzed by instrumental neutron activation analysis or atomic absorption spectrophotometry (15) in the finest fraction have been determined: Cd(4.6), Se(198), As(132), Sb(20.6), Mo(50), Pb(278), Co(21), Cu(137), Be(10.3), Ni(40), Mn(309), and Fe(32,000). The inverse dependence of concentration on particle size has been explained, for the most part, as being due to condensation of vol-

Table 2. Effect of EDTA treatment and serum fractionation on the number of TA1538 His⁺ revertants per plate. The concentrations of fly ash incubated with serum was 78 mg/ml (as in Table 1). The mean values \pm S.E.M. were for five determinations. The number of spontaneous revertants per plate was 5 ± 1 . Controls were serum samples with EDTA added and treated in a manner analogous to the test materials. Abbreviation: UF, unfractionated.

Serum filtrate fraction	Fly ash	Fly ash + EDTA	Control
UF	162 ± 18	261 ± 25	8 ± 2
Fraction 1	79 ± 11	94 ± 10	7 ± 1
Fraction 2	21 ± 4	11 ± 4	11 ± 2
Fraction 3	7 ± 2	22 ± 3	4 ± 1

atile metals and their oxides on the surface of fly ash particles (16). Therefore, although average concentrations of potentially toxic materials on the surface of these aluminosilicate spheres (17) may be on the order of tens or hundreds of micrograms per gram, surface concentrations may be as high as 1 to 5 percent (18). Of the metals found in fly ash, a number have been demonstrated to be mutagenic in the *Salmonella* reversion assay (8). These include compounds of chromium (10, 11), iron (12), manganese (13), and selenium (10). Sirover and Loeb have suggested that the mechanism of damage by many mutagenic and carcinogenic metals is due to decreased fidelity of DNA synthesis (19). Sodium bi-

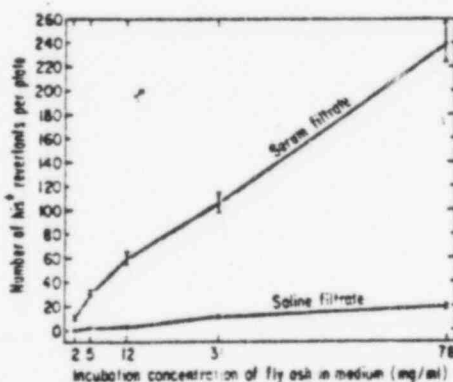


Fig. 1. Dose response curves for mutagenicity of fly ash filtrates with strain TA1538. The number of his⁺ revertants per plate is the mean of 5 to 20 replicate determinations minus the mean of the appropriate background revertants (serum or saline). The background reversion was defined as the group mean of the spontaneous revertants and the appropriate media control after it was determined that the number of his⁺ revertants in all negative controls was not significantly different from that of spontaneous revertants. The means (\pm S.E.M.) of the background revertants were $5.8 (\pm 0.4)$, $6.9 (\pm 0.9)$, $4.0 (\pm 0.6)$ for the spontaneous revertants, serum controls, and saline controls, respectively. Filtrate (100 μl) was added to 2 ml of soft top agar before plating. Plates were incubated for 2 days at 37°C. The vertical bars are 1 S.E.M.

sulfite, which may be present on the surface of fly ash (20), has also been shown to be mutagenic (21).

Although we have not analyzed for organic compounds, they (particularly polynuclear aromatic hydrocarbons) have been reported to be present on the surface of fly ash (22). Studies of suspended particulates in urban aerosols have also resulted in the identification of polynuclear aromatic hydrocarbons, as well as oxidized species, including polycyclic quinones (23). Although most polynuclear aromatic hydrocarbons require metabolic activation, some of the oxides do not (24). It has been postulated (25) that, in addition to polynuclear aromatic hydrocarbons, urban aerosols contain other extractable organic components that are mutagenic in the Ames test system. Since our fly ash samples were collected at 100°C from the power plant smokestack, concentrations of organic compounds were probably lower than would be present if the fly ash were cooled rapidly to ambient temperatures as occurs in the smokestack plume; however, the organic compounds may be altered by interaction with effluent gases or light and other environmental constituents (22).

In summary, evidence has been presented that filtrates from a respirable fraction of coal fly ash collected from a power plant over a 30-day period contain substances that cause frameshift mutations in a bacterial strain lacking normal excision repair. These substances apparently include both organic and inorganic compounds. Increased mutagenicity of the serum filtrate compared to the other filtrates may indicate that extraction with serum increases the sensitivity of the Ames technique for detecting mutagenicity of complex mixtures. It may be expected that substances on the surface of fly ash deposited in the deep lung should be similarly soluble in alveolar fluid. The prospect of a large increase in the amount of coal burned for energy production warrants specific identification of these mutagenic substances and a careful assessment of the possible carcinogenic properties of respirable fly ash.

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Pierce's Disease of Grapevines: Isolation of the Causal Bacterium

Abstract. A Gram-negative, rod-shaped bacterium has been consistently isolated from grapevines with Pierce's disease. Grapevines inoculated with the bacterium developed Pierce's disease, and the bacterium was reisolated from the plants. The bacterium was serologically and ultrastructurally indistinguishable from the one in naturally infected plants, and also indistinguishable from a bacterium isolated from almonds with almond leaf scorch disease.

The etiological agent of Pierce's disease (PD), an important and often devastating disease of grapevines (*Vitis vinifera* L.) (1), is also considered to cause alfalfa dwarf (2) and almond leaf scorch diseases (3). Prior to 1971, PD was considered to be a viral disease (4), but chemotherapy, thermotherapy, and electron microscopy subsequently implicated the "rickettsia-like" organism seen in the xylem vessels of diseased grapevines as the etiological agent (2, 5, 6). Many investigators have reported failure to isolate the PD pathogen from diseased plants using artificial media (2, 6, 7). Similar insect-vectored bacteria have recently been associated with a number of other plant diseases, and although determination of their pathogenicity and taxonomic position has been delayed by the inability of investigators to culture these bacteria, they apparently

constitute a new group of plant pathogenic bacteria (8).

Recently, a Gram-positive, catalase-negative bacterium that could be isolated from infectious leafhopper vectors but not from diseased plants was reported to be the etiological agent of PD (7). However, this bacterium did not infect healthy plants following direct inoculation, and contradictory evidence as to its causal role has been reported (9).

We now report the consistent culture of a Gram-negative, catalase-positive bacterium from grapevines with PD, and evidence that this bacterium causes PD.

A rod-shaped, Gram-negative bacterium was first isolated on our JD-1 medium (Table 1) from grapevines experimentally inoculated by the leafhopper vector, *Hordnia circellata* (Baker). Initially, the inoculum was collected by centrifugation of sap from surface-sterilized peti-

oles; in later isolations, inoculum was obtained by expressing sap from petioles with forceps. The inoculum was blotted directly from the petioles onto the media. Colonies on the JD-1 medium appeared after 2 to 3 weeks of aerobic incubation at 28°C. Progressive refinements in the culture medium shortened the necessary incubation period. On the JD-3 medium (Table 1), small but distinct colonies are visible without magnification within 6 days. Colonies are circular with entire margins, white, smooth, and convex, and reach a diameter up to 1.0 mm within 2 weeks.

We have consistently isolated the PD bacterium from diseased grapevines. In one isolation experiment, single petioles from 195 rooted cuttings of eight European grapevine varieties (Pinot Noir, Mission, Ruby Cabernet, Flora, Cabernet Sauvignon, White Riesling, Barbera, and Thompson Seedless) were used. Pierce's disease had been transmitted with leafhopper vectors to 116 plants. Of the 79 remaining plants categorized as healthy, 52 had been subjected to feeding by leafhoppers but did not develop PD, and 27 were noninoculated controls. Positive isolations on the JD-2 medium (Table 1) of the PD bacterium determined on the basis of colony characteristics were obtained from 97.4 percent (111/116) of the diseased plants. Only one plant in each group of healthy plants, or a total of 2.5 percent (2/79), yielded bacteria with colonies resembling those of the PD bacterium. Other bacteria were rarely isolated from diseased or healthy plants.

The pathogenicity of the PD bacterium was tested by inoculating green stem cuttings of the grapevine varieties Pinot Noir, Mission, and Ruby Cabernet. The upper end of each two- or three-node cutting with leaves intact was attached to a vacuum pump, and 0.1 to 0.2 ml of a turbid suspension of the PD bacterium (approximately 5×10^8 bacteria per milliliter) in sterile tap water was drawn into each cutting. Controls consisted of noninoculated cuttings and cuttings inoculated with sterile tap water alone, or with suspensions of *Erwinia amylovora* (8×10^8 bacteria per milliliter). After inoculation, the cuttings were rooted on a heated bench under intermittent mist for 14 days and transplanted. Typical PD symptoms (1) developed in 86 percent (43/50) of the cuttings inoculated with the PD bacterium within 2 to 4 months, and many of these plants died within 5 months. All 47 of the control plants remained healthy throughout the study. Colonies characteristic of the PD bacterium were reisolated from 35 of 36

Fig. 2 show that the mean absolute refractory periods of CMA neurons were significantly shorter in castrated rats after treatment with TP ($U = 5$, $P < .002$, two-tailed). Comparisons of refractory periods between the first and second experiments show no significant difference between the mean refractory period of intact (experiment 1) and testosterone-treated (experiment 2) animals ($U = 71$, $N = 12$ and 13 , not significant). This experiment shows, therefore, that testosterone reverses the effect of castration observed in the first experiment.

In a third experiment we measured refractory periods of CMA neurons stimulated antidromically not from the MPH but from the VMC. Refractory periods were determined for 57 neurons from 13 intact rats and 59 neurons from 13 castrated rats. The results show no significant difference in mean refractory period between the two groups. Means and ranges are 1.23 and 0.84 to 2.11 msec for intact rats and 1.21 and 0.97 to 1.79 msec for castrated rats ($U = 81$, not significant).

All the neurons for which results are given were located in the cortical and medial nuclei of the amygdala as defined in (13). In accordance with anatomical evidence (8), the neurons driven from the MPH and VMC were encountered in the same caudal region of the CMA. The refractory period is altered, therefore, in amygdala neurons projecting via the dorsal stria to the MPH, but not in adjacent amygdala neurons projecting via the dorsal stria to the VMC. So the effect of castration is restricted to the pathway known on other grounds to be involved in the control of sexual behavior. The effect of castration must be due to the removal of testosterone, since it is reversed by testosterone injections. Testosterone must be affecting these neurons directly, since it is the refractory period that is altered, and a change in refractory period implies a membrane change.

The change in refractory period that we have demonstrated would alter the output of the pathway to high-frequency inputs. Presumably these inputs would be olfactory. This interpretation receives support from a previous study (4), which shows that testosterone does alter pre-optic neuron responses both to electrical stimulation of the olfactory bulb and to natural sexual odors.

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Physical Factors Affecting the Mutagenicity of Fly Ash from a Coal-Fired Power Plant

Abstract. The two finest, most respirable coal fly ash fractions collected from the smokestack of a power plant were more mutagenic than two coarser fractions. Mutagenicity was evaluated in the histidine-requiring bacterial strains TA 1538, TA 98, and TA 100 of *Salmonella typhimurium*. Ash samples collected from the hoppers of an electrostatic precipitator in the plant were not mutagenic. The mutagens in coal fly ash were resistant to x-ray or ultraviolet irradiation, possibly as a result of stabilization by fly ash surfaces. All mutagenic activity is lost with heating to 350°C.

In 1977, fly ash produced and collected by coal-fired power plants was considered to be the sixth most abundant mineral in the United States (1). Of the 50 million metric tons of fly ash produced, 13 percent was reused commercially, predominantly as a partial replacement for cement or as fill material in construction; of the remainder, most was deposited in landfills. Electrostatic precipitators (ESP's) are used in most coal-fired power plants for in-plant collection of aerosolized particulate matter. The total mass collection efficiencies of the ESP's vary from 95 to 99.5 percent, with the lowest relative efficiency for collecting respirable, submicron-sized particles (2). Because vast quantities of fly ash are produced in the generation of electricity, detailed studies are required of the potential public and occupational health hazards of fly ash released from smokestacks and collected in power plants.

We have demonstrated that extracts from a stack-collected, respirable fly ash sample were mutagenic in the Ames bacterial assay (3); moreover, because of the correlation between mutagenicity and carcinogenicity (4), our study indicated that fly ash is potentially carcinogenic. We describe here physical factors af-

fecting the mutagenicity of (i) four size-classified, stack-collected fly ash samples; (ii) one size-classified, ESP-collected sample; and (iii) one unsized, ESP-collected sample.

The stack sampling was performed at 95°C; two measurements of the stack gas temperature during the 30-day sampling period varied from 107° to 115°C (5). The volume median diameters (VMD's) of these four size-classified samples, fractions 1 through 4, are 20, 6.3, 3.2, and 2.2 μm , respectively. All have geometric standard deviations (σ_g) of approximately 1.8.

We also collected fly ash from the power plant's ESP hoppers (6). Three measurements of the temperature of the ESP's during 2 days of collection varied from 104° to 107°C. Because the ESP fly ash is predominantly composed of relatively large particles, it was aerodynamically size-classified to obtain a fraction with a VMD of 2.3 μm and $\sigma_g = 1.4$. The physical and chemical properties of the stack-collected samples and of similarly collected unsized ESP ash have been reported (7).

We evaluated the relative mutagenicity of serum filtrates from the four stack-collected fractions using TA-1538 because our previous studies indicated it

were observed at temperatures above 200°C and 300°C, respectively. For the three bacterial strains studied, \pm S-9, no mutagenic activity was observed for filtrates from fly ash heated to 350°C.

Our studies of physical factors affecting the mutagenic activity of coal fly ash extracts provide insight into the chemical properties of fly ash mutagens. The finding that the greatest activity is associated with the finest fractions of stack-collected ash is consistent with the observations of Natusch (13) that PAH are adsorbed on particle surfaces during cooling of the effluent stream. The observation that ESP-collected fly ash was not mutagenic (whether size-classified or not) suggests that condensation of mutagens on fly ash particles occurred after passage through the ESP but before or within the stack sampling system. Natusch and Tomkins (14) have predicted that a temperature near 100°C is critical for the adsorption of PAH onto fly ash. Our observations of the complete loss of mutagenic activity with experimental heating to 350°C are consistent with the hypothesis that the bulk of the mutagenic activity of the fly ash samples is associated with organic compounds. This loss of activity from stack-collected fly ash appears to begin at temperatures greater than the operating temperatures of the ESP. The temperature difference probably reflects the fact that organic compounds are chemisorbed to fly ash surfaces and therefore require higher temperatures for desorption. This hypothesis is supported by our observations that the mutagens in fly ash are resistant to photochemical decomposition upon UV- or x-ray irradiation. Similarly, Natusch and his co-workers (8, 15) have observed that PAH adsorbed from the vapor phase on fly ash surfaces may be stabilized against photochemical decomposition at solar radiation wavelengths; photodecomposition occurred with irradiation of PAH as dry powders, in solution, or adsorbed onto silica, alumina, or glass.

