Environmental Health Perspectives
Vol. 22, pp. 79–90, 1978

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

by D. F. S. Natusch*

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*).

*Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

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 (HCOH). Representative contributions are indicated in Table 2 (*13*). In addition, minor emissions of mercury occur, and it has been suggested that bromine (Br_2),

Table 1. Concentrations of known and suspected carcinogens in urban and rural atmospheres.

Substance[a]	Status	Urban air[b] Range	Urban air[b] Average[c]	Rural air (range)[b]	References
Inorganic cases, $\mu g/m^3$					
SO_x	Reactant	20–1200	70	0.1–5	(2, 4)
NO_x	Reactant	50–400	100	2–6	(2, 4)
O_3	Reactant	20–400	100	20–100	(2, 4)
Hg	Suspected	0.001–0.20	0.007	—	
Inorganic particulates, ng/m^3					
As	Recognized	2–130	10	< 0.5–5	(5, 6)
Asbestos	Recognized	10–100	20	—	(7)
Be	Recognized	< 0.2–8	5	—	(5, 6)
Cd	Recognized	4–250	10	—	(5, 6, 8)
Co	Suspected	0.5–15	2	< 0.5–2	(5, 8)
Cr	Recognized	5–120	15	< 1–10	(5, 8)
Cu	Suspected	10–4000	60	1–280	(5, 8)
F[d]	Suspected	< 50–2000	300	< 50–150	(5)
Fe	Suspected	1000–2000	1400	10–1000	(5, 8)
Ni	Recognized	10–1000	100	< 10	(5, 6, 8)
Pb[e]	Suspected	500–3000	1500	10–100	(5, 6, 8)
Se[f]	Suspected	< 1–10	1	—	(5)
SO_4^{2-}	Suspected	1000–100,000	5000	—	(2, 5)
U	Recognized	0.01–2	0.2	—	(9)
V[g]	Suspected	50–2000	500	< 1–50	(5, 6, 8)
		1–100	10		
Total particulates	Reactant	$(60–220) \times 10^3$	140×10^3	$(5–60) \times 10^3$	(4, 5)
Radionuclides, Ci/m^3					
^{210}Pb	Recognized	$(1–30) \times 10^{-15}$	20×10^{-15}	$(55–10) \times 10^{-15}$	(9)
^{212}Pb	Recognized	$(0.1–4) \times 10^{-15}$	2×10^{-15}	$(0.03–0.06) \times 10^{-15}$	(9)
^{226}Ra	Recognized	$(50–100) \times 10^{-18}$	—	—	(9)
^{222}Rn	Recognized	$(20–1000) \times 10^{-12}$	200×10^{-12}	$(0.1–20) \times 10^{-12}$	(9)
^{228}Th	Recognized	$10–50) \times 10^{-18}$	30×10^{-18}	—	(9)
^{230}Th	Recognized	$(20–70) \times 10^{-18}$	50×10^{-18}	—	(9)
^{232}Th	Recognized	$(10–50) \times 10^{-18}$	30×10^{-18}	—	(9)
$^{234}U + ^{238}U$	Recognized	$(100–400) \times 10^{-18}$	200×10^{-18}	—	(9)
Gaseous and particulate organic species					
Alkanes, ng/m^3[i]					(3, 4)
n-Butane	Reactant	5–80	10	—	
n-Pentane	Reactant	1–40	15	—	
2-Methylbutane	Reactant	5–60	25	—	
Alkenes, ng/m^3[i]					(4)
2-Butene	Reactant	1–5	6	—	
1,3-Butadiene	Reactant	1–5	2	—	
Propene	Reactant	1–20	6	—	
Aldehydes and ketones, ng/m^3					(3, 7)
Formaldehyde	Suspected	5–100	20	0.5–5	
Acrolein	Suspected	< 1–20	5	—	
Nitrosamines,[j] ng/m^3					(10)
Dimethylnitrosamine	Recognized	20–100	—	—	
Peroxides, ng/m^3					(3, 4)
Peroxyacylnitrates	Suspected	2–30	—	—	
Aromatic hydrocarbons, ng/m^3					(3, 7)
Benzene	Recognized	5–90	20	—	
Toluene	Reactant	10–100	40	—	
1,2-Dimethylbenzene	Suspected	5–100	40	—	
1,3-Dimethylbenzene	Suspected	5–100	40	—	
1,4-Dimethylbenzene	Suspected	5–100	40	—	
Polyaromatic hydrocarbons,[k] ng/m^3					(2, 11, 12)
Anthracene	Reactant	0.5–700	1	—	
Benzo[a]pyrene	Recognized	1–50	10	—	
Benzo[e]pyrene	Suspected	0.1–50	5	—	
1,2-Benzanthracene	Recognized	1–70	20	—	
1,12-Benzperylene	Reactant	0.1–20	3	—	
Coronene	Reactant	0.2–50	1	—	
Chrysene	Suspected	0.5–200	5	—	
Pyrene	Reactant	0.2–50	10	—	

