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Chemical and Biological Characterization of Emissions from Coal- and Oil-Fired Power Plants

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Emission samples were obtained from two medium-sized power plants, one fired with oil and the other with pulverized coal. Particles obtained by a miniscale plume stack gas sampler (MIPSGAS), simulating the dilution process in the plume, were subjected to detailed physical, chemical and biological characterization. Studies by scanning electron microscopy and by Coulter counter demonstrated that the particles from the oil-fired boiler were considerably larger than the particles from the coal-fired boiler. Chemical analyses revealed more organic substances and more S, Ni, V, in the oil than in the coal particles. The latter contained a larger proportion of Al, Si, Cl, K, Ca, Ti, Mn, Fe, Se, Rb, Y, Zr, Ba and Pb.

Biological testing revealed a greater acute and subacute toxicity by the intratracheal route in the hamster, a greater toxicity to alveolar macrophages and a greater lung retention of BaP coated on the particles from oil combustion than on those from coal combustion.

In another sampling line, employed simultaneously with the MIPSGAS-particulate sampler, the total emissions were collected, i.e., both particle and gas phase. These samples were used for chemical analyses and Ames mutagenicity test. Analyses of specific PAHs in emissions from both plants demonstrated that concentrations were below the detection limit (< 4 ng/m^3 of benzo(a)pyrene), which is in accord with an efficient combustion of the fuel. The mutagenicity of the samples were below the detection limit of the mutagenicity assay.

Introduction

Sweden is heavily dependent on oil as a source of energy. In order to reduce this oil dependence it has been considered useful to reintroduce coal for energy production purposes. While the present usage of coal for production of heat and electricity is negligible, it is foreseen that approximately 6 million tons of coal will be used in 1990, with a further increase later on. In order to assess the potential health effects of increased coal utilization, a comparison between the health effects of emissions from coal- and oil-fired boilers is one main objective. In this context it seemed pertinent to perform a detailed biological and chemical characterization of the respective emissions.

The sampling of particulate and gaseous material in a representative manner constitutes an important consideration, since it is known that particulate emissions may be considerably changed with regard to their chemical composition during the dilution and cooling process that takes place in the stack gas plume. In order to sample particulate material that would, as far as possible, be representative of the particles as they occur in the environment, a probe was used that simulates the plume process. Particles thus obtained were characterized through morphological studies by scanning electron microscopy (SEM), determination of particle size distribution, chemical analysis of organic and inorganic constituents and studies of the retention properties of the particles in the lungs of

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experimental animals, their influence on phagocytosis of alveolar macrophages as well as their toxicity by the intratracheal route of administration. The design of a long-term carcinogenicity study in animals is also reported.

In order to include the gas phase of the emissions also, another sampling line was used in which particulates were separated at the temperature of the stack gases. These samples were used for chemical analyses and for short-term bioassay in the form of the Ames mutagenicity test. Although individual characteristics of emissions from oil- and coal-burning facilities have previously been reported (*1–4*), there seems to be no similarly complete comparative study reported in the literature.

Sampling

Two different power plants were chosen for this study. The first was an oil-fired boiler (Sulzer once through) equipped with turbo generators with a nominal electric power of 250 MW and a heat power production between 150 and 200 MW. The boiler was fired with heavy fuel oil with an ash content of 0.06% and a sulfur content of 2%. The sampling was done after the heat exchange and before the electrostatic precipitator. The second was a boiler fired with pulverized coal (Benson once through VKW AG) equipped with turbogenerators for the production of electric power, 265 MW nominal effect. The boiler was equipped with electrostatic precipitators with a guaranteed separation efficiency of 99.1%. The boiler was fired with Polish coal which had an ash content of 13% and a sulfur content of 0.8%. The sampling was done after the electrostatic precipitator.

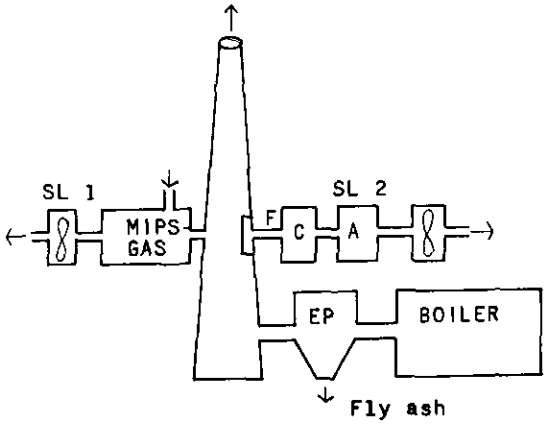

FIGURE 1. Schematic of the sampling arrangement for sampling line 1 (SL 1) and sampling line 2 (SL 2) at the coal-fired power plant. At the oil-fired power plant the sampling was done before the electrostatic precipitator (EP).

Methods

Sampling Methods

At each power plant the stack gases were sampled by two different extractive stack gas sampling methods simultaneously (Fig. 1). Carbon monoxide, carbon dioxide, nitrogen oxides and total hydrocarbons were monitored continuously during the sampling.