These studies demonstrate that (i) the most respirable stack-collected fly ash samples are the most mutagenic, (ii) the ESP-collected fly ash from the same power plant is not mutagenic, (iii) the surface-associated mutagens are resistant to photodecomposition with UV- or x-ray irradiation, and (iv) the mutagenicity of fly ash is completely removed by heating to 350°C. The observation that mutagens were associated with fly ash particles when collected at temperatures below 100°C suggests a possible improvement in control technology. Fly

ash could be collected at lower temperatures than normally present in ESP's. However, if such an approach were used, the industry would be confronted in 1980 with a predicted 100 million tons (1) of weakly mutagenic solid waste. A reasonable strategy, therefore, would consist of high-temperature, high-efficiency collection of particulate matter from the flue stream, followed by subsequent condensation and in-plant collection of volatilized organic matter:

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Estimating Fatness

Part of the controversy between Frisch and Trussell (1) hinges on the manner in which Frisch has estimated fatness as a linear function of height and weight rather than measuring it physiologically. It appears that the random variability of the estimator has an impact on the arguments which has not been fully appreciated heretofore. Rather than actual measurements of fatness, Frisch uses the Mellits and Cheek equation (1):

$$TW = -10.313 + 0.252WT \text{ (kg)} + 0.154HT \text{ (cm)}$$

to predict a girl's total body water (TW) (assumed proportional to fatness) from her height (HT) and weight (WT) at menarche. Since this regression line has a multiple $r^2 = .97$, one might be tempted to suppose that the random variability is negligible, but this is not the case. Examination of the Mellits and Cheek data (2) shows that one needs to provide a band of 3.03 liters to either side of the line to cover 90 percent of the individuals in the Mellits and Cheek study. With this error band one has:

$$TW = -10.313 + 0.252WT + 0.154HT \pm 3.03$$

and thus,

$$WT = \frac{-10.313 + 0.154HT \pm 3.03}{TW/WT - 0.252}$$

Now, according to Frisch, the minimum required weight for the onset of menarche is given by the 10th percentile fatness line, where $TW/WT = 0.598$, and thus we have,

$$\begin{aligned} \text{Minimum required weight} &= \\ &= \frac{-10.313 + 0.154HT \pm 3.03}{0.598 - 0.252} \end{aligned}$$

From this it can be seen that about 9 kg of uncertainty is added to or subtracted from the predicted minimum required weight by the error bands. Clearly, this 9-kg variability in estimated minimum weight occurs for all heights and weights involved, rendering this procedure for determining fatness rather questionable and undermining any support these data might be thought to give to a critical fatness hypothesis.

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Potentially Carcinogenic Species Emitted to the Atmosphere by Fossil-Fueled Power Plants

by D. F. S. Natusch*

*a good paper
on the trace
elements of fine
fly ash*

The identities and physicochemical characteristics of potentially carcinogenic species emitted to the atmosphere by fossil-fueled power plants are presented and discussed. It is pointed out that many so-called carcinogens are preferentially concentrated on the surface of respirable fly ash particles thus enabling them to come into intimate contact with lung tissues when inhaled. Relatively little information is available about the identities of particulate polycyclic organic compounds whose emission from coal fired power plants may well be substantially greater than hitherto supposed. The importance of chemical changes, which several species may undergo following emission (but prior to inhalation) in determining their potential carcinogenic impact, is stressed.

Introduction

Production of electric power from the combustion and conversion of fossil fuels represents a ubiquitous and increasing means of obtaining energy in most countries throughout the world. It is now well established that such power plants emit substantial quantities of many carcinogenic and potentially carcinogenic chemical species to the atmosphere. Consequently, it is of considerable importance to establish whether these materials are active in promoting the occurrence of lung cancer in populations resident in the vicinity of fossil-fueled power plants.

In order to make any assessment of risk it is necessary to have knowledge of the nature, concentrations, and physicochemical characteristics of potentially carcinogenic material emitted from the various types of fossil fueled power plants. This paper, therefore, presents a brief survey of the information currently available. Special emphasis is placed on what is known about the physical and chemical characteristics and behavior of each species since these properties may have a profound influence on the inhalation toxicology of individual species (1, 2).

Fossil-fueled power plants are considered to be those utilizing gases, liquids, or solids as primary fuels derived, respectively, from natural gas, oil, or coal. Some difficulty is encountered in specifying individual pollutant species since definitive data on carcinogenicity are sparse. For the purpose of this paper, therefore, compounds are classified as known carcinogens, suspected carcinogens, and reactants. Compounds classified as reactants are those which are considered likely to be involved in chemical reactions which may result in the production or removal of carcinogenic species or which may interact synergistically with known carcinogens. In Table 1 are given examples of concentrations of known and suspected carcinogens in urban and rural atmospheres.

Gaseous Emissions

Gaseous emissions from fossil-fueled power plants generally contribute more material to the atmosphere than do particulate emissions (except in the now rare case of uncontrolled coal combustion). The major emissions, in terms of mass, involve carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NO_x), sulfur oxides (SO_x), and oxygenated species often classified as formaldehyde (HCHO). Representative contributions are indicated in Table 2 (13). In addition, minor emissions of mercury occur, and it has been suggested that bromine (Br₂),

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Table 1 (cont'd.)

Polycyclic nitrogen compounds, ng/m ³					
Acridine	Suspected	0.1-0.5	—	—	(2, 12)
Fluorene carbonitrile	Suspected	0.02-0.1	—	—	
Lead tetraalkyls, ng/m ³					
Tetraethyllead	Suspected	50-2000	75	—	(6)
Benzene-soluble organics, ng/m ³					
	Recognized	1000-20,000	7000	200-3000	(2, 4, 7)

*The substances listed include both known and suspected carcinogens for which reasonably reliable atmospheric concentration data are available. Also listed are several compounds which are considered to be capable of promoting carcinogenic activity in noncarcinogenic compounds or modifying that of carcinogens as a result of chemical reaction.

*Most values represent 24-hr averages established over periods ranging from several days to one or more years.

*Approximate average values have been estimated for urban air noting that individual areas may exhibit atmospheric concentrations which differ considerably from the average. Due to paucity of data it is considered inappropriate to estimate similar averages for rural atmospheres.

*Fluorine is present in the atmosphere as both fluorine gas and particulate fluorides. The values listed refer to the sum of both forms.

*Values listed for lead refer to concentrations measured in countries utilizing lead alkyl gasoline additives. Significantly lower values are encountered in countries which do not use leaded gasoline.

*Selenium is present in the atmosphere in both gaseous and particulate form. The values listed refer to the sum of both forms. Also, selenium has not been implicated as a causative agent of bronchial carcinoma but only of liver and kidney cancers.

*The two sets of values listed for vanadium refer, respectively, to urban areas where considerable use is made of fuel oil for power generation and domestic heating, and to urban areas where oil burning is minimal.

*A very large number of organic compounds have been implicated as causative agents for bronchial carcinoma. Only a few of these are listed here, however, since reliable atmospheric concentration data are unavailable. In general, compounds are listed by class with specific examples being given where data are available.

*These hydrocarbons are not in themselves considered to be carcinogenic. They may, however, promote formation of photochemical smog which contains several carcinogenic components.

*The data for nitrosamines are very tenuous; they are, however, included because of the considerable current interest in these compounds.

*Several noncarcinogenic polycyclic compounds are listed, since some of these are known to react photochemically to produce oxygenated derivatives (such as quinones, phthalates, and endoperoxides) which are suspected carcinogens. It will be noted that some very wide concentration ranges are listed for the polyaromatic hydrocarbons. The upper ends of these ranges correspond to values measured in European cities where extensive coal burning is practiced.

Table 2. Average air pollution emissions from power plants according to fuel type.*

Fuel	Particles*	Emissions, lb/1000 lb fuel				
		CO	HC	NO _x	SO _x	HCNH
Coal	85 (1 - E) ^b	0.25	0.1	10	19 S ^c	0.002
Oil	1.7 (1 - E)	0.07	0.5	17	19 S	0.1
Natural gas	2.7 (1 - E)	neg.	neg.	70	19 S	0.2

*Data of Goldstein and Waddams (13).

^bE is the mass collection efficiency of the control equipment.

^cAs the percent sulfur content of the fuel by weight.

hydrochloric acid (HCl), selenium dioxide (SeO₂), arsenic trioxide (As₂O₃), and organometallics such as nickel carbonyl (Ni[CO]₄) may be emitted as vapors (6, 14).

Sulfur Oxides

Sulfur oxides are not, in themselves, thought to be carcinogenic. They are, however, quite reactive and are known to react with, for example, polycyclic aromatic species (2) and to promote lung damage when associated with airborne particles. In the ab-

sence of controls the amounts of sulfur oxides emitted from a fossil-fueled power plant are directly related to the sulfur content of the fuel burned (Table 2). In this case, typical SO_x emissions lie in the range 500-3000 ppm with 1000-2000 ppm being most commonly encountered (15). Nowadays, however, most major installations utilize control equipment which typically achieves 85-90 percent removal of SO_x. Generally, about 1-2% of the emitted sulfur oxides are in the form of SO₃, which reacts rapidly with water vapor to produce sulfuric acid mist. A small amount of the SO₂ is also chemisorbed by fly ash particles to form metallic sulfates (primarily calcium sulfate and alkali iron trisulfates) (16).

The rate and extent of sulfur dioxide conversion to sulfuric acid mist and solid particulate sulfate in a power plant plume are unknown; however, current thinking is that these processes occur fairly extensively, so that a significant proportion of the gaseous sulfur oxides produced actually occur in urban atmospheres as sulfuric acid mists or as particulate sulfate (4). This is an important consideration, since it means that the health hazard presented by gaseous sulfur oxides may be partly manifest through inhalation of sulfuric acid and sulfate particles.

many countries the proportion is even higher. As indicated by the data in Table 2, particulate emissions from coal-fired power plants are much greater than those derived from oil or natural gas combustion. Some idea of particle mass emission factors can be obtained by noting that modern electrostatic precipitation equipment usually operates with mass removal efficiencies in excess of 98%.

Assessment of the carcinogenic hazard associated with airborne particulate material such as fly ash is very much more difficult than is the case for a gaseous pollutant. This is because particles contain a large number of potentially carcinogenic chemical species including both organic and inorganic compounds. The relative amounts of these species, and thus their net carcinogenicity, can vary significantly with the type and origin of the fuel burned and even with the operating characteristics of individual power plants. Furthermore, the way in which a given chemical species is distributed among different particles and even within a single particle can strongly influence its potential health impact. Finally, it must be recognized that, although many potentially carcinogenic compounds may be associated with solid fly ash particles these compounds are unlikely to constitute a hazard to health unless they can be mobilized into solution, e.g., body fluids.

The extent to which information is available about each of the above factors is discussed in the following sections. For convenience, different classes of chemical compounds are considered separately even though all may be present together. In this regard it is useful to note that a single particle effectively concentrates many chemical species in a localized microregion so that its influence is likely to be exerted over a very localized area of lung tissue when inhaled. This is in contrast to the more generalized influence of inhaled gases.

Particle Morphology, Size Distribution, and Matrix Composition

Particles emitted to the atmosphere from fossil fueled power plants are more or less spherical. In the case of coal combustion both solid and hollow spheres occur and some of the latter have small respirable spheres encapsulated inside them (15, 19). Particles derived from oil and natural gas combustion have a highly porous structure rather like that of a sponge (20).

The aerodynamic size of a particle is a major factor in determining the efficiency with which it can be collected by control equipment, its atmospheric transport characteristics and lifetime, and its deposition and clearance behavior when inhaled (1). In

addition, the size of a particle determines the specific surface area which can come into intimate contact with body fluids and tissues. The size distributions of particles produced by different power plants exhibit considerable variation; however, a typical size distribution of fly ash emitted from a coal fired power plant equipped with an electrostatic precipitator is presented in Figure 1 (21). It is apparent from this figure that much of the emitted fly ash falls in the respirable size range.

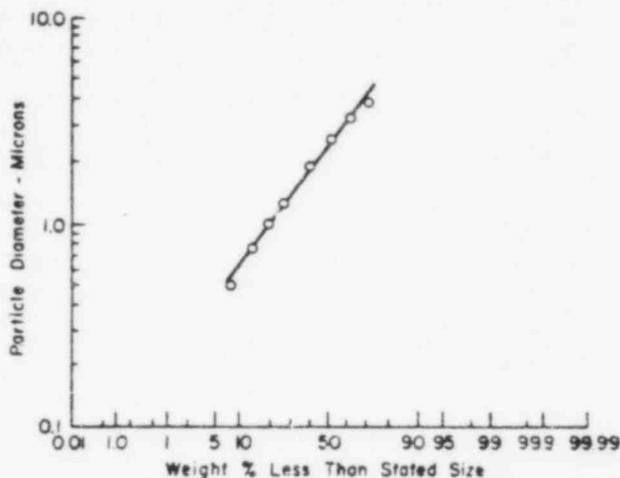


FIGURE 1. Representative aerodynamic particle size distribution of fly ash emitted from a coal fired power plant equipped with an electrostatic precipitator (21).

Relatively few measurements have been made of particle size distributions in power plant plumes. As a rough indication, however, particulate material collected at a distance of 5 miles downwind from a coal-fired power plant plume under stable plume conditions has an aerodynamic mass median diameter in the range 0.08–0.25 μm . Such samples usually exhibit a bimodal distribution, with the two modes being centered around 0.04 μm and 0.3 μm . The smaller modal particles are thought to represent a secondary aerosol consisting primarily of sulfate particles. Comparable information is not, to our knowledge, available for oil or natural gas-fired power plants, although similar general behavior would be expected.

The major matrix elements present in coal fly ash are Al, Si, and Fe, with minor amounts of Ca, Mg, K, Na, Ti, and S. Some typical composition ranges, expressed as weight percent as the oxides, are presented in Table 4 (22). The matrix elements in oil fly ash are C, Ca, Fe, S, Si, Ti, and V (23), whose relative proportions vary considerably in individual particles. Coal fly ash consists primarily of a semi-transparent aluminosilicate glass with small amounts

Table 5. Specific concentrations and volume concentrations of elements in coal and oil fly ashes.

Element	Coal fly ash		Oil fly ash	
	Specific concn, $\mu\text{g/g}$	Volume concn, $\mu\text{g/m}^3$	Specific concn, $\mu\text{g/g}$	Volume concn, $\mu\text{g/m}^3$
Al	70,000-140,000	5000-10,000	100-5000	130-300
As	2-500	60-90	30	4-7
Au	0.004-0.1	—	—	—
B	10-600	—	—	—
Ba	500-7000	30-110	—	—
Be	1-10	—	500-10,000	1600
Br	0.3-20	1-5	—	—
Ca	6000-180,000	300-1000	—	—
Cd	0.1-50	—	10-1000	500-700
Ce	100-300	—	—	—
Cl	10-500	—	—	1-2
Co	5-100	1-5	—	—
Cr	50-300	8-20	90	16
Cs	1-20	—	66	12
Cu	50-650	—	—	0.1
Fe	25,000-300,000	4000-10,000	50-2000	—
Ga	10-250	2-10	10,000-100,000	700-1000
Hf	5-10	—	—	—
Hg	0.02-0.4	—	—	—
I	0.5-7	—	—	—
In	0.1-0.3	15-40	—	—
K	1500-35,000	—	—	—
La	35-100	2-10	1000	—
Lu	0.5-2	—	—	2.5
Mg	11,000-60,000	300-1000	—	—
Mn	50-500	—	500-5000	—
Mo	5-40	70-200	1-100	8
Na	1200-18,000	—	2000-50,000	4000-7000
Ni	5-100	10-25	—	—
Pb	5-1000	10-20	200-2000	—
Rb	40-300	—	—	—
Sb	1-15	0.5-3.0	5	1
Sc	10-40	2-4	—	—
Se	1-20	5-15	5	0.03
Sm	10-20	—	—	0.6
Sn	30-30	—	—	0.15
Sr	50-4000	—	—	—
Ta	0.5-1.5	—	—	—
Th	15-70	0.5-3.0	—	—
Ti	3500-8500	300-700	—	0.13
Tl	2-30	—	—	—
U	5-20	—	—	—
V	100-500	10-60	100-200,000	1000-1200
W	3-10	—	—	—
Yb	3-7	—	—	—
Zn	50-5000	20-70	200-3500	680

concentrations are employed. This is because volume concentrations depend upon the way in which the bulk particulate mass is distributed with respect to aerodynamic particle size. Some typical elemental size distributions determined in the stack gas of a coal fired power plant are presented in terms of volume concentration ($\mu\text{g/m}^3$) in Figure 2 (23).