Table 1 (cont'd.)

Polycyclic nitrogen compounds, ng/m³					(2, 12)
Acridine	Suspected	0.1–0.5	—	—	
Fluorene carbonitrile	Suspected	0.02–0.1	—	—	
Lead tetraalkyls, ng/m³					(6)
Tetraethyllead	Suspected	50–2000	75	—	
Benzene-soluble organics, ng/m³	Recognized	1000–20,000	7000	200–3000	(2, 4, 7)

[a]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.

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

[c]Approximate averages 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.

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

[e]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.

[f]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.

[g]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.

[h]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.

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

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

[k]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.[a]

		Emissions, lb/1000 lb fuel				
Fuel	Particles[a]	CO	HC	NO_2	SO_2	HCOH
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

[a]Data of Goldstein and Waddams (*13*).

[b]*E* is the mass collection efficiency of the control equipment.

[c]As the percent sulfur content of the fuel by weight.

hydrochloric acid (HCl), selenium dioxide (SeO_2), arsenic trioxide (As_4O_6), 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 absence 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 SO_3, which reacts rapidly with water vapor to produce sulfuric acid mist. A small amount of the SO_2 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.

Nitrogen Oxides

As in the case of sulfur oxides, the oxides of nitrogen are not carcinogenic but may produce carcinogenic materials as a result of chemical reactions such as those involved in photochemical smog formation. By contrast with sulfur oxides, which are derived from sulfur present in the fuel, nitrogen oxides are derived primarily from fixation (oxidation) of atmospheric nitrogen present in the combustion feed air. Consequently, nitrogen oxides cannot be effectively controlled by selection or pretreatment of the fuel.

Representative emission factors for nitric oxide (NO) and nitrogen dioxide (NO_2) combined are given in Table 2, 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, the temperature, and the fuel-air mixing characteristics. Actual concentrations of NO_x are normally in the range 300–1300 ppm in stack emissions. Significantly higher concentrations are produced during natural gas combustion than during combustion of coal or oil (Table 2).

The amount of NO_2 formed during combustion is generally much less than that of NO; however, conversion of NO to NO_2 occurs fairly rapidly in a power plant plume following emission. From the standpoint of human health, therefore, it is reasonable to presume that the primary direct exposure will be to NO_2.

Organic Gases

The amounts of organic material emitted as gases or vapors from fossil-fueled power plants are quite small (2.5%) when compared with those from other anthropogenic sources. For example, transportation accounts for some 53% of the gaseous organics emitted in the United States. Consequently, rather little work has been done to determine the identities and amounts of individual organic gases emitted from power plants. Primary emissions consist of hydrocarbons, aldehydes, and organic acids for which representative emission factors are given in Table 3. Of these materials only certain aldehydes (e.g. formaldehyde and acrolein) are suspected carcinogens. Hydrocarbons and organic acids are, however, quite reactive (hydrocarbons in photochemical smog production) and are thus worthy of consideration in the present context (*3*).

Table 3. Typical emission of several classes of compounds from stationary combustion sources.[a]

Compounds	Emission, lb/ton of fuel		
	Coal	Oil	Gas
Hydrocarbons	0.3	1.0	1.0
Aldehydes	Unknown	0.5	0.5
Formaldehyde	0.0003	0.006	0.008
Organic acids	10	5	2

[a]Data from National Academy of Sciences (*3*).