Sampling Line 1 (SL 1): Miniscale Plume Stack Gas Sampler (MIPSGAS). To obtain a gas particulate sample with a chemical composition which closely resembles the chemical composition of particles released to the environment, a miniscale plume stack gas sampler was used (Fig. 2) (*5*). The sampler employs a dilution probe to imitate the dilution and cooling process in the flue gas plume.

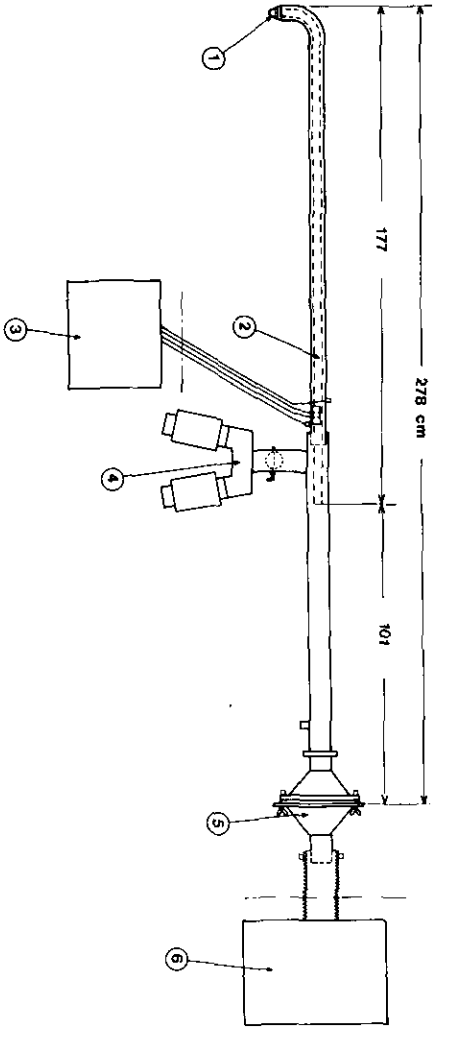

FIGURE 2. Miniscale plume stack gas sampler (MIPSGAS) used for the sampling with dilution cooling in sampling line 1.

The flue gases were sampled isokinetically and transported through a porous tube in which filtered air (aerosol filter) diffuses through the walls to keep wall losses low (approximately 10%). The flow gases were cooled by dilution with filtered ambient air, dilution ratio 1/10, to a temperature slightly above ambient. Typical flow rates were: sampling flow, 80 L/min, sheath air 20 L/min and dilution air 1000 L/min. The particulates in the diluted and cooled flue gas were thereafter collected in a Sierra high volume impactor equipped with a final high volume filter sampler. As a final filter Gelman glass fiber filters were used. The residence time in the system was about 0.4 sec.

The samples collected in sampling line 1, denoted coal fly ash 1 and oil soot 1, respectively, were used for the investigations outlined in Figure 3.

Sampling Line 2 (SL 2): Filter–Condenser–Absorber (FCA). During the sampling period the emission was characterized by discrete stack gas samples taken in an all-glass sampling train system (Figs. 1 and 3). The flue gases were sampled isokinetically at a rate of about 60 L/min. Sampling times varied between 4 and 7 hr. All parts of the sampling equipment were made of glass or Teflon. The particulate matter in the flue gases was at first collected "in-stack" on a borosilicate fiber filter thimble. The filter temperature was about 150–200°C. The filtered flue gas was thereafter cooled to about 5–10°C, and the condensate was collected in 50 mL of a buffered pH 7 aqueous solution. (To prepare the buffer, 10*M* NaOH is added to 1*M* KH_2PO_4 until pH 7 is reached.) The dried flue gas was then finally passed through a column containing Amberlite XAD-2 adsorbent (bed volume 50 mL). The XAD-2 adsorbent had been precleaned by ultrasonic rinsing in ethanol until no white turbidity in the ethanol remained, thereafter Soxhlet-extracted with acetone (24 hr) and then dried in a nitrogen flow at 150°C until no acetone smell remained.

The filter (after weighing) and the XAD-2 adsorbent were Soxhlet-extracted with acetone (at least 100 cycles). The water condenser, the filter holder and the Teflon tubing were rinsed with 20 mL of ethanol. The condensate with the ethanol rinse was extracted with methylene cloride. The extracts were concentrated at reduced pressure to a volume of 5 mL. Aliquots of the particulate extract, the adsorbent extract and the condensate extract were combined and were further concentrated at reduced pressure to a volume of 0.5 mL total extract. This total extract was then dissolved in a small volume of acetone (5 mL) and concentrated at reduced pressure to strip off the methylene chloride.

To identify aldehydes, separate flue gas samples were taken out through Teflon tubing. The aldehydes were absorbed in two impingers in series containing 20 mL of 2,4-dinitrophenyl hydrazine in 2*M* hydrochloric acid solution. At no time were aldehydes detected in the second impinger.

Samples for volatile components were taken in 0.5 L gas pipets. To determine benzene and toluene in some samples, small adsorption columns containing Carbopack C/activated carbon was used. The