As mentioned previously, coal combustion results in the emission of several carcinogenic radionuclides in particulate form. Specific concentrations of ^{210}Pb , ^{226}Ra , ^{228}Ra , ^{228}Th , ^{232}Th , and ^{238}U

have been measured in coal fly ash (25-28); however, only ^{210}Pb and ^{238}U are enriched with respect to the levels found in soil. Measurements of ^{226}Ra , ^{228}Th , and ^{232}Th in the plume 6 km downwind from a coal fired power plant show that these elements are enriched over normal background levels by factors of 9, 4, and 28, respectively (29). These authors have assessed the lung doses from a 1000 MW coal fired power plant to be approximately 10 man-rad per year.

ready availability. (2) Conventional bulk analyses of particulates provide a poor measure of the actual concentrations of toxic trace elements to which the external environment is exposed. This fact must be considered in designing toxicity studies using synthetic particulates. (3) Since the surface layer contains an increasing fraction of the total particle mass with decreasing size, small, lung depositing particles will have a greater proportion of their associated toxic species in immediate contact with lung tissues than will large particles, i.e., as indicated earlier, lung-depositing particles definitely constitute the most potentially carcinogenic fraction of all fly ash particles.

Solubility

Probably one of the most important properties of particulate matter emitted by fossil fueled power plants is its solubility. Indeed, unless the associated toxic chemical species can be extracted by lung fluids their ability to act as chemical carcinogens is probably negligible. Surprisingly, this point is frequently overlooked.

It is now well established that only about 2-3% of the mass of both coal and oil fly ash is soluble in water. Very little more is soluble in most dilute acids or bases. However, while the fly ash matrix is effectively insoluble, the so-called surface layer, in which many potentially carcinogenic elements are highly concentrated, is quite soluble. This is illustrated for the case of Pb in Figure 3, which shows

the dependence of concentration on radial depth into coal fly ash particles before and after leaching with water (16).

The factors controlling the rate and extent of solubility of individual elements associated with fly ash are complex (32); however, it is apparent that a substantial fraction (probably ~50%) of most potentially carcinogenic elements is extractable from respirable particles.

It is appropriate here to draw attention to the distinction between the concentration and amount of a species extracted from a particle. Thus, the total amount of a given species may be quite small and unlikely to constitute a hazard. On the other hand, the localized concentration of that species may be very high (due to its surface predominance) and quite capable of causing damage in a micro-region surrounding each particle. The question is whether or not such local effects are important. If not, then the surface predominance of carcinogenic trace elements may be of little consequence.

Particulate Organic Compounds

Particulate associated organic material emitted from fossil fueled power plants is known to contain both aliphatic and aromatic compounds. To date essentially all studies have been directed towards the latter class of compounds with special emphasis being given to polycyclic aromatic species which include many well established carcinogens (2). Even within this group, primary emphasis has been

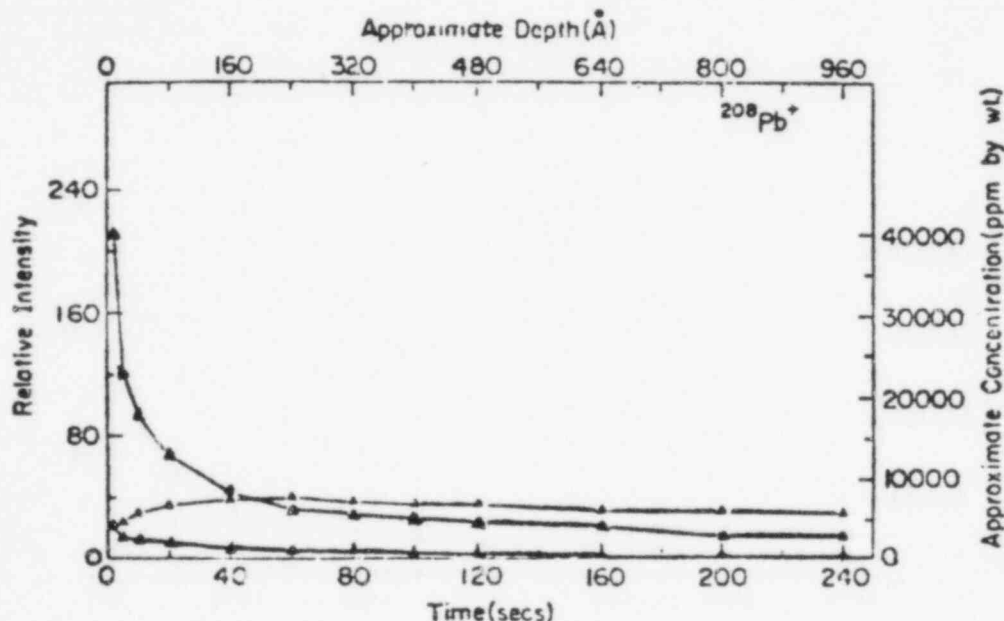


FIGURE 3. Depth profiles of Pb associated with coal fly ash recorded (a) before, and (b) after leaching the fly ash with water and dimethyl sulfoxide (16).

Chemical Conversion of POM

A number of studies have shown that particulate polycyclic organic species can be modified in the atmosphere as a result of photochemical decomposition or reaction with sulfur or nitrogen oxides (2). This is of considerable importance, since such reactions may significantly alter the carcinogenic potential of POM. Indeed, the chemical compounds actually inhaled may be quite different from those originally emitted to the atmosphere.

Recent studies (34) of the photochemical decomposition of several polycyclic aromatic compounds adsorbed onto the surface of coal fly ash indicate that some compounds, e.g., phenanthrene and pyrene, do not decompose appreciably under the influence of solar radiation. A second group, e.g., anthracene and benzo[a]pyrene, decompose with half lives of several hours, giving the corresponding quinone as the major product. Interesting behavior is observed in the case of fluorene, which decomposes to fluorenone in the absence of light.

Data such as these illustrate the point that estimates of the carcinogenic potential of POM emitted from fossil fueled power plants must necessarily be based on analyses of particulate material collected from the plant plume at some distance from its origin. Until the results of such analyses are available, very little can be inferred about the nature and amounts of potentially carcinogenic organic species likely to be present.

Conclusions

It is apparent from the foregoing remarks that the identities and amounts of most air pollutants emitted by fossil fueled power plants are reasonably well established. The major gap in knowledge of this type concerns the emission of particulate polycyclic organic matter (POM) which probably includes the most potentially carcinogenic species.

It is also apparent that simple knowledge of the identity of a toxic substance is scarcely adequate to enable assessment of its significance as a health hazard. This is of primary importance in the case of particulate matter for which such factors as aerodynamic size distribution and surface predominance may play a major role in determining toxicity. In this regard, the information which would be of most value is a quantitative measure of the availability of carcinogenic species associated with particles.

While there is considerable information about potentially carcinogenic species which are actually emitted from fossil fueled power plants only

rudimentary knowledge is available about the changes that these species undergo prior to inhalation. Consequently, contemporary estimates of human hazards must, of necessity, be based on what is known about emitted species plus what can be inferred or guessed about the ways in which their carcinogenicity may be modified prior to inhalation.

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SIZE DEPENDENCE OF THE PHYSICAL AND CHEMICAL PROPERTIES OF FLY ASH

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and
D.F.S. Natusch

* good information
on fine particles
can stay in air
inhalated by man
& stay in lung
longer

Radiobiology

Laboratory

p 34 - toxic metals - higher concentration in smaller
fine particles

SIZE DEPENDENCE OF THE PHYSICAL AND CHEMICAL PROPERTIES OF COAL FLY ASH

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I. INTRODUCTION

In order to assess the environmental significance and potential health hazards associated with exposure to environmental pollutants, detailed studies of physical and chemical properties are required. It is these properties that determine the route and biological consequences of exposure. The aerodynamic behavior of aerosols released during coal combustion will determine the potential for atmospheric transport and subsequent human exposure. Large particles ($>10\text{ }\mu\text{m}$) escaping the power plant's control technology will fall out near the plant, which may ultimately result in general population exposure by ingestion of agricultural products or water. Thus, exposure of agricultural products by soil or foliar deposition or contamination of water sources in the environs of the power plant will reflect, for the most part, the chemical composition of the larger particles. Long-range transport and general population exposure will be associated with the more stable aerosols. These fine particles ($<10\text{ }\mu\text{m}$) are of special interest because they are less efficiently collected by existing control technologies, have a relatively long atmospheric residence time, and upon inhalation, are efficiently deposited and slowly removed from the pulmonary region of the respiratory tract.

In a review of particulate abatement technologies, Vandegrift et al. (1973) described collection efficiency as a function of particle size for a variety of control technologies including electrostatic precipitators, fabric filters, wet scrubbers, and cyclones. Average collection efficiencies for a medium-efficiency electrostatic precipitator (ESP) were 90, 70, and 35% for 1.0, 0.1, and 0.01 μm particles, respectively. Interestingly, the Venturi wet scrubber (VWS) was more efficient (99.5%) for 1.0 μm particles and less efficient ($<1\%$) for 0.01 μm particles. A crossover in the ESP- and VWS-efficiency curves was observed at 0.35 μm .

Respiratory tract deposition of inhaled particles is determined by the physics and chemistry of aerosols, the anatomy of the respiratory tract, and the airflow patterns in the lung airways (Yeh et al., 1976). The most important physical factors affecting lung deposition of inhaled particles are the aerodynamic properties of the aerosol and the chemical reactivity in the airways. Lung deposition is generally described in terms of fractional particulate deposition by mass or number in the three major regions of the respiratory tract: the nasopharyngeal, tracheobronchial, and pulmonary regions (Task Group on Lung Dynamics, 1966). The nasopharyngeal region is composed of the nose and throat, extending to the larynx; the tracheobronchial region consists of the trachea and bronchial tree, including the terminal bronchioles; and the pulmonary region consists of the respiratory bronchioles and the alveolar structures. Particles greater than 10 μm are effectively collected in the nasopharyngeal region; tracheobronchial and pulmonary deposition generally increase with decreasing particle size. Fractional deposition in the pulmonary region ranges from 30 to 60% of the inhaled aerosol for particles ranging in size from 1.0 to 0.01 μm (Task Group on Lung Dynamics, 1966). Similarly, tracheobronchial deposition ranges from 5 to 30% for inhaled aerosols from 1.0 to 0.01 μm , respectively. Respiratory tract deposition profiles have been calculated for iron, lead, and benzo(a)pyrene in urban aerosols (Natusch and Wallace, 1974). The hygroscopicity or

reactivity of an aerosol in the airways may dramatically alter the particle size and the regional deposition. Parks et al. (1977) have shown that, upon inhalation, ammonium sulfate aerosols with initial aerodynamic diameters of $0.8 \mu\text{m}$ and 8% relative humidity may rapidly grow to $2.3 \mu\text{m}$ in the water vapor saturated atmosphere of the respiratory tract. The rapid growth of the aerosols resulted in deposition predominantly in the nasopharyngeal region and lower than expected deposition in the tracheobronchial and pulmonary regions.

The rate of clearance of deposited particulate matter from the respiratory tract will be determined, in part, by the chemical behavior in the lung's unique microenvironment in the vicinity of the particle. Hygroscopic particles deposited in the respiratory tract will be rapidly cleared by dissolution and subsequent passage into the bloodstream for ultimate exposure of internal organs. Less soluble particles deposited on the mucocilliary escalator of the tracheobronchial region and on the ciliated epithelium of the nasopharyngeal region will be rapidly cleared with half-times on the order of one day and a few minutes, respectively (Task Group on Lung Dynamics, 1966). Relatively insoluble particles deposited in the pulmonary region will be phagocytized by the pulmonary alveolar macrophages (PAM). These particles will be slowly removed by either dissolution within PAM or transport within PAM to the mucocilliary escalator. The biological half-time of material in the pulmonary region is very much a function of particulate chemical composition; half-times of hundreds of days have been reported for insoluble particles.

It should be emphasized, however, that dissolution of surface-associated chemical components need not be a requisite for their interaction with the biological system. For example, inhaled particles may be phagocytized by macrophages where direct particle surface-cell interaction will take place. A reasonable comparison of "insoluble" particle interaction may be made with asbestos.

In this chapter, the size dependence of physical and chemical properties of coal fly ash is reviewed. Because the size dependence of many of the chemical properties results from surface-associated chemical phenomena, a detailed description of surface analysis is provided. An understanding of the bioenvironmental significance of ambient fly ash requires a detailed understanding of its chemical reactivity and biological interactions with fly ash surfaces. This chapter reproduces the material found in a DOE report published through NTIS (Fisher and Natusch, 1979).

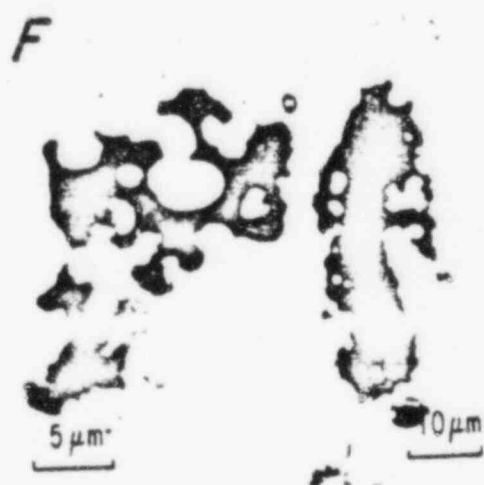
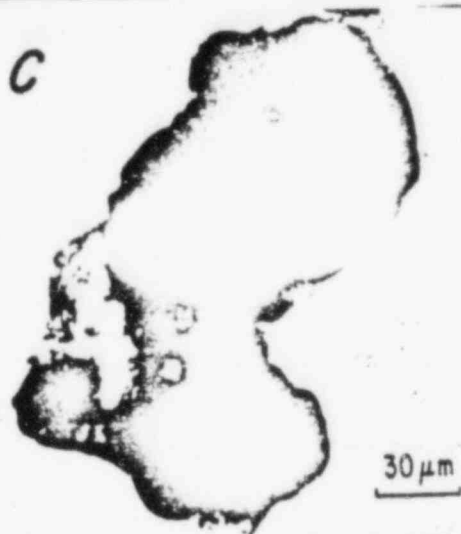
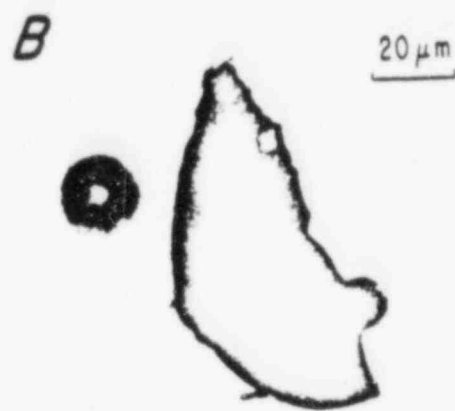
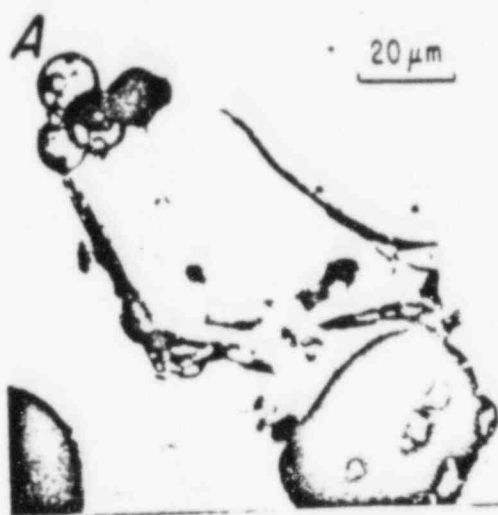
II. MORPHOLOGY AND FORMATION OF COAL FLY ASH

A. Morphological Analysis

Morphological studies by light and electron microscopy have described the heterogeneity and structural complexity of coal fly ash. Based on morphological appearance, much can be inferred concerning origin, formation, and chemical composition. McCrone and Delly (1973) indicate that particulate matter derived from combustion products is readily identified under the light microscope. The fused glassy spheres in coal fly ash are the result of exposure to boiler temperatures $>1200^{\circ}\text{C}$. Aside from the water-white glassy spheres, McCrone and Delly (1973) also describe the presence of opaque "magnetite" spheres and spheres containing trapped gas bubbles.