Other Gaseous Emissions

With the exception of elemental mercury vapor, very little is known about gaseous emissions other than those already discussed. Mercury is, however, a suspected carcinogen.

Mercury levels in coal and fuel oil average about 1 μg/g and 0.1 μg/g, respectively. When the coal is burned, about 90–95% of the mercury present is emitted to the atmosphere as elemental vapor. The remainder is associated with fly ash. There is no apparent tendency for mercury vapor to become adsorbed or otherwise associated with fly ash or atmospheric aerosols. Consequently, mercury is transported long distances from a coal fired power plant. This behavior is exactly opposite to that of other, particulate associated, metals.

The actual concentrations of mercury vapor emitted from a given power plant will depend on the type and origin of the fuel burned; however, because of the almost quantitative release of mercury to the atmosphere, stack concentrations can be readily calculated where stack gas flow rates are known. Typical stack exit concentrations are around 1 $\mu g/m^3$ for a coal fired power plant. Plume concentrations depend, of course, on atmospheric conditions but concentrations around 80 ng/m^3 have been measured (*17*) at ground level on the plume center line 1.2 miles downwind of a coal fired power plant. Representative concentrations in urban atmospheres lie in the range 2–100 ng/m^3, most of which is present as mercury vapor (*18*).

Fossil fuel combustion also results in the release to the atmosphere of several radioactive species including the gas radon (^{222}Rn), which, with its daughter products, is a known carcinogen. The few available measurements indicate that natural gas contains 10–20 pCi/l of ^{222}Rn and that coal contains 0.1–0.4 pCi/g. While quantitative release of radon to the atmosphere will occur, present estimates suggest that fossil fuel combustion does not contribute significantly to the natural ^{222}Rn background even in the vicinity of power plants (*9*).

Particulate Emissions

Fossil-fueled power plants contribute approximately 25% of the anthropogenic particulate matter emitted to the atmosphere in the United States. In

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.

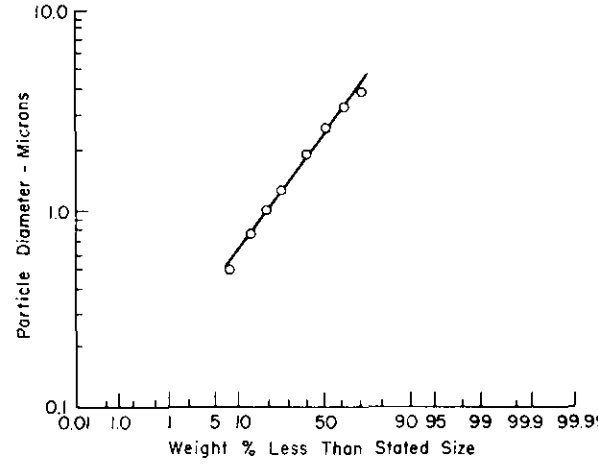

FIGURE 1. Representative aerodynamic particle size distribution of fly ash emitted from a coal fired power plant equipped with an electrostatic precipitator (*21*).

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

of microcrystalline hematite (Fe_2O_3) magnetite (Fe_3O_4), α-quartz (SiO_2), mullite ($3Al_2O_3 . 2SiO_2$), anhydrite ($CaSO_4$), and lime (CaO). In addition some elemental carbon (soot) particles are present. All these compounds have low solubility in water which accounts for the low bulk solubility of fly ash. The compounds present in fly ashes derived from oil and natural gas combustion have not been established although it is known that such particles are highly carbonaceous in nature.

Table 4. Typical matrix element composition ranges of some U. S. coal fly ashes expressed as weight percentages of the oxides.

	Matrix element composition, wt-% of oxide
Major constituent	
Al_2O_3	14–30
SiO_2	22–60
Fe_2O_3	3–21
K_2O	0.2–3.5
CaO	0.5–31.0
Minor constituents	
Li_2O	0.01–0.07
Na_2O	0.2–2.3
MgO	0.7–12.7
TiO_2	0.6–2.6
P_2O_5	0.1–1.1
SO_4[b]	0.1–2.2

[a]Data of Natusch (*15*).
[b]Soluble sulfate.