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Light microscopy has been used to define 11 major morphological classes of coal fly ash particles (Fig. 1) in stack-collected, size-fractionated material (Fisher et al., 1978). The characteristics employed in morphological characterization were particle shape and degree of opacity. The 11 classes include (a) amorphous, nonopaque particles, (b) amorphous, opaque particles, (c) amorphous, mixed opaque and nonopaque particles, (d) rounded, vesicular, nonopaque particles, (e) rounded, vesicular, mixed opaque and nonopaque particles, (f) angular, lacy, opaque particles, (g) cenospheres (hollow spheres), (h) plerospheres (sphere filled with other spheres), (i) nonopaque, solid spheres, (j) opaque spheres, and (k) spheres with either surface or internal crystals. A morphogenesis scheme (Fig. 2) has been developed relating the 11 morphological classes to extent and duration of exposure to combustion zone temperatures and probable matrix composition. Opaque amorphous particles and angular, lacy, opaque particles were tentatively classified as unoxidized carbonaceous material or iron oxides (Fisher et al., 1978). Subsequent SEM-x-ray analysis (Fisher et al., 1979a) indicated that these opaque particles were composed of low atomic number matrices. Furthermore, calculation of the effective atomic number of class b particles based upon Bremstrahlung production indicated that this class is predominantly composed of elemental carbon (Fisher et al., 1979b). The opaque spheres (class j) appear to be predominantly magnetite and may be identified by (1) magnetic separation or passing a magnet near a liquid mount of the sample under a microscope and (2) by observation of small clusters of these particles. The amorphous and rounded-vesicular, nonopaque particles (classes a and d) appear to be aluminosilicate particles. Rounding and vesicularity reflect increased exposure to boiler conditions. Further heating of these particles will give rise to nonopaque spheres that are either solid, hollow, or packed with other particles. Similarly, the mixed opaque, nonopaque, amorphous, or rounded classes will give rise to spherical particles upon increased exposure to combustion conditions in the boiler. The nonopaque, solid spheres ranged in color from water white to yellow to orange and deep red. Analysis of single particles in this class by SEM-x-ray techniques indicated that the variation in color was associated with iron content (Fisher et al., 1979b). Cenosphere and plerosphere formation will be discussed in detail in the following sections. Crystals within glassy spheres (as determined by light microscopy) are probably formed by heterogeneous nucleation at the surface of the molten silicate droplet (Fisher et al., 1979a). In this regard, Gibbon (1978) has demonstrated the presence of mullite crystals within and on the surface of fly ash particles (Fig. 3). Crystal formation within glassy spheres was demonstrated by transmission electron microscopy (TEM) of hydrofluoric acid-etched replicas. In this process the original glassy material is dissolved, but the insoluble mullite remains. Mullite structure was confirmed by electron-diffraction analysis.



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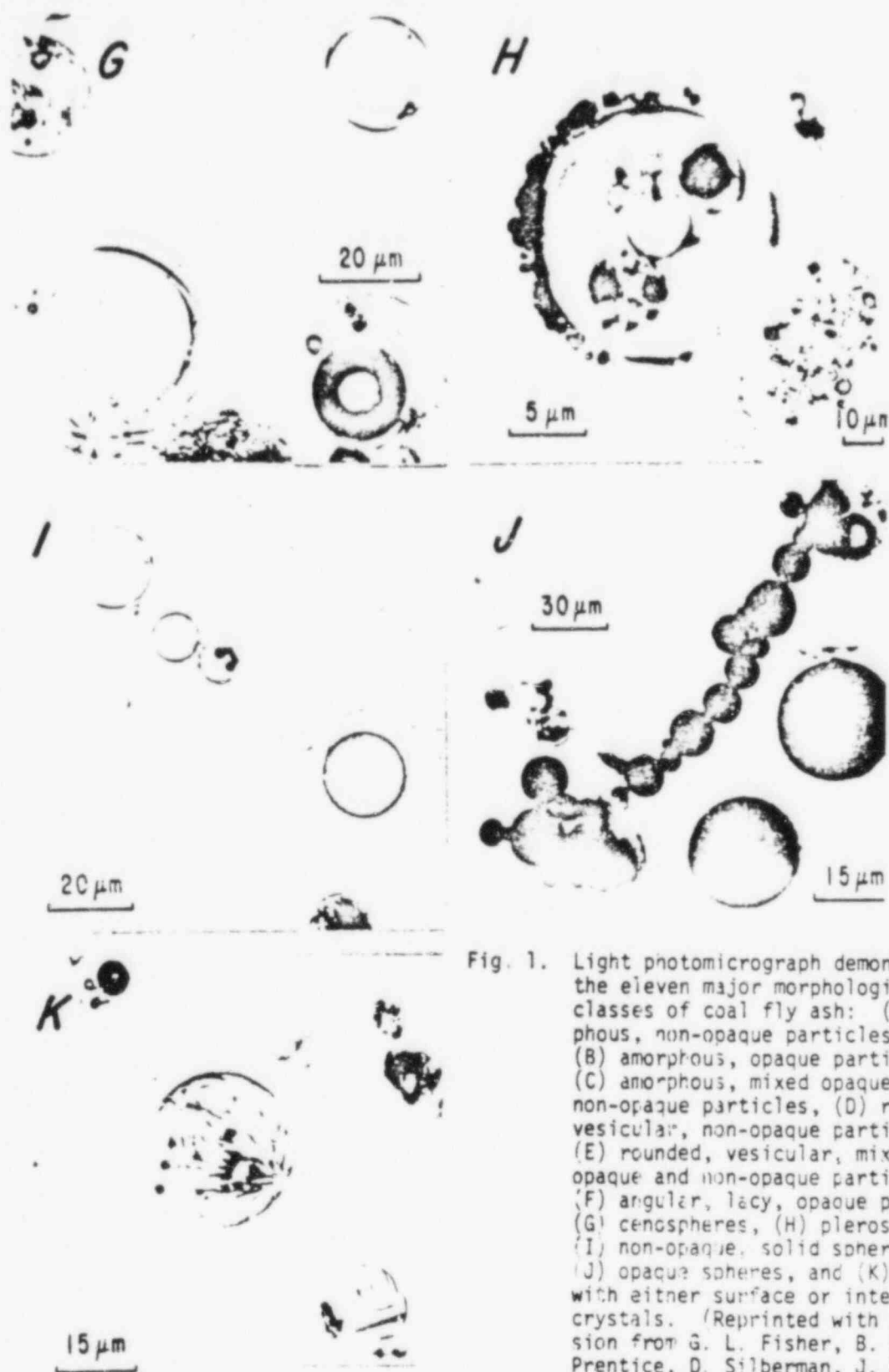


Fig. 1. Light photomicrograph demonstrating the eleven major morphological classes of coal fly ash: (A) amorphous, non-opaque particles, (B) amorphous, opaque particles, (C) amorphous, mixed opaque and non-opaque particles, (D) rounded, vesicular, non-opaque particles, (E) rounded, vesicular, mixed opaque and non-opaque particles, (F) angular, lacy, opaque particles, (G) cendrospheres, (H) plerospheres, (I) non-opaque, solid spheres, (J) opaque spheres, and (K) spheres with either surface or internal crystals. (Reprinted with permission from G. L. Fisher, B. A. Prentice, D. Silberman, J. M. Ondov, A. H. Biermann, R. C. Ragaini, and A. R. McFarland, *Environmental Science and Technology* 12, 449 (1978). Copyright 1978 by the American Chemical Society)

Fig. 2. Fly ash morphogenesis scheme illustrating probable relationship of opacity to particle composition, and relationship of particle shape to exposure in combustion chamber (Reprinted with permission from G. L. Fisher, B. A. Prentice, D. Silberman, J. M. Ondov, A. G. Biermann, R. C. Ragaini, and A. R. McFarland, *Environmental Science and Technology* 12, 450 (1978). Copyright 1978 by the American Chemical Society.)

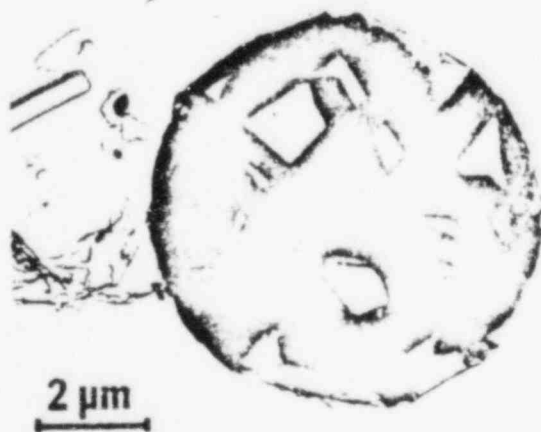
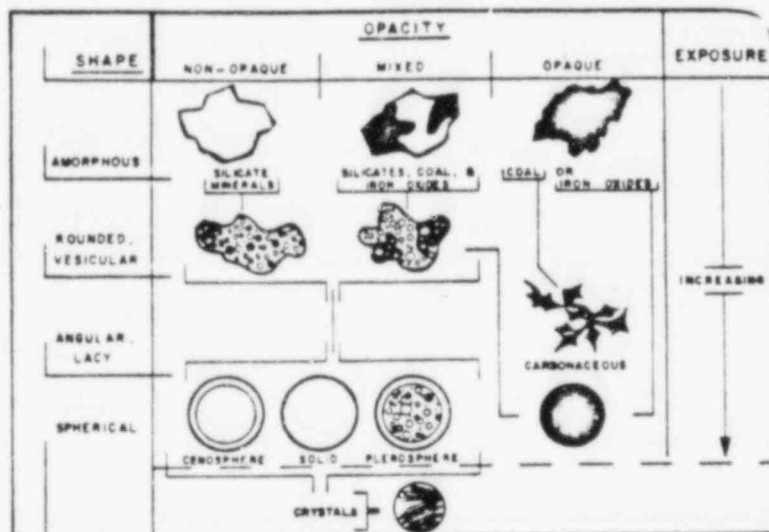


Fig. 3. Transmission electron micrograph of a replica of a fly ash sphere showing abundant mullite needles. The association of crystals-within-sphere is retained by the replica; the original glassy material is dissolved during the replication process, but mullite is insoluble in HF. (Photos courtesy of G. A. Waits, D. S. McKay, and D. L. Gibbon, Lyndon B. Johnson Space Center, Houston, Texas.)

EXPOSURE

Fisher et al. (1978) have quantified the relative abundances of the 11 light-microscopically defined morphological classes in four size-classified, stack-collected fly ash fractions (McFarland et al., 1977). The four fractions had volume median diameters (VMD's) of 2.2, 3.2, 6.3, and 20 μm with associated geometric standard deviations (σ_g) of approximately 1.8 for all fractions. The data in Table I demonstrate that the relative abundances of all particle classes are size dependent. In particular, only the nonopaque solid spheres increased in abundance with decreasing particle size; all other morphological classes appeared to increase in frequency with increasing particle size. Amorphous and vesicular particles (classes a, b, c, d, e, and g) predominated in the coarsest fraction (66% by number), while solid, nonopaque spheres predominated in the finest fraction (87% by number).

Table I. Relative Abundance (%) of Morphologic Particle Classes in Four Fly Ash Fractions^a

Particle class	Fraction			
	VMD ^b = 20 μm	VMD = 6.3 μm	VMD = 3.2 μm	VMD = 2.2 μm
(A) Amorphous, nonopaque	7.25	2.13	0.79	0.33
(B) Amorphous, opaque	0.42	0.18	--	--
(C) Amorphous, mixed opaque and nonopaque	0.77	0.09	--	--
(D) Rounded, vesicular, nonopaque	12.39	6.67	2.91	2.99
(E) Rounded, vesicular, mixed opaque and nonopaque	2.27	0.24	--	0.03
(F) Angular, lacy, opaque	1.34	0.57	0.27	0.33
(G) Nonopaque, cenosphere	41.11	25.22	13.20	7.91
(H) Nonopaque, plerosphere	0.51	0.21	--	--
(I) Nonopaque, solid sphere	25.58	56.01	79.16	86.99
(J) Opaque sphere	1.56	0.90	0.33	0.24
(K) Nonopaque sphere with crystals	6.80	6.79	3.18	0.95

^a From Fisher et al. (1978c).

^b Volume median diameter.

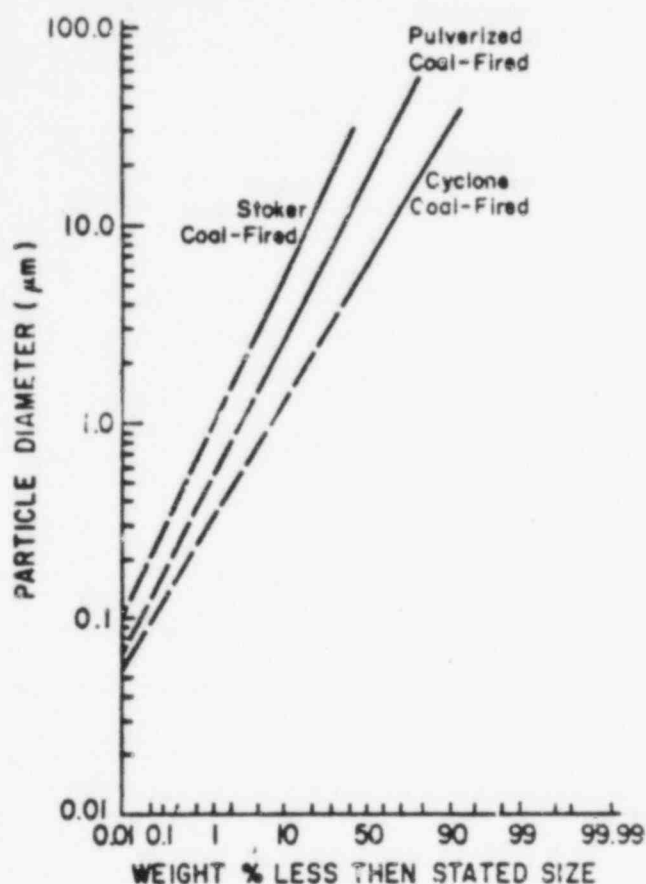


Fig. 8. Size distributions for boiler particulate emissions from coal combustion in a chain grate stoker, a pulverized coal fed unit and a cyclone fired unit. (Reproduced by permission of Southern Research Institute, 1975, and Electric Power Research Institute.)

From a practical standpoint, one is primarily interested in the aerodynamic size distribution of the fly ash that is actually emitted from a coal-fired power plant. This is, of course, largely determined by the collection efficiency of the particle control equipment. Specifically, the size distribution of the emitted fly ash is determined by the product of the functions describing the size dependence of fly ash mass entering a control device and describing the dependence of collection efficiency of this device on particle size. Examples of the aerodynamic size distribution of fly ash mass emitted from a coal-fired power plant equipped with different control devices are presented in Fig. 9.

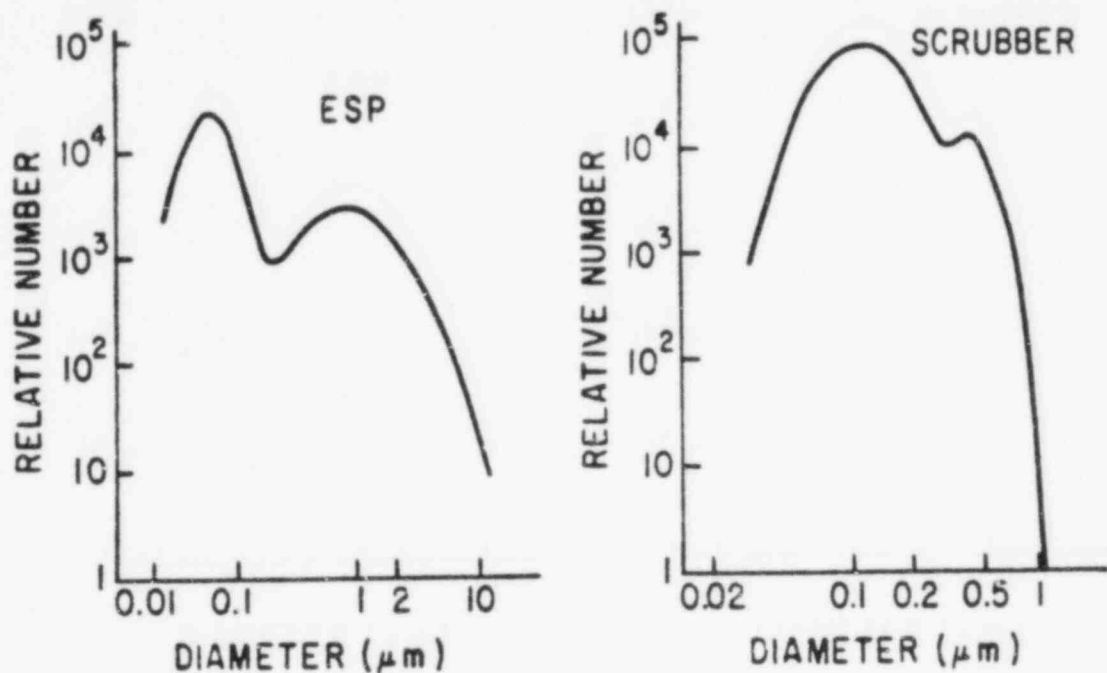


Fig. 9. Size distributions for particulate emissions from similar production units with either electrostatic precipitator (ESP) or a Venturi wet scrubber at the same power plant (Modified with permission from Ondov, et al. 1976).

B. Density and Magnetic Distributions

Determination of the density of coal fly ash as a function of particle size is largely of interest in obtaining an understanding of aerodynamic behavior and of the factors responsible for the intrinsic heterogeneity of coal fly ash. Thus, determination of the densities of different fly ashes, and subfractions thereof, provides a means of interconverting aerodynamic and physical sizes according to Eq. (8). In addition, some differentiation between distinct morphological and compositional characteristics can be achieved. For example, cenospheres can readily be distinguished from solid particles on the basis of density as can predominantly carbonaceous particles from aluminosilicates.

Determination of fly ash particle density is most simply achieved by means of the traditional "float-sink" method that employs a series of liquids of different densities to separate particles of greater and lesser density than the liquid (Ruch et al., 1974; Olsen and Skogerboe, 1975). Alternatively, separation can be achieved by placing the particles in a liquid in which a density gradient has been established.

While determination of particle density is of considerable interest in its own right, more definitive insights are obtained if density separations are carried out in conjunction with sequential size separations and with differentiation between ferromagnetic and nonferromagnetic particles. Such a three-dimensional fractionation scheme has been presented by Natusch et al. (1975), and resulting mass distributions are presented in Tables II and III for fly ashes derived from typical midwestern United States

Table II. Mass distribution of size-classified, magnetic and nonmagnetic fractions of a midwestern bituminous coal fly ash (%)^a

Size (μm)	Nonmagnetic						Magnetic					
	<1.6	1.6-2.0	2.0-2.3	2.3-2.7	2.7-3.0	>3.0	<2.1	2.1-2.5	2.5-2.9	2.9-3.4	3.4-3.6	>3.6
<20	b	b	0.2	28.0	b	b	b	0.6	0.4	1.3	14.9	0.5
20-60	1.4	1.3	12.1	12.9	0.1	b	0.2	0.6	1.8	11.5	3.1	0.1
60-90	0.7	1.0	0.6	1.1	0.6	0.1	0.5	0.8	1.0	0.2	b	b
>90	0.1	0.1	0.1	0.6	0.5	0.2	0.1	0.2	0.3	0.2	0.1	b

^a From Natusch (1978c), unpublished results.

^b Less than 0.05%.

Table III. Mass distribution of size-classified, magnetic and nonmagnetic fractions of a western sub-bituminous coal fly ash (%)^a

Size (μm)	Nonmagnetic						Magnetic					
	<1.6	1.6-2.0	2.0-2.3	2.3-2.7	2.7-3.0	>3.0	<1.6	1.6-2.0	2.0-2.3	2.3-2.7	2.7-3.0	>3.0
<20	b	b	b	0.7	b	b	b	b	b	b	b	b
20-44	0.2	0.4	0.5	21.3	0.3	0.2	b	b	b	1.0	b	b
44-74	0.5	0.8	1.0	45.6	0.6	0.5	0.1	0.1	0.2	6.8	0.1	0.1
>74	0.2	0.3	0.4	16.1	0.2	0.2	b	b	b	1.5	b	b

^a From Natusch (1978c), unpublished results.

^b Less than 0.05%.

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bituminous and western sub-bituminous coals. These data were obtained by separating bulk fly ash into several physical size fractions by sieving. Each size fraction was then subdivided into a number of density fractions that were, in turn, separated into magnetic and nonmagnetic fractions according to whether the particles adhered to a magnet or not. The designation of magnetic and nonmagnetic is entirely operational in nature.

A number of characteristics of coal fly ash can be distinguished from the data presented in Tables II and III. It is apparent that both fly ashes are compositionally extremely heterogeneous, although there are very considerable differences between the mass distributions for these two fly ashes. As discussed in the previous section, much of the variation in densities observed is attributable to morphological rather than compositional characteristics. This is rather well illustrated by the data in Fig. 10, where density distributions have been determined as a function of particle size both before and after crushing the fly ash. The observed shift to higher density on crushing indicates the presence of vesicular particles and cenospheres in the larger size fractions, as discussed previously.

Interestingly, determination of the x-ray powder diffraction patterns of each of the subfractions presented in Tables II and III reveals no convincing differences in matrix composition that depend upon either size or density (Natusch et al., 1975). This finding further supports the contention that the density distributions in fly ash are largely determined by morphology rather than by composition. There are, however, very distinct differences between the amount of magnetite (Fe_3O_4) present in the magnetic and nonmagnetic fractions (Fig. 11). This suggests that magnetite is primarily responsible for the ferromagnetic susceptibility of coal fly ash.

C. Electrical Resistivity Distribution

The electrical resistivity of coal fly ash is an important physical property from the standpoint of control. Thus, it has been established (Bickelhaupt, 1974, 1975) that the collection efficiency of electrostatic precipitators increases with decreasing fly ash resistivity. Bickelhaupt (1974, 1975) has further shown that both the surface and volume resistivities of fly ash, at precipitator operating temperatures, are inversely proportional to the specific concentrations of alkali metals, which are thought to act as charge carriers. These studies have shown that considerable differences in electrical resistivity occur between different fly ashes, and correlations are observed between fly ash resistivity and alkali metal content, but no measurements have been made relating resistivity directly to particle size.

Some insight into the dependence of resistivity on particle size can be obtained by considering the data presented in Table IV. This table lists concentrations of potassium measured in fly ash that has been fractionated sequentially according to size, density, and ferromagnetism as described previously. It can be seen that in the nonmagnetic fractions (that account for 64% of this fly ash) there is a pronounced increase in the concentration of potassium (and also of sodium), both with decreasing particle size and with decreasing density. This suggests that, for this fly ash sample,

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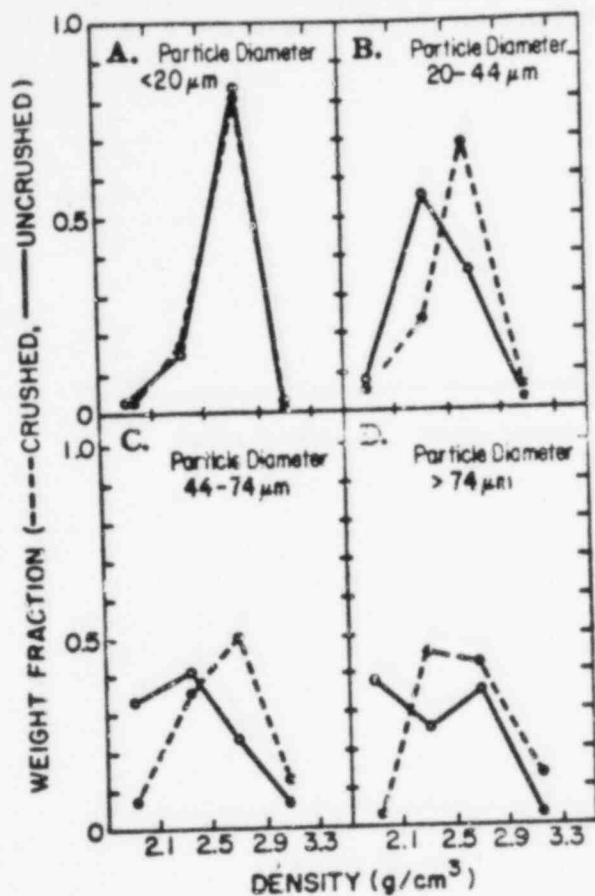


Fig. 10. The effect of crushing on the mass distribution of size-classified fly ash fractions. The shift to higher densities indicates the presence of hollow or vesicular particles (figure by courtesy of D. F. S. Natusch).

Fig. 11. X-ray powder diffraction patterns demonstrating the compositional differences between magnetic and non-magnetic fly ash fractions (figure by courtesy of D. F. S. Natusch).

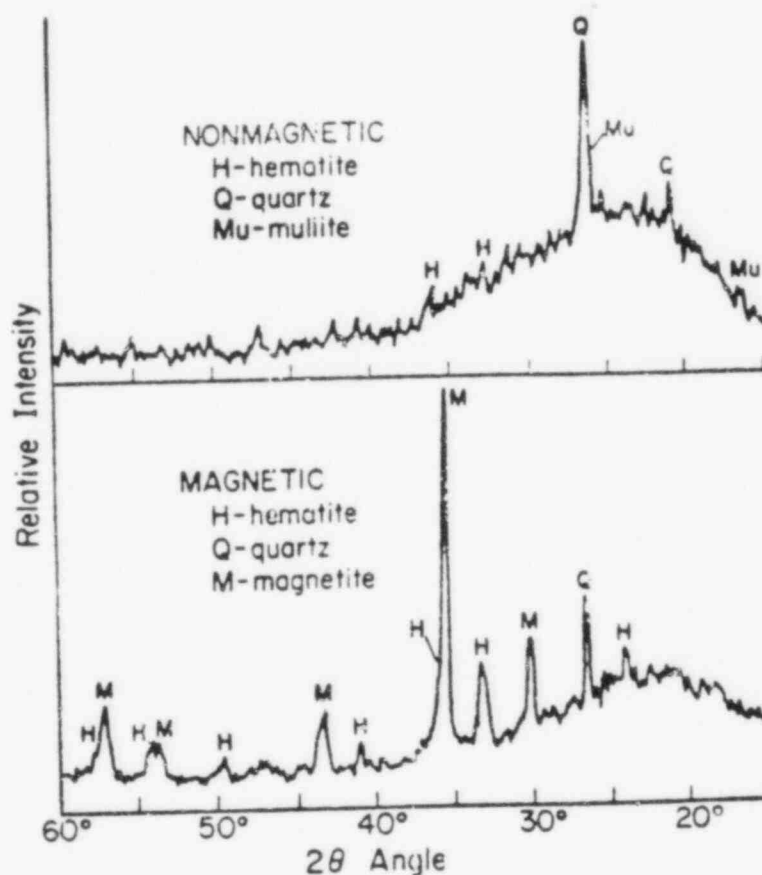


Table IV. Concentration (%) of Potassium in Fly Ash Separated Sequentially by Size, Density, and Ferromagnetism^a

Particle type	Particle size (μm)	Density (g/cm^3)			
		<2.1	2.1-2.5	2.5-2.9	>2.9
Nonmagnetic	<20	2.69	2.34	2.22	1.73
	20-44	2.63	2.28	1.33	1.09
	44-74	1.89	1.63	1.05	0.45
	>74	1.79	1.48	1.06	0.13
Magnetic	<20	-- ^b	--	0.76	0.70
	20-44	--	1.92	1.48	0.73
	44-74	1.78	1.60	1.27	0.85
	>74	1.37	1.62	1.49	0.83

^a From Natusch et al. (1975).

^b No meaningful data.

resistivity decreases with particle size and with density. Similar, though less pronounced, density dependencies are observed in the magnetic fractions, but size dependencies, if any, are obscure. Since both decreasing density and decreasing physical size contribute to decreasing aerodynamic size, it is apparent that the efficiency of electrostatic precipitation per unit mass of these size-classified fly ashes increases with decreasing aerodynamic particle size. This is an extremely desirable characteristic. It should be pointed out, however, that these studies require extension to respirable particle sizes.

D. Surface Area Distribution

The specific surface area of fly ash particles is an important parameter in determining a number of the behavioral characteristics of coal fly ash. It is the surface area of a particle that determines the number of electrostatic charges that can be placed on that particle in an electrostatic precipitator (White, 1963; Bickelhaupt, 1974, 1975); it is the surface area of a particle that determines the extent of condensation or adsorption of species from the gas phase (Davison et al., 1974; Natusch and Tomkins, 1977); and it is the surface area of fly ash that determines the rate and extent of its aqueous leaching (Natusch et al., 1975; Matusiewicz and Natusch, 1979).

To a reasonable approximation, one would expect the specific surface area (square meters per gram) of fly ash to increase linearly with decreasing particle diameter since the particles are predominantly spherical. Similar trends would also be expected for nonspherical particles having similar shape factors (Butcher and Charlson, 1972).

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In fact, the expected trend is observed; however, two important points are noted. First, the surface areas that are measured for spherical fly ash particles are considerably greater than those calculated from measured particle diameters. Even taking into account the assumptions inherent in surface area measurements, it appears that coal fly ash has a significant "internal" surface area. This is probably in the form of pores or cracks or a porous surface layer, although, as previously described, surface crystal formation may contribute significantly to the measured surface area. However, several fly ashes show no significant dependence of surface area on particle diameter (Table V), especially for small particles. These data indicate the existence of substantial internal surface area that is effectively proportional to particle volume rather than external surface area. In this regard, it has recently been suggested (Natusch, 1978a) that collisionally efficient condensation processes may result in deposition of material from the gas phase predominantly onto the external particle surface, whereas much less efficient adsorption processes (Natusch and Tomkins, 1977) can deposit gases and vapors on both the internal and external surfaces of a particle.

Table V. Comparison of Measured and Calculated Specific Surface Areas of Size-Classified Fly Ash Fractions^a

Physical size (μm)	Measured (m^2/g)	Calculated (cm^2/g)
<45	2.02	>267
45- 63	3.55	191-267
63- 90	2.55	133-191
90-125	2.43	96-133
125-180	1.20	67- 96
>180	3.11	<67

^a From Kim and Natusch (1978). Unpublished results.