Trace Elements

As a result of their geological origins coal and petroleum oil contain essentially all known stable elements in minor or trace amounts. Of these, the elements As, Be, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb, Se, and V are regarded as either known or suspected carcinogens. It must be strongly emphasized, however, that the chemical and toxicological properties of any element depend upon the nature of the chemical compound in which that element is present. Unfortunately very little is known about the identities of metal compounds emitted in particulate form from fossil fueled power plants. Consequently it is accepted, though strictly incorrect, practice to refer to the metallic elements themselves.

The specific concentrations (μg/g) of individual trace elements found in coal and oil fly ashes depend primarily on the trace element content of the original fuel. However, the relative concentrations of elements differ significantly between fly ash and fuel due to the different partitioning characteristics of individual elements between bottom ash and fly ash. Thus, in the case of coal fly ash, it is not reasonable to assume that because a given fraction of one element ends up in emitted fly ash that the same fraction of other elements will do likewise. This assumption is, however, reasonable in the case of an oil fired power plant which produces very little combustion residue.

Some representative specific (μg/g) and volume ($\mu g/m^3$) concentrations of trace elements emitted from coal and oil fired power plants are presented in Table 5. It should be noted that volume concentrations will be highly dependent on individual plant operating conditions. It should also be noted that vanadium, V, is emitted in substantial amounts from the combustion of fuel oil. This is because the element is concentrated in the form of several vanadium porphyrins in the original fuel (*24*).

At this point it is appropriate to comment on the partitioning of different elements in coal-fired (and probably also oil-fired) power plants. The most important aspect in this regard is that several potentially carcinogenic elements or their compounds are apparently volatilized at the combustion temperatures (1400–1600°C) encountered. These elements then condense or absorb onto the surface of co-entrained fly ash particles as both particles and vapors leave the combustion region. Since small particles have a greater specific surface area than do large particles this phenomenon results in the volatile elements becoming preferentially associated with small particles (*14*). Table 6 presents data showing how the specific concentrations of several potentially carcinogenic elements depend on aerodynamic particle size in fly ash both emitted and retained by a representative coal-fired power plant.

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 the bulk fly ash with the following important results: (1) many potentially carcinogenic trace elements are most concentrated in the small, pulmonary depositing, fly ash particles which are least effectively collected by existing particle control devices; (2) the concentrations of volatilizable trace elements determined by analyzing fly ash collected by control devices are very much lower than the concentrations of those elements actually emitted. Trace element emission factors cannot, therefore, be obtained by multiplying the specific concentration of an element measured in retained fly ash by the bulk particle emission factor.

It should be pointed out that, although the specific concentrations of volatilizable elements increase more or less linearly with inverse particle diameter (*14, 25*), the same is not true when volume

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

Element	Coal fly ash		Oil fly ash	
	Specific concn, μg/g	Volume concn, μg/m³	Specific concn, μg/g	Volume concn, μg/m³
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	500–10,000	1600
Be	1–10	—	—	—
Br	0.3–20	1–5	—	—
Ca	6000–180,000	300–1000	10–1000	500–700
Cd	0.1–50	—	—	—
Ce	100–300	—	—	1–2
Cl	10–500	—	—	—
Co	5–100	1–5	90	16
Cr	50–300	8–20	66	12
Cs	1–20	—	—	0.1
Cu	50–650	—	50–2000	—
Fe	25,000–300,000	4000–10,000	10,000–100,000	700–1000
Ga	10–250	2–10	—	—
Hf	5–10	—	—	—
Hg	0.02–0.4	—	—	—
I	0.5–7	15–40	—	—
In	0.1–0.3	—	—	—
K	1500–35,000	—	1000	—
La	35–100	2–10	—	2.5
Lu	0.5–2	—	—	—
Mg	11,000–60,000	300–1000	500–5000	—
Mn	50–500	—	1–100	8
Mo	5–40	70–200	—	—
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	—	0.03
Se	1–20	5–15	5	0.6
Sm	10–20	—	—	0.15
Sn	30–30	—	—	—
Sr	50–4000	—	—	—
Ta	0.5–1.5	—	—	—
Th	15–70	0.5–3.0	—	0.13
Ti	3500–8500	300–700	—	—
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 (μg/m³) 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, ^{238}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, ^{232}Th, and ^{238}U 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.