IV. ELEMENTAL COMPOSITION OF COAL FLY ASH: PARTICLE SIZE DEPENDENCE

Studies of the size dependence of the elemental concentration of fly ash can be classified into two categories. The first category consists of those studies that relate the elemental concentration to the particle size of size-classified material. For these studies, sufficient mass of size-classified material is collected to allow gravimetric determination prior to elemental analysis. The second category are the many studies that have employed inertial cascade impactor systems for aerodynamic size classification. Aerosol sampling is performed isokinetically to avoid anomalous alteration of the particle size distribution. Because impactor stages are often coated with sticky adhesive to prevent particle bounce off and reentrainment effects and because only small masses of material may be collected on the stages, accurate gravimetric determination of sample mass is difficult. To obviate this complication, specific elemental masses of deposited particles on each stage are often ratioed to the mass of an element that does not demonstrate a marked concentration dependence with particle size. In this regard, Ondov et al. (1977a) have analyzed four size-classified, stack-collected fly ash samples ranging in particle size (VMD) from 2.2 to 20 μm (McFarland et al., 1977). The elements Al, Si, Ca, K, Ce, La, Rb, Nd, Hf, Sm, and Cs varied in concentration by less than 20% among all fractions and should therefore be suitable for mass estimation. A second approach that has been used in the analysis of impactor data, reports the size distribution for the mass of each element analyzed, thus avoiding the compounded errors in data derived from elemental ratios. Impactor studies also report elemental concentrations in terms of mass per unit volume of aerosol sampled. Thus, because of the limitation of gravimetric determination, results from impactor studies are often reported as ratios of elemental masses or mass-to-volume ratios rather than specific concentrations.

Many studies employ the enrichment factor (EF) of Gordon and Zoller (1973). The EF is defined as the ratio of an elemental concentration in the fly ash sample to the elemental concentration in the coal. To provide normalization relative to total mineral content, EF's are often calculated from the ratios of specific elemental contents in the fly ash samples and coal, respectively, to those of mineral matrix elements in the fly ash samples and coal, respectively. Thus, the EF may be calculated from:

$$EF = ([X]_s/[M]_s)/([X]_c/[M]_c), \quad (9)$$

where $[X]_s$ and $[X]_c$ represent the mass of element X in the sample and coal, respectively, and $[M]_s$ and $[M]_c$ represent the content of the matrix element in the sample and coal, respectively. A number of "matrix" elements have been used in the EF calculation: Al (Gordon et al., 1974), Fe (Ragaini and Ondov, 1977), Sc (Ondov et al., 1977c), Ce (Coles et al., 1979), and ^{40}K (Coles et al., 1978). In the following section, studies of fly ash analyses using gravimetrically determined masses will be discussed separately from studies employing smaller masses.

A number of analytical techniques have been employed in the determination of the elemental composition of coal fly ash. For complete analysis of the major, minor, and trace elements, a combination of analytical techniques is usually employed. The physical and chemical heterogeneity in terms of particle size, chemical distribution within and among individual particles, and the fused aluminosilicate matrix provide a unique combination of difficulties for the analyst. The techniques employed for elemental analysis may be divided into two categories: (1) single element techniques that generally require matrix dissolution and (2) multielement techniques that generally are performed on the undissolved ash. A detailed and extensive review of the elemental analysis of particulate matter has recently been published by Natusch et al. (1978). See also Chapters 11 through 14 in Volume I, and Chapter 46 in this volume.

A. Studies of Specific Concentrations

Davison et al. (1974) published the first detailed elemental analysis of coal fly ash as a function of particle size. The ash was collected from a power plant using southern Indiana coal. Two types of fly ash samples were analyzed: (1) fly ash collected by the plant's cyclonic precipitator and (2) stack-collected material. The precipitator ash was size separated by sieving the larger particles and aerodynamically separating the remaining mass. The stack-collected fly ash was aerodynamically classified using an Anderson impactor. These authors presented the elemental concentrations in three categories based on the degree of concentration dependence on particle size. The elements showing "pronounced" concentration trends of increased concentration with decreasing particle size were Pb, Tl, Sb, Cd, Se, As, Ni, Cr, Zn, and S. Elements classified as showing limited concentration trends were Fe, Mn, V, Si, Mg, C, Be, and Al. Iron concentrations decreased with particle size for the precipitator ash, while no trend was observed in the stack-collected samples. The elements described as showing no concentration trends were Bi, Sn, Cu, Co, Ti, Ca, and K. The mechanism of concentration enhancement has been postulated to be volatilization of the element (or compound) at combustion temperatures (1400°-1600°C) followed by condensation on particle surfaces (Natusch et al., 1974; Davison et al., 1974). Thus, fine particles with their large ratio of surface area to mass will preferentially concentrate volatile inorganic species. In particular, those elements displaying the greatest concentration dependence with particle size generally are associated with elemental forms that boil or sublime at coal combustion temperatures.

Fisher et al. (1977) and Fisher and Chrisp (1978) have described the size dependence of the elemental concentrations in coal fly ash collected from the stack of a power plant burning low-sulfur, high-ash, western United States coal. The fly ash was size classified in situ, downstream from the ESP, using a specially designed instrument employing two cyclone separators in series followed by a 25 jet centripeter (McFarland et al., 1977). Elements were classified into two categories: elemental concentrations (1) dependent on particle size and (2) independent of particle size. Concentration dependence with particle size was determined qualitatively with the criterion that constant concentration trends beyond experimental uncertainty were observed for each of the four

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fractions analyzed. In order of decreasing dependence on particle size, the elements Zn, As, Sb, W, Mo, Ga, Pb, V, U, Cr, Ba, Cu, Be, and Mn displayed increased concentration with decreasing particle size. Silicon was the only element to decrease in concentration with decreasing particle size.

The elements not displaying clear-cut concentration dependence on particle size for all fractions analyzed were Al, Fe, Ca, Na, K, Ti, Mg, Sr, Ce, La, Rb, Nd, Th, Ni, Sc, Hf, Co, Sm, Dy, Yb, Cs, Ta, Eu, and Tb. Of these elements, Na, Sr, Ni, and Co displayed marked enhancement in the finest fraction relative to the coarsest fraction. Coles et al. (1979) have described the elemental behavior in the four size-classified fractions in terms of elemental enrichment factors relative to the parent coal.

The elements were grouped into three classes: group I elements displayed little or no enrichment in fine particles and were lithophilic; group II elements displayed marked enrichment and were chalcophilic (sulfur associated); and group III consisted of elements with behaviors intermediate to groups I and II. Group I elements included Al, Ca, Cs, Fe, Hf, K, Mg, Mn, Na, Rb, Sc, Ta, Th, Ti, Ce, Dy, Eu, La, Nd, Sm, Tb, and Yb; group II elements were As, Cd, Ga, Mo, Pb, Sb, Se, W, and Zn; and group III consisted of Ba, Be, Co, Cr, Cu, Ni, Sr, U, and V.

In a separate report, Coles et al. (1978) described enrichment factors for ^{228}Th , ^{228}Ra , ^{210}Pb , ^{226}Ra , ^{238}U , and ^{235}U , relative to ^{40}K in the four size-classified fractions of stack fly ash. Although the EF's for all radionuclides appeared to increase with decreasing particle size, ^{210}Pb , the most volatile radionuclide, showed the greatest size dependence. The authors proposed the U is present as either a carbonate [$\text{Na}_2\text{UO}_2(\text{CO}_3)_2$ or $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$] that upon heating in an oxidative atmosphere may give rise to either volatile UO_3 from oxidation of uranite (UO_2) or the silicate-soluble, nonvolatile mineral, coffinite [$\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$]. Thus, U behavior would be expected to display an intermediate behavior depending on the relative concentrations of uranite and coffinite. The behavior of Th was rationalized to be due to coexistence in submicron zircon grains in the coal. The authors suggested that ^{226}Ra enrichment may have been due to ^{238}U , while no explanation of ^{228}Ra enrichment was presented.

Campbell et al. (1978) have studied the elemental distribution of size-classified ESP-collected coal fly ash from a western United States power plant. Reaerosolized ESP fly ash was separated into nine size fractions ranging in size (VMD) from 0.5 to 50 μm . The authors describe fine particle enhancement for elements "volatilized during combustion," i.e., As, Co, Cr, Ga, Pb, Se, and Zn. Their data also demonstrate that K, Al, Mn, Mg, Na, Ba, S, Ni, V, Cu, Cs, Rb, Sb, Br, Mo, and Sn display an inverse concentration dependence on particle size. Silicon and possibly Zn were reported to increase in concentration with increasing particle size. The concentrations of Ca and Sr demonstrated a maximum at approximately 5 μm . A similar concentration pattern was reported for Ce, Eu, and Yb.

These studies are in basic agreement with the hypothesis of Natusch et al. (1974) in that the most volatile elements (or their oxides), Cd, Zn, Se, As, Sb, W, Mo, Ga, Pb, and V, displayed the greatest size dependence. Furthermore, the least volatile elements

the elements, the concentration, the size, Th, Ni, and Co.

did not display a strong particle size dependence. With regard to enhancement of Ba and U, Coles et al. (1979) postulated that Ba may form the volatile species $Ba(OH)_2$ and U may be volatilized in part as UO_3 . Fisher et al. (1977) have proposed that the presence of Cr in the organic fraction of coal, Mn and Sr as carbonate minerals, and Cu as sulfides, may explain the behavior of these relatively refractory elements. Campbell et al. (1978) speculated that the concentration profiles exhibiting maximum particle sizes of approximately 5 μm for Ca, Sr, and the rare earth elements were because of the presence of these elements in apatite.

B. Studies of Relative Concentrations

Most studies of the chemical properties of size-classified fly ash have employed cascade impactors for stack or plume sampling. Zoller et al. (1974) reported enrichment factors relative to Al for stack-collected fly ash. The ash studied was collected downstream from the ESP at a power plant burning pulverized coal containing 10% ash and 1% S. In agreement with the previously described studies, enhancement of the volatile elements, Sb, Se, As, Pb, Zn, Ni, and I, was observed in the stack fly ash relative to their concentrations in the coal. Bromine was depleted in the stack ash relative to the coal. The authors point out that the EF's for Se, I, and Br are underestimates because portions of these elements were probably in the vapor phase. Elements not displaying enrichments included Ti, Sc, Th, Ta, Na, K, Rb, Mg, Sr, Ca, Ba, V, Cr, Mn, Fe, Co, and six rare earth elements. It should be pointed out that although the stack sample was not size classified, a relatively fine particle distribution (i.e., MMD 5-10 μm) may be presumed for this post-ESP material. In a subsequent report (Gladney et al., 1976), the research team described the size dependency of the EF's in the stack fly ash.

Three patterns of elemental behavior were described. The elements Na, K, Rb, Mg, Ca, Sr, Ba, Sc, Ti, V, Mn, Co, Zr, Nb, Hf, Ta, and all rare earths except Ce displayed an EF distribution that was not size dependent. Interestingly, the authors also report that the relatively volatile elements, Cr, Zn, Ni, and Ga, also exhibited little size dependence. A definite increase in EF of fine particles was observed for Pb, As, and Sb. The volatile elements, Se, Br, I, and, to a lesser extent, Hg, displayed bimodal activity. An enrichment minimum was observed from 0.7 to 5.0 μm . Iron and Ce displayed EF's that decreased with decreasing particle size.

Klein et al. (1975) described the pathways of 37 trace elements through a cyclone-fed power plant burning coal of 3% S and 11% ash. Concentration ratios for ESP outlet versus inlet ash indicated enhancement of As, Cd, Cr, Pb, Sb, Se, V, and Zn in the finer fly ash fraction. The authors point out that the ESP efficiency was 96.5% during their first sampling trip, as compared to 99.5% during their second sampling trip. Interestingly, the removal of the major elements was more complete during the second trip, although no change in capture efficiency was observed for Cd, Pd, and Zn because of association with fine particles. The authors estimate that 60-90% of the Hg was released from the stack as a vapor. In a subsequent study, Andren and Klein (1975) presented extensive data on the mass balance and chemical form of selenium emissions from the same power plant. The authors concluded that 68% of the Se was incorporated into fly ash. Based on an ESP efficiency of 99.6%, the authors also concluded that 93% of the

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Se released to the environment is in the vapor phase. The oxidation state of Se was determined to be Se^0 based upon inefficient extraction in HCl and complete elemental extraction in Br/Br^- -redox buffer, 16M HNO_3 , 18M H_2SO_4 , or 1:1 $\text{HNO}_3:\text{HClO}_4$.

Mercury emissions from coal-fired power plants have been described in detail. Billings and Matson (1972) and Billings et al. (1973) studied mercury emission from a power plant burning low sulfur (<1%), high ash (21%) pulverized coal. The authors concluded that 90% of the Hg was released from the stack as a vapor and that fly ash particles represented less than 1% of the Hg emissions. The annual release of Hg from all coal-fired United States power plants was estimated to be 10^3 metric tons in 1971. Similarly, Diehl et al. (1972) studied Hg emissions from a 100-g/hr pulverized coal combustor and a 500-lb/hr pulverized coal combustor. Although these authors experienced difficulties in their collection of Hg from the flue gas, 35 and 60% of the total Hg was found in the fly ashes generated from combustion of coals having ash contents of 21.6 and 6.9%, respectively, and sulfur contents of 5.2 and 1.2%, respectively. Subsequent studies in the larger combustor using coal with 10.1% ash and 2.1% S, resulted in fly ash containing 12% of the total Hg. The authors present calculations for two Illinois power plants, indicating that the Hg content of ash contained within the plants accounted for 7 and 19% of the total Hg in the coal. Thus, in agreement with Billings' work, most of the Hg in coal is volatilized and released as a vapor to the atmosphere. Similarly, Kalb (1975) has reported that the major portion of Hg in coal is volatilized during combustion and released to the atmosphere. Approximately 10% of the volatilized Hg was found to be adsorbed onto fly ash; organomercury compounds were not observed. The author points out that Hg emissions could be reduced by coal cleaning, which results in removal of higher density minerals, including pyrite that is relatively high in Hg contents.

In a review of trace element studies related to low sulfur, high ash coal combustion in Four Corners, New Mexico, Wangen and Wienki (1976) described enrichment factors for electrostatic precipitator ash relative to bottom ash. Enhancement in the precipitator ash was observed for the following elements in order of decreasing magnitude: Se, As, F, Sb, Zn, Tl, Hg, Mo, Ga, B, Pb, V, and Cr. Enrichment factors near unity were observed for the other 22 elements studied.

Kaakinen et al. (1975) studied the behavior of 17 elements in the inlets and outlets of a power plant burning pulverized coal containing 0.6% S and 6% ash. Although particle size was not reported, the author described the specific surface area of his samples. The surface areas measured by nitrogen adsorption for the bottom ash, mechanical collector hopper ash, electrostatic-precipitator hopper ash, and electrostatic-precipitator-outlet fly ash were 0.38, 1.27, 3.06, and $4.76 \text{ m}^2/\text{g}$, respectively. Enhancement in trace element concentration relative to Al was observed for Pb, Mo, As, Zn, Sb, and Cu.

The magnitude of the EF's correlated with relative distance of each outlet downstream from the boiler and the specific surface area of the ashes. The authors point out that As enrichment depends on the Ca content of the coal; As_2O_3 is associated with low Ca coals while As_2O_5 is associated with high Ca. Zirconium was the only element displaying a decrease was thought to be because of the occurrence of Zr as zircon, a relatively high density mineral that may be more efficiently captured by the mechanical collector. Contrary to this observation, little or no enrichment was reported for Nb, Sr, Fe, Rb, and Y.

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Ondov et al. (1977b,c) have performed extensive analyses of element enrichments in fly ash as a function of particle size. In the study of two large western power plants burning high ash, low sulfur, pulverized coal, Ondov et al. (1977c) reported considerable enrichment of W, U, Ba, Zn, V, In, Ga, Br, As, Se, Sb, and Mo in fine particles for the plant with an ESP rated at 99.5% efficiency. In the second plant, with a 97% efficient ESP, EF distribution tended to be bimodal for these elements, with a broad maximum of 2-10 μm . The authors also point out that Br, Se, Cr, Mn, Ta, Co, and Zn displayed enrichment in both the fine and the large particles, i.e., an EF minimum was observed from approximately 1 to 8 μm . The authors indicate that the biphasic distributions may be the result of artifacts in collection because the larger particles will be collected on the first impactor stages, through which vapor containing volatile elements is initially drawn.

Fisher et al. (1979d) also reported data supporting bimodal elemental distributions. Filtration studies with neutron-activated, stack-collected fly ash (VMD = 2.2 μm ; $\sigma_g = 1.8$) were performed by dispersing ash samples in buffer at pH 7.4 and filtering through a membrane with pore size of 5, 2, 0.8, 0.4, 0.2, 0.1, 0.05, or 0.03 μm . The elements were classified into four groups based on their behavior: (1) Na, Ca, Co, Se, Mo, and Ba were partially soluble and did not display filtrate concentrations that were pore-size dependent; (2) Sb, As, Zn, W, Cr, and U displayed a pattern of filtrate concentrations that appeared to be bimodal; (3) K, Si, Fe, Ce, Sm, Eu, and Th were only detected in filtrates from membranes >2 μm in pore size; and (4) Zr, Cs, Nd, Rb, Tb, Yb, Hf, and Ta were not detected in the filtrates. For those elements displaying bimodal behavior, a relatively large increase in concentration was observed in filtrates derived from the 0.4 μm membrane. The concentration profile remained constant thereafter. These data suggest a concentration maximum for Sb, As, Zn, W, Cr, and U in fine particles less than 0.4 μm in diameter.

Ondov et al. (1977c) have compared enrichment factors for the two power plants to those published by Klein et al. (1975), Kaakinen et al. (1975), and Gladney et al. (1976). The comparison (Table VI) for EF's for elements in stack-collected fly ash indicates relatively good agreement between studies of different power plants with ESP control systems employing a wide variety of coals. In light of the uncertainties, only Mo, Se, and Mn showed significant differences between plants. The volatile elements Sb, As, and Pb were clearly enhanced in samples from all power plants; Zn, Se, Cr, and V were enhanced in stack ash from those plants with the most efficient ESP's, i.e., those plants presumably releasing the finest ash. Bromine was the only element displaying a significant fractional EF. Ondov et al. (1977c) point out that the EF's for stack ash collected from a unit with a venturi wet scrubber (VWS) are generally much higher than those for plants with ESP's. The authors attribute these findings, in part, to the high efficiency ($>99\%$) of removal of particles >2 μm and the low efficiency (40%) of removal of particles <2 μm by the VWS. In another study, Ondov et al. (1979b) indicated that the ratio of VWS-to-ESP fractional emissions of submicron, supermicron, and total suspended particles were 1:6, 11:1, and 10:1, respectively. They also proposed that

Table VI. Enrichment Factors for Elements in Stack Fly Ash from Coal-Fired Power Plant

	Western U.S. plant A ^b	Western U.S. plant B (ESP) ^c	Allen Steam plant ^d	Chalk point ^e	Valmont ^f	Western U.S. plant (VWS) ^g
Si	7.0	5.3	6.7	4.0	--	120
Cd	--	6.0	--	--	--	--
W	--	4.9	--	--	--	70
As	6.6	7.9	6	6.3	--	100
In	5.5	3.7	--	--	--	20
Zn	4.3	4.3	7.8	1.5	2.5	19
Pb	--	3.8	8.1	3.7	3.1	--
Ga	4.3	3.0	--	1.2	--	--
U	3.3	2.5	--	--	--	13.5
Se	3.0	5.3	5.5	5.7	1.7	400
Ba	2.5	2.7	0.7	0.92	--	13
Cr	2.5	2.6	3.0	1.1	--	100
Co	2.3	1.7	1.4	1.0	--	4.3
V	2.0	2.5	2.5	0.75	--	21
Mo	1.8	3.5	--	--	3.0	43
Hg	1.1	0.8	0.54	--	--	2.7
Fe	1.1	0.90	0.84	0.83	1.0	2.0
Na	1.0	1.1	0.99	--	--	3.2
Sc	1.0	1.0	1.0	1.0	--	1.0
K	1.0	0.7	0.95	0.83	--	0.86
Th	0.95	0.90	0.76	--	--	0.89
Al	0.86	0.75	0.44	0.83	0.94	1.3
Ca	0.76	0.89	--	0.92	--	7.6
Mn	0.68	1.1	0.78	--	--	21
Be	--	0.6	--	0.64	--	--
Br	0.2	0.1	--	0.17	--	57

^a Modified from Ondov et al. (1977c).

^b Plant A employed an ESP with removal efficiency of 99.6% (Ondov et al., 1977c).

^c Plant B employed an ESP with efficiency of 97% on one unit and a venturi wet scrubber (VWS) on a second unit (Ondov et al., 1979).

^d Employed an ESP with 99.5% efficiency (Klein et al., 1975). *Pulver's Allen?*

^e Employed an ESP with 75% efficiency (Gladney et al., 1976).

^f Employed a mechanical collector and an ESP with 91% efficiency (Kzakinen et al., 1975).

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corrosion may enhance VWS emissions of Cr, Co, Cu, and Zn. Thus, although the VWS may have a higher removal efficiency of total suspended particulate matter, the ESP may more efficiently remove respirable particles.

Ondov et al. (1977b) have reported enrichment factors for plume samples collected from a power plant with five generating units, of which two units were equipped with ESP's and the other three with VWS's. Elemental enrichment factors were relatively constant as a function of distance from the stack for Sc, Na, K, Cu, and the lanthanides. Enrichments for Mo, V, Ba, U, Ga, In, As, W, and Se increased from the stack to the plume. Subsequent plume samples indicated decreased EF's with distance from the point of release. The only elements displaying increased enrichments with increased distance from the stack were Br, Sb, Zn, and Co. The increased EF for Br was postulated to be because of mixing of plume aerosols with high background concentrations of Br, possibly because of automotive sources (Ondov et al., 1977b).

In a further comparison of the stack fly ash from an ESP unit with that from a VWS unit, Ondov et al. (1979b) reported that the mass median aerodynamic diameters (MMAD's) for the elements As, Ba, Sb, Se, U, V, and W in the ESP ash were approximately tenfold higher than in the VWS ash, which ranged from 0.47 to 0.59 μm . The authors concluded that despite an eleven-fold higher total particulate emission, the ESP unit is far more efficient at removing submicron particles than is the VWS unit. Thus, the scrubber unit tested appeared to be less effective at reducing potential inhalation hazards than the precipitator unit.

C. Surface Deposition Models

A number of investigators have presented mathematical models relating the concentrations of relatively volatile elements to geometric parameters associated with fly ash particles. Assuming a volatilization-condensation mechanism, Davison et al. (1974) proposed a simple mathematical model for elemental concentration as a function of particle size. Their model predicts that the elemental concentration of a volatile species will be inversely dependent on particle size. Kaakinen et al. (1975) presented a similar mathematical dependence based on the specific surface area (square meters per gram) of fly ash. If the specific surface area is proportional to the surface area:volume ratio and if particle sphericity is assumed, then elemental concentration is inversely proportional to particle size. Based on mass transfer arguments, Flagan and Friedlander (1976) indicated that concentration should be inversely dependent on particle size for Knudsen numbers >1 (i.e., for condensation when the particle size is greater than the mean free path of the depositing gas) and inversely dependent on the square of the particle size for Knudsen numbers <1 . Application of this model fits existing data equally as well as the model of Davison et al. (1974). Smith et al. (1978) extended the Flagan and Friedlander (1976) and the Davison et al. (1974) models to include fine particles in which the thickness of the deposited surface layer approached the diameter of the total particle. This modification resulted in concentrations that asymptotically approached maxima at particle size $<1 \mu\text{m}$. The models were demonstrated to fit the concentration dependence on particle size of re-aerosolized, ESP-collected

fly ash. Biermann and Ondov (1978) have proposed a model with an inverse square dependence and an asymptotic maximum for concentration as a function of surface thickness. Their results indicated that the thickness of surface-deposited chemicals is inversely proportional to particle size and that total elemental composition is proportional to $1/d^2$, where l is the thickness of the surface layer and d the diameter of the particle. Analysis of 12-stage impactor data with increased resolution in the submicron region supported the mathematical model. Further studies are required, however, to extend the presently available data on concentration as a function of particle size thus allowing evaluation of the validity of the existing mathematical models.

D. Summary

In summary, most studies of the size dependence of elemental concentrations in coal fly ash support the hypothesis of Natusch et al. (1974); the more volatile elements (or chemical forms) are preferentially associated with fine particles. The fine particle mode ($<1.0 \mu\text{m}$) in the bimodal elemental distributions is generally considered to be because of coagulation of primary particles (Whitby, 1977). Bimodal size distributions may also result from the presence of multiple mineral forms, some of which may decompose or may be associated with a fine mineral grain size. It should be noted, however, that the bimodal distribution of the very volatile elements (Se, Br, and I) observed in impactor samples may be artifacts due to vapor condensation on the larger particles collected on the first impactor stages. Also, the bimodal distribution of metallurgical elements may be associated with entrainment of corrosion products in the flue gases. Similarly, small particle enhancement of relatively nonvolatile elements may be because of a combination of decomposition, chemical reaction, mineral grain size, or elemental association in the organic phase of coal.

V. MATRIX AND SURFACE COMPOSITION OF COAL FLY ASH

A. Matrix Composition

Elemental analyses of coal fly ash show that the major matrix elements are Al, Si, and Fe together with a few percent of Ca, K, Na, and Ti. Fly ashes derived from western United States sub-bituminous coals generally contain higher levels of calcium than do bituminous coals and lignites.

The actual compounds that constitute the fly ash matrix have been identified only for a comparatively small fraction of the mass. The techniques that have proved most useful for this purpose are x-ray powder diffraction and infrared spectroscopy (Natusch et al., 1975). In addition, selected area electron diffraction has been employed in the identification of small crystals often found associated with the surface of fly ash.

X-Ray powder diffraction studies have demonstrated the presence of α -quartz (SiO_2), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), hematite (Fe_2O_3), magnetite (Fe_3O_4), lime (CaO), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in aged fly ash (Natusch et al., 1975; Miguel, 1976). However, there is evidence to suggest that crystalline species, associated with aged fly ash may differ from those in the freshly collected material (Fisher et al., 1976, 1978) because of

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either the presence or lack of moisture in storage atmospheres. In addition to these crystalline species, x-ray powder diffraction patterns indicate the presence of a substantial amount of material that is amorphous to x-rays (Fig. 11). The composition of this material has not been established with certainty; however, it is widely accepted that it consists of an impure aluminosilicate glass and constitutes the bulk of the fly ash matrix (Natusch et al., 1975; Walt and Thorne, 1965; Simons and Jeffery, 1960).

Infrared spectroscopic identification of inorganic compounds present in coal fly ash has largely been restricted to the tentative identification of residues of evaporated aqueous leachates (Jakobsen et al., 1978). Several sulfate species have been identified; however, it is not clear whether these represent the actual compounds that existed prior to removal from the fly ash. In addition, studies have been made of glass melts derived from oxides of aluminum, iron, and silicon (Henry et al., 1978). These have provided information that supports the contention that the matrix of coal fly ash is predominantly an aluminosilicate glass.

B. Trace Elemental Distribution

Further insights into the factors that determine the distribution of elements in a bulk fly ash sample have been obtained from multielemental analyses of the 32 subsamples presented in Table IV. Specific concentrations of the elements Al, As, Ba, Ca, Co, Cr, Cs, Dy, Eu, Fe, Ga, Hf, K, La, Mg, Mn, Na, S, Sb, Sc, Si, Sm, Sr, Ta, Ti, Th, Y, and Zn were determined. In addition, x-ray powder diffraction patterns and BET surface areas (by nitrogen adsorption) were obtained (Natusch et al., 1975).

As an aid to the interpretation of the extensive data sets obtained, multivariate statistical analyses, in the form of both common-factor analysis and hierarchical aggregative cluster analysis (Harmon, 1967; Blackith and Reyment, 1971) were employed. Common factor analysis makes it possible to determine the way in which each measured variable in the system is related to a set of n factors common to the system as a whole. The important causalities that give rise to the observed data can thus be inferred. By comparison, cluster analysis permits an objective assessment of the similarity between individual subsamples.

The results obtained indicated that the distributional pattern of trace elements in fly ash is controlled by five major factors. These factors have been interpreted to include particle size, particle composition, and the geochemical behavior of the elements.

Thus, specific distributional patterns are observed for the chalcophile, lithophile, and siderophile elements as classified by Goldschmidt's Geochemical Series (Bertine and Goldberg, 1971; Coles et al., 1979b). It would appear, therefore, that the size factor arises as a result of the volatilization and condensation of certain trace metals as described earlier (Davison et al., 1974). The dependence on particle composition possibly reflects the association of some elements (e.g., As and Mn) with certain types of mineral inclusions. The dependence on geochemical class of the elements, in all probability, reflects the different chemical characteristics of each of these classes under high temperature combustion conditions.

SEM-x-ray analysis has provided further insight into the complexity of the matrix composition of coal fly ash. Elemental analysis of morphologically similar fly ash particles from the NBS fly ash reference material indicated extreme matrix heterogeneity (Pawley and Fisher, 1977). Particles rich in K, Ti, Fe, S, or Ca were observed. Indeed, nearly all of the Ti in a field of 100 particles could be accounted for by a single Ti-rich particle. It is interesting to note the extreme matrix heterogeneity of individual particles in the NBS fly ash, a material that is well documented as being homogeneous by macroscopic analytical techniques.

C. Surface Composition

As pointed out in previous sections, the inverse dependence of trace elemental concentration on fly ash particle size is generally held to be due to condensation of metallic species onto particle surfaces from the vapor phase (Davison et al., 1974). One would expect, therefore, to find certain volatilizable elements preferentially concentrated on particle surfaces. This has been observed (Linton et al., 1976, 1977; Keyser et al., 1978).

The techniques that have been employed, to date, in analyzing the surface regions of coal fly ash are electron spectrometry for chemical analysis (ESCA), Auger electron spectrometry (AES), and secondary ion mass spectrometry (SIMS). In addition, some surface analytical information is available using electron microprobe x-ray spectrometry. The operational characteristics of these techniques are summarized briefly as follows (Czanderna, 1975; Kane and Larrabee, 1974; Keyser et al., 1978).

The electron microscope (EM) and microprobe (EP) bombard the sample with a focused beam of electrons to stimulate emission of x-rays characteristic of the elements present. The technique is useful for analyses of individual micrometer-size particles and has a lateral and depth resolution of about 1 μm , determined by the x-ray emission volume. The electron probe microanalyzer is described in Chapter 48.

Surface analysis capabilities of EM and EP are poor since the depth resolution is very much greater than the thickness of the surface layer normally of interest. Indeed, information about elemental surface predominance can be obtained only by varying the energy of the electron beam (depth penetration) or by ion etching of the outer surface and by comparing elemental ratios for inner and outer surfaces.

The ESCA technique employs an x-ray source to eject core-level electrons from the sample. Energy analysis of the resulting photoelectrons provides chemical bonding information since the bonding energies of the core electron are sympathetic to changes in the electronic structure of the valence level. Elements present at levels greater than 1 at. % in the uppermost 20 Å are detected. Depth profiling is achieved by etching the surface with an ion beam between analyses. For details on ESCA (or XPS) see Volume I, Chapter 11.

The utility of ESCA for individual particle analysis is limited because of the difficulty of focusing x-rays to a beam diameter smaller than 1 mm, although recent advances indicate that lateral resolutions of 10 μm are feasible. Normally, the sensitivity of ESCA is insufficient to enable observation of trace constituents unless considerable surface enrichment is encountered.