Table 6. Specific concentrations of several potentially carcinogenic elements in coal fly ash as a function of particle size.[a]

	Particle diameter, μm	Specific concentration, μg/g					
		Pb	Cd	Se	As	Ni	Cr
Fly ash retained in plant							
Sieved fractions							
	< 74	140	< 10	< 12	180	100	100
	44–74	160	< 10	< 20	500	140	90
Aerodynamically sized fractions							
	< 40	90	< 10	< 15	120	300	70
	30–40	300	< 10	< 15	160	130	140
	20–30	430	< 10	< 15	200	160	150
	15–20	520	< 10	< 30	300	200	170
	10–15	430	< 10	< 30	400	210	170
	5–10	820	< 10	< 50	800	230	160
	< 5	980	< 10	< 50	370	260	130
Airborne fly ash							
	> 11.3	1100	13	13	680	460	740
	7.3–11.3	1200	15	11	800	400	290
	4.7–7.3	1500	18	16	1000	440	460
	3.3–4.7	1550	22	16	900	540	470
	2.1–3.3	1500	26	19	1200	900	1500
	1.1–2.1	1600	35	59	1700	1600	3300

[a]Data of Davison (*14*).

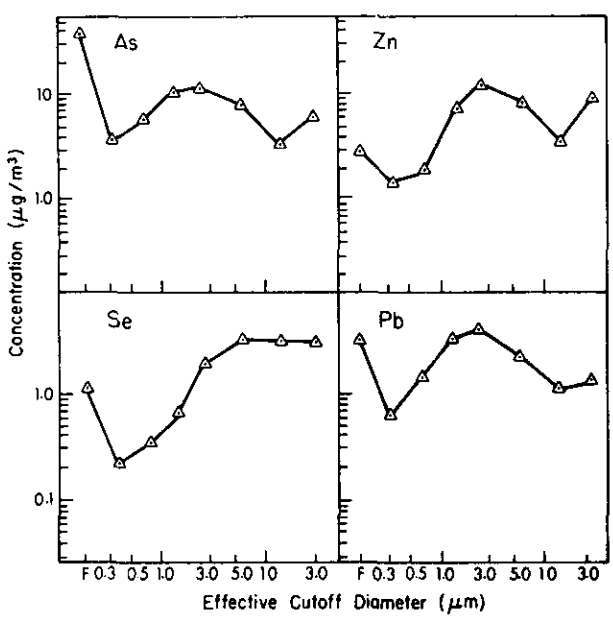

FIGURE 2. Representative aerodynamic particle size dependences of the elements As, Pb, Se, and Zn in fly ash emitted from a coal fired power plant. F refers to the final filter employed with the cascade impactor used in sampling (*23*).

Surface Association of Trace Elements

Recent results (*30*) have established that a number of trace elements, including several potential carcinogens are more highly concentrated on the surfaces of coal fly ash particles than in their interior. This phenomenon is probably due to particle surface deposition of elements volatilized during combustion and is found to occur for particles derived from a variety of high temperature combustion or smelting operations, e.g., automobile exhaust particulates and blast furnace dusts (*31*).

It is difficult to make quantitative measurements of surface concentrations. However, some semiquantitative estimates of specific concentrations of several potentially carcinogenic elements present in a shell 300 Å thick at the surface of coal fly ash particles are compared to bulk concentrations in Table 7 (*31*). It should be stressed that these data are presented primarily for the purposes of illustration and should not be regarded as definitive. This surface association is considered to be of considerable importance in determining the toxicity of trace elements in coal fly ash. The following reasons are cited. (1) Since it is the surface of a particle which comes into immediate contact with the external environment (e.g. body fluids and tissues), the surface predominance of toxic trace elements ensures their

Table 7. Estimated surface concentrations of elements in coal fly ash.

Element	Bulk concentration, μg/g	Estimated surface concentrated in 300 Å layer, μg/g
As	600	1,500
Cd	24	700
Co	65	440
Cr	400	1,400
Pb	620	2,700
S	7,100	252,000
V	380	760

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 microregion 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

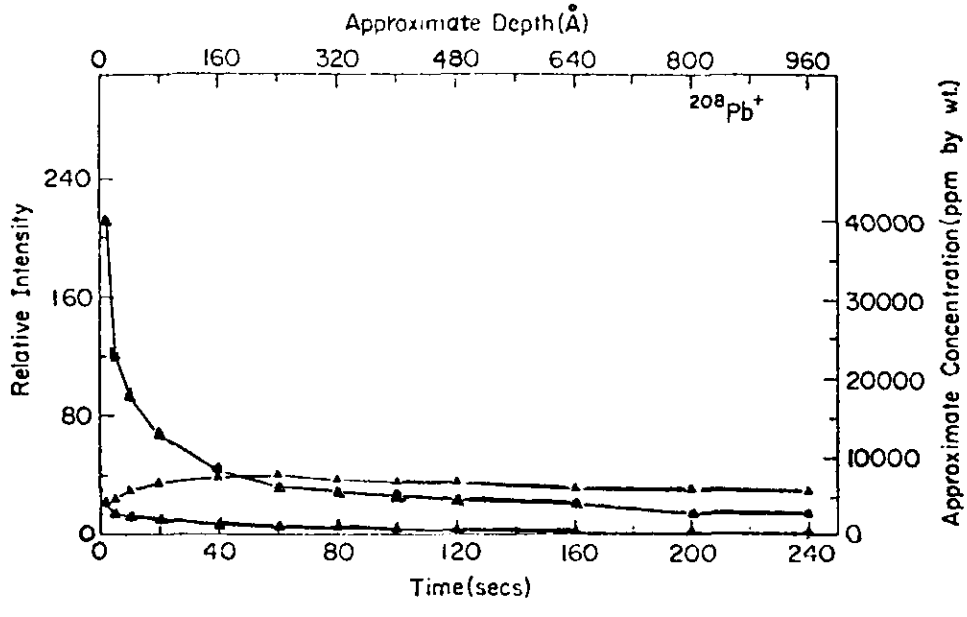

FIGURE 3. Depth profiles of Pb associated with coal fly ash recorded (*a*) before, and (*b*) after leaching the fly ash with water and dimethyl sulfoxide (*16*).

placed on hydrocarbons and little attention has been paid to heterocyclic compounds containing oxygen, nitrogen, or sulfur. Similarly, derivatives containing substituents such as carboxylic, nitro, sulfonic acid, or phenolic groups (if, indeed, they occur) have received little attention. At this time, therefore, the only polycyclic organic compounds which have been uniquely identified as being associated with fly ash emitted by fossil fuel power plants are listed in Table 8 (*15, 16, 33*). It should be noted that many more compounds have been tentatively identified but have not yet received full confirmation.

Table 8. Polycyclic organic compounds identified in stack and plume particulates from coal-fired power plants.[a]

	Polycyclic organic compounds		
	In stack,	In plume, ng/m³	
Compound	ng/m³	0–5 miles	5–10 miles
Fluoranthene	2.7	5.0	4.4
Pyrene	16.4	60	9.0
Benzo[a]anthracene	69	232	14.4
Chrysene	48	68	10.8
Perylene	< 2	7.0	8.6
Benzo[e]pyrene	9.8	15.8	13.2
Benzo[a]pyrene	12.9	16.2	8.2
Benzoperylene	12	13	—
1,2,4,5-Dibenzopyrene			
3,4,7,10-Dibenzopyrene			
Phenanthrene			
Dimethylbenzanthracene			
Anthracene			
Benzo[k]fluoranthene			
9,10 dimethyl anthracene			
Benzo[b]phenanthrene			
Fluorene			
Triphenylene			

[a]Data of Stahley (*33*) and Korfmacher et al. (*34*).

A number of studies of particulate polycyclic organic matter (POM) emitted by fossil fueled power plants have concluded that total emissions are negligibly small compared with those from other sources (*2*). A summary of reported emission factors for several coal combustion operations is presented in Table 9. These figures translate to a total emission of 1 ton of benzo[a]pyrene from all coal-fired power plants in the United States. The much higher emission factors associated with hand stoked furnaces are attributed to inefficient combustion.