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In AES the emission of Auger electrons is stimulated by bombarding the sample with a beam of electrons. The energy of the secondary Auger electrons is characteristic of the emitting element. Spectra are recorded in the first derivative mode to discriminate against a background of inelastically scattered electrons. Elemental detection limits lie in the range 0.1-1.0 at. % within the analytical volume (depth ~20 Å). Depth profiling is achieved by etching the sample surface with an ion beam (normally Ar⁺) as in ESCA. Most AES spectrometers possess microprobe capabilities with incident beam diameters of 1-5 µm.

In SIMS the sample is bombarded with a stream of ions (most commonly, negative oxygen ions) and surface material is physically removed. About 1-10% of the sputtered material is in the form of secondary ions that are mass analyzed by a conventional mass spectrometer.

The ion microprobe represents a special configuration of SIMS in which the primary ion beam can be focused to a diameter of about 3-5 µm. Both individual particle analysis and elemental-mapping capabilities are thus available. Depth profiling constitutes an integral part of the process of secondary ion generation.

A major advantage of SIMS is its extremely high sensitivity, with elemental detection limits ranging from 10⁻² - 10⁻⁶ at. %, depending on the element and the primary ion used. Typically, it is possible to observe as little as 1 µg/g in the analytical volume, thereby enabling studies of species present at trace levels. Secondary ion mass spectrometry is, however, subject to several types of interferences and artifacts. In particular, spectral interferences from molecular- and multiple-charged ions make the high resolving power of a double-focusing mass spectrometer desirable. Also, volatilization losses and migration of sample ions under the influence of the primary ion beam can give rise to spurious depth profiles. Such effects are often difficult to identify in SIMS since removal of surface material is an integral part of the detection process.

Of the above techniques, AES and SIMS are generally most useful for surface analysis and the depth-profiling studies, owing to their sensitivity and good lateral and depth resolution. Electron spectrometry for chemical analysis, however, has the important advantage of providing information about the identity of molecular species present. With all the techniques, difficulties are encountered in establishing even semiquantitative depth scales, which are normally attempted by calibrating the rate of removal of surface material against that obtained for a standard having a surface layer of known thickness. The main problem, however, lies in matching the matrix composition of the standard to that of the material being studied, which, in the case of coal fly ash, is not well defined.

Surface analysis and depth profiling studies of both individual coal fly ash particles and groups of particles have established that a number of trace elements, including C, Cr, K, Mn, Na, Pb, S, Ti, V, and Zn, are substantially surface enriched, whereas the matrix and minor elements, Al, Ca, Fe, Mg, Si, and Tl, are not (Linton et al., 1977). This observation clearly supports the hypothesis that the more volatile elements, or their compounds, are vaporized during combustion and then condense on the surfaces of coentrained fly ash particles at lower temperature.

Fig. 1

Depth profiling studies of fly ash have also demonstrated the utility of using instrumental techniques in conjunction with solvent leaching to remove soluble surface material. An example of this approach is presented in Fig. 12 for the elements Pb and Tl. This study demonstrated that extraction of fly ash with water or dimethyl sulfoxide removes the surface layer of both elements. Determination of the amounts of Pb and Tl in solution then enables estimation of the amounts present in the surface layer. Assuming a surface layer thickness of 300 Å, one obtains average concentrations of 2700 µg/g for Pb and 920 µg/g for Tl in the surface layer as compared to bulk particulate concentrations of 620 µg/g and 30 µg/g for these elements. Similar estimates for several other trace elements are presented in Table VII (Natusch, 1978a).

Solvent leaching can also provide some insight into the chemical forms of elements present. For example, although AES and SIMS indicate little surface enrichment of iron, aqueous leaching rapidly removes this element from the surface region, thereby indicating its presence in a readily soluble form. Similarly, comparison of the leaching and depth profiles of K, Fe, Na, and S suggests that these elements may be associated with each other in the surface layer, possibly as alkali-iron sulfates. Further support of the existence of simple and/or complex sulfates is provided by ESCA studies that show that the oxidation states of Fe and S in the surface region are +3 and +6, respectively (Wallace, 1974).

Surface analytical results, such as those presented in Fig. 12 and Table VII demonstrate the considerable differences in composition that exist between the interior of fly ash particles and their external surface. Since it is the particle surface that is in contact with the external environment, determination of surface composition is of considerable importance, as previously discussed. Finally, it should be remarked that there are no coherent data that relate surface composition to particle size for fly ash. However, if the volatilization-condensation process is primarily responsible for surface enrichment of trace elements, then one would not expect surface concentrations to vary greatly with particle size. This is because the amount of vapor deposited is proportional to surface area, thereby resulting in a constant elemental concentration per unit surface area. Of course, if other mechanisms are responsible for or contribute to surface enrichment (e.g., agglomeration of accumulation mode particles with coarse particles or thermal diffusion of trace species to the surface of molten particles), then some dependence on particle size would be anticipated.

D. Solubility and Leachability

A number of workers (Shannon and Fine, 1974; Theis and Wirth, 1977; James et al., 1977; Dreesen et al., 1977) have reported that the bulk solubility of coal fly ash in water is very low and rarely exceeds 2-3% by weight. The bulk solubility is clearly a property of both the glassy and crystalline matrix materials identified earlier, and one would expect elements that are either chemically or physically trapped within this matrix to exhibit low solubility. On the other hand, at least some of the material present in the surface skin is readily soluble in water (Fig. 12). Indeed, it is now quite well established (Linton et al., 1977; Natusch, 1978a; Fisher et al., 1978e) that most of the soluble fraction of fly ash is derived from this surface layer and is thus very rich in trace elements.

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Fig. 12. Ion microprobe depth profiles for Pb and Tl for un-extracted and ex-tracted fly ash samples (reprinted with permission from R. W. Linton, P. Williams, C. A. Evans, Jr. and D. F. S. Natusch, Anal. Chem. 49, 1514 (1977). Copyright 1977 by the American Chemical Society).

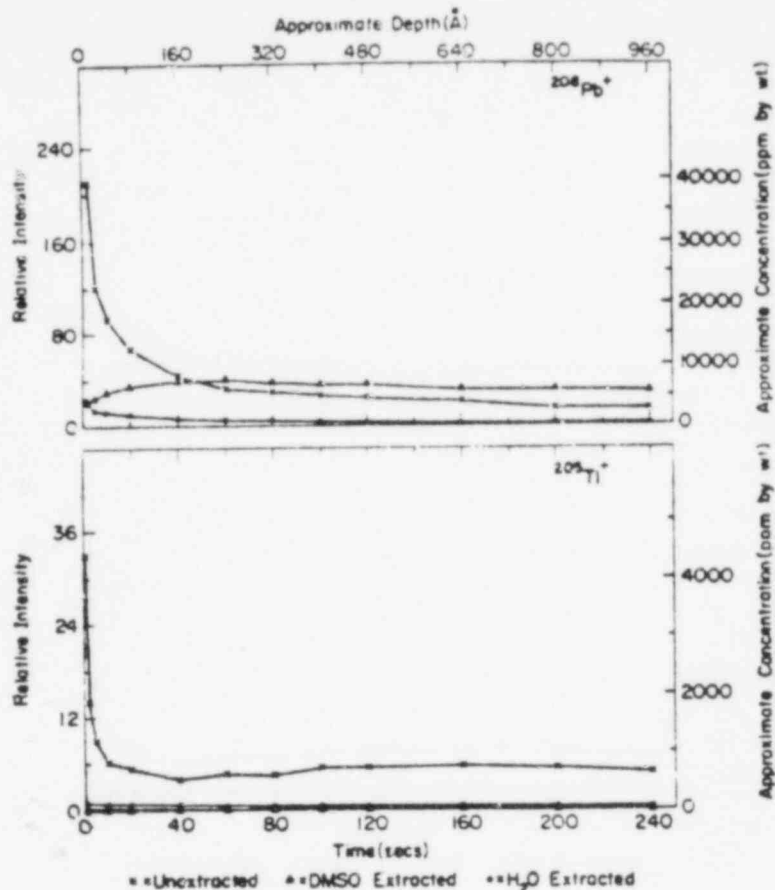


Table VII. Estimated Surface Concentrations of Elements in Coal Fly Ash^a

Element	Bulk concentration (μg/g)	Estimated surface concentration in 300 Å layer (μg/g)
As	600	1500
Cd	24	700
Co	65	440
Cr	400	1400
Pb	620	2700
S	7100	252,000
V	380	760

^a From Natusch (1978a).

At the present time, there is considerable confusion involved in interpreting and understanding results obtained from different studies of fly ash solubility. Specifically, quite different results are obtained by workers using apparently similar laboratory leaching techniques and none are readily transferrable to field studies. It is appropriate, therefore, to consider the factors that control leachate composition under both laboratory and field conditions and to standardize one or more laboratory leaching techniques whose results bear some relationship to real field conditions.

Some insight into leaching behavior can be obtained by recognizing that soluble inorganic species $M_i A_i$ associated with fly ash particles can dissociate into their component cations M_i and anions A_i in aqueous solution, and that both dissolution and deposition (e.g., precipitation) processes can occur. Furthermore, cations and anions present in solution can interact so as to set up multiple equilibria that may involve ion pairing, complexation, precipitation, or acid-base behavior ($M_i A_j$ or $M_j A_i$). The result can be expressed, simplistically by the equations



Here P represents the parent particles and k_n , k_{-n} are the rate constants for forward and reverse reactions, respectively. It is apparent from Eq. (10) that, when leaching studies are conducted under batch conditions, such that the amount of fly ash and solvent are maintained constant, an equilibrium will be established between particulate and solution species. Consequently, only a fraction of the potentially soluble material will enter solution. On the other hand, if conditions are such that soluble material is continuously removed by provision of fresh solvent or by providing a large solution sink in the form of complexing ligands or acids, then all potentially soluble material will ultimately enter solution.

Matusiewicz and Matusch (1979) have conducted very extensive studies to demonstrate the validity of Eq. (10). They have established that the rate and extent of leaching depend upon the leaching method, the fly ash:solution ratio, temperature, pH, complexing agents, particle size, and fly ash origin exactly as predicted from Eq. (10) for both equilibrium and nonequilibrium conditions. When equilibrium is established between particulate and solution species, as in batch leaching, little dependence on particle

size is observed since the amount of a given element is determined by its solution concentration (solubility) that is only weakly related to the amount of solid phase present. Exhaustive (nonequilibrium) leaching, however, removes all soluble material, the amount of which is directly related to particle size because of its presence in fly ash surface layer.

It is apparent from the foregoing remarks that any leaching process that establishes the solid-solution equilibrium given in Eq. (10) will result in changes in solution composition with equilibrium position. It is hardly surprising, therefore, that widely differing results are obtained by workers who use different leaching conditions. Nevertheless, some significant generalizations can be made. First, it is readily apparent that much higher proportions of most trace elements are soluble than is the case for matrix elements (Table VIII). This is due, in part, to the predominance of trace elements in the particle surface layers in quite soluble forms (probably sulfates, oxides, and carbonates). Second, it is clear that, under batch leaching conditions, such as are most likely to occur in the field, the amount of each element entering solution is strongly dependent on the dilution (fly ash:water ratio) and the initial pH (Matusiewicz and Natusch, 1979; Dreesen et al., 1977; Theis and Wirth, 1977).

Table VIII. Percentage of Elements Leached from a Typical Coal Fly Ash^a

Element	% Leached
Al	0.2
B	5
Ba	4
Ca	35
Cr	30
K	40
Mg	0.2
Mn	0.4
Mo	85
Na	10
P	6
Pb	100
Si	0.1
Sr	6
Zn	6

^a From Matusiewicz and Natusch (1979).

E. Organic Constituents

To date, no exhaustive determination of organic species associated with coal fly ash has been reported. Rather, emphasis has been placed primarily on the determination of polycyclic organic matter (POM) in fly ash, due to the potential carcinogenicity of several compounds of this type (Committee of Biological Effects of Atmospheric Pollutants, 1972). For the most part, the several studies of POM in fly ash have indicated either extremely low or undetectable levels (Committee on Biological Effects of Atmospheric Pollutants, 1972).

In a survey of fly ashes representing several coals and combustion conditions, Aslund et al., (1978) found no individual species of POM to be present at concentrations greater than 20 ng/g. A number of other unidentified organic compounds were, however, observed at somewhat higher (10x) concentrations. It is important to note that all of these studies have considered fly ash collected in bulk from power plant control devices.

Only a few studies have been made of POM present in fly ash that was actually emitted and collected from the atmosphere (Natusch, 1978b; Tomkins, 1978; Stahley, 1976). However, all have indicated concentrations that are very much greater than encountered in fly ash collected within the plant. This apparent paradox has been explained by Natusch and Tomkins (1977) who postulate that POM (and probably other organic species) are present as gases at the temperatures encountered within a power plant but rapidly and quantitatively adsorb onto surfaces of emitted fly ash particles as the temperature falls on leaving the stack. Both laboratory (Miguel et al., 1979) and field (Miguel, 1976; Natusch, 1978b) studies support this hypothesis.

The actual compounds that have been identified in emitted fly ash are listed in Tables IX and X, which present the results of two separate studies in which specific concentrations inside and outside the plant, and volume concentrations in the plume, were determined. To our knowledge, only one study has actually measured POM concentrations as a function of particle size for emitted fly ash (Natusch, 1978b). The results indicated little convincing dependence of concentration on aerodynamic particle size over the range <1.1 to >7.0 μ m. However, the fly ash in question was derived from a small plant that employed a chain grate stoker, and the particles were found to be extremely irregular in outline. Furthermore, there was very little change in specific surface area over the size range collected. We do not, therefore, consider these results to be conclusive.

In fact, if the temperature dependent adsorption mechanism proposed by Natusch and Tomkins (1977) is correct, one would expect the specific concentration of organic species to vary in proportion to the surface area of the fly ash particles. There is some indirect evidence for this behavior (Chrisp et al., 1978; Fisher et al., 1979c), but further work is clearly required. It has been established, however, that adsorption of POM (pyrene) onto fly ash under laboratory conditions occurs, to significantly different extents, on different fly ashes and on magnetic and nonmagnetic fractions of a given fly ash (Miguel, 1976; Korfmacher et al., 1979a).

Table IX. Measurement of Polycyclic Organic Matter Emitted from a Coal-Fired Power Plant Stack^a

Compound	Specific concentration (μg/g)	
	Inside stack	Outside stack
Fluorene	ND ^b	Trace
Phenanthrene	ND	9
Fluroanthene	ND	19
Pyrene	ND	12
Benzofluorene	ND	2
1-Methylpyrene	ND	1
Benzophenanthrene	ND	3
Benzo[a]pyrene	ND	5
Total fluorescence	3.61 x 10 ⁻³ units	3.68 units

^a From Tomkins (1978).

^b Not detectable.

Table X. Emission Factors for Polycyclic Organic Matter from Coal Fired Furnaces in (pounds/ton of coal) x 10⁴ ^a

Species	Pulverized firing	Chain grate stoker	Hand fired
Benzo[a]pyrene	0.2-0.52	0.3	3520
Pyrene	0.8-1.6	3.5	5260
Benzo[e]pyrene	0 -2.3	1.1	880
Perylene	0 -0.6	--	526
Fluoranthene	--	6.0	8800

^a Committee on Biological Effects of Atmospheric Pollutants, 1972.

Finally, it should be mentioned that POM associated with fly ash may undergo chemical transformation following adsorption and emission. In this regard, Korfmacher et al., (1979b) have shown that adsorption onto coal fly ash effectively stabilized most POM against photochemical decomposition, but actually promotes rapid (hours to days) non-photochemical oxidation of polycyclic aromatic compounds possessing one benzylic carbon atom. Furthermore, Hughes and Natusch (1978) have shown that exposure of POM adsorbed on fly ash to typical plume concentrations of sulfur dioxide and nitrogen oxides results in very rapid formation of a variety of derivatives having sulfur or nitrogen containing substituents. It is possible, therefore, that the chemical nature of POM associated with coal fly ash emitted from a power plant is likely to change dramatically with time and distance from the plant.

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