Table 9. POM emission factors for coal-fired furnances.[a]

	POM emission factors, lb/ton coal × 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[e]pyrene	0–2.3	1.1	880
Perylene	0–0.6	—	526
Fluoranthene	—	6.0	8800

[a]National Academy of Sciences data (*2*).

There is now substantial evidence indicating that most, if not all, organic material remains in the vapor phase so long as the stack gases are within a power plant stack system (*15, 32, 33*). With the temperature decrease which occurs following emission to the atmosphere, however, rapid adsorption of organics onto the surfaces of co-entrained fly ash particles takes place. What this means is that fly ash retained by control equipment or collected within a power plant stack contains only a small fraction of the total organic material emitted. Conversely, emitted fly ash contains much higher specific concentrations (μg/g) of organics than the same fly ash prior to emission. In establishing POM emission factors, therefore, it is vitally important to ensure that material present in both vapor and particulate form be included when samples are collected from within a plant.

In view of the high carcinogenic potential of POM (*2*), this vapor-to-particle conversion process is of more than academic interest since it has the following ramifications.

Since polycyclic organic compounds appear to associate with fly ash by adsorption they will be present primarily on particle surfaces which can make intimate contact with lung tissues and fluids. Furthermore, preliminary indications are that extraction into solution is quite facile (*31*).

Since adsorption depends upon the available surface area of particulate adsorbent the highest specific concentrations of POM will be found associated with small particles in the respirable range. In fact size distribution studies indicate that the aerodynamic mass median diameter of benzo[a]pyrene in fly ash emitted from a coal fired power plant is around 0.1 μm (*1, 33*). In short, it is reasonable to assume that essentially all POM derived from fossil fueled power plants is capable of pulmonary deposition.

Since particulate association of POM apparently occurs primarily following emission, analysis of particulate material collected inside a power plant stack may provide a gross underestimate of POM emissions (*16*). This point is illustrated by the data in Table 8, which show that when account is taken of dilution, significantly (possibly several orders of magnitude) higher concentrations of POM are found in emitted fly ash than in that collected in a power plant stack (*33*). While there is no reason, at this time, to disbelieve the mission estimates presented in Table 9, it is of considerable importance that they be fully substantiated by additional measurements relating to modern fossil fueled power plants.

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.

Part of the research described herein was supported by grants ERT-74-24276, MPS-74-05745, and DMR-73-030206 from the United States National Science Foundation and by grant R-803950-01 from the United States Environmental Protection Agency.

REFERENCES

1. Natusch, D. F. S., and Wallace, J. R. Urban aerosol toxicity: the influence of particle size. Science 186: 695 (1974).
2. National Academy of Sciences (U.S.). Particulate Polycyclic Organic Matter. Committee on Biological Effects of Atmospheric Pollutants, Division of Medical Sciences, National Research Council, National Academy of Sciences, Washington, D. C., 1972.
3. National Academy of Sciences (U. S.). Vapor Phase Organic Pollutants. Committee on Biological Effects of Atmospheric Pollutants, Division of Medical Sciences, National Research Council, National Academy of Sciences, Washington, D. C., 1976.
4. American Chemical Society. Cleaning our Environment: The Chemical Basis for Action. American Chemical Society, Washington, D. C., 1969.
5. Rhan, K. A. The chemical composition of the atmospheric aerosol. Technical report, Graduate School of Oceanography, University of Rhode Island, Kingston, R. I., 1976.
6. Schroeder, H. A. Trace metals in the air. Environment 13: 18 (1971).
7. Sax, N. I. Toxicological effects of non-nuclear pollutants. In: Atmospheric Science and Power Production. D. Randerson, Ed., US-ERDA. Washington, D. C., in press.
8. Lee, R. E., Jr., et al. National air surveillance cascade impactor network II. Size distribution measurements of trace metal components. Environ. Sci. Technol. 6: 1025 (1972).
9. National Council on Radiation Protection and Measurements. Natural Background Radiation in the United States. NCRP.
10. Shapley, D. Nitrosamines: Scientists on the trail of prime suspect in urban cancer. Science 191: 268 (1976).
11. Kertész-Sáringer, M., and Morlin, Z. On the occurrence of polycyclic aromatic hydrocarbons in the urban area of Budapest, Atmos. Environ. 9:831 (1975).
12. Lao, R. C., et al. Application of gas chromatography–mass spectrometry–data processor combination to the analysis of the polycyclic aromatic hydrocarbon content of airborne pollutants. Anal. Chem. 45: 908 (1973).
13. Goldstein, R. F., and Waddams, A. L. The Petroleum Chemicals Industry, 3rd ed. E. and F. Spon Ltd., London, 1967.
14. Davison, R. L., et al. Trace elements in fly ash: dependence of concentration on particle size. Environ. Sci. Technol. 8: 1107 (1974).
15. Natusch, D. F. S. Characterization of atmospheric pollutants from power plants. In: Proceedings of the Second Federal Conference on the Great Lakes. Great Lakes Basin Commission, 1976.
16. Linton, R. W., et al. Determination of the surface predomi-

nance of toxic elements in airborne particles by ion microprobe mass spectrometry and auger electron spectrometry. Anal. Chem., 49: 1514 (1977).
17. Skogerboe, R. K. Department of Chemistry, Colorado State University, Fort Collins, Colorado, personal communication, 1976.
18. Johnson, D. L., and Braman, R. S. Distribution of atmospheric mercury species near ground. Environ. Sci. Technol. 8: 1003 (1974).
19. Natusch, D. F. S., et al. Characterization of trace elements in fly ash. Proceedings, International Conference on Trace Metals in the Environment. Toronto, Canada, Oct. 1975. Vol. II, Part 2, p. 535.
20. McCrone, W. C., and Delly, J. G. The Particle Atlas. Ann Arbor Science Publishers, Ann Arbor, Mich., 1973.
21. Jones, H. R. Fine dust and particulates removal. Pollution Control Rev. No. 11, Noyes Data Corp., Park Ridge, N. J., 1972.
22. Bickelhaupt, R. E. Surface resistivity and the chemical composition of fly ash. J. Air Pollut. Control Assoc. 25: 148 (1975).
23. Gordon, G. E. Study of the Emissions from Major Pollution Sources and their Interaction. Progress Report Nov. 1972 to October 1974, Univ. Maryland, College Park, Md., 1977.
24. Gordon, G. E., et al. The sources and distribution of vanadium in the atmosphere. In: Trace Elements in the Environment. (Adv. Chem. Ser. No. 123) E. L. Kothny, Ed., American Chemical Society, Washington, D. C. 1973, p. 31.
25. Kaarkinen, J. W., et al. Trace element behavior in a coal fired power plant. Environ. Sci. Technol. 9: 862 (1975).
26. Bayliss, R. J., and Whaite, H. M. A study of the radium alpha-activity of coal, ash and particulate emission at a Sydney power station. Air Water Pollut. Int. J. 10: 813 (1966).
27. Pensko, J., and Stpiczynska, Z. Internal report 0-310/XIX/75, Swierk, Poland, 1975.
28. Klein, D. H., et al. Pathways of thirty-seven trace elements through a coal fired power plant. Environ. Sci. Technol. 9: 973 (1975).
29. Martin, J. E., Harvard, E. D., and Oakley, X. International Atomic Energy Association Publication STI/PUB/261, Vienna, 1971.
30. Linton, R. W., et al. Surface predominance of trace elements in airborne particles. Science 191: 852 (1976).
31. Natusch, D. F. S. Unpublished results, 1977.
32. Natusch, D. F. S. Characteristics of pollutants from coal combustion and from coal and oil shale conversion processes. In: Toxic Effects on the Aquatic Biota from Coal and Oil Shale Development, Natural Resources Ecology Laboratory, Colorado State University, Fort Collins, Colo., 1976.
33. Stahley, S. (Department of Chemistry, University of Maryland, College Park, Md.), personal communication, 1976.
34. Korfmacher, W. A., Natusch, D. F. S., and Wehry, E. Unpublished results, 1977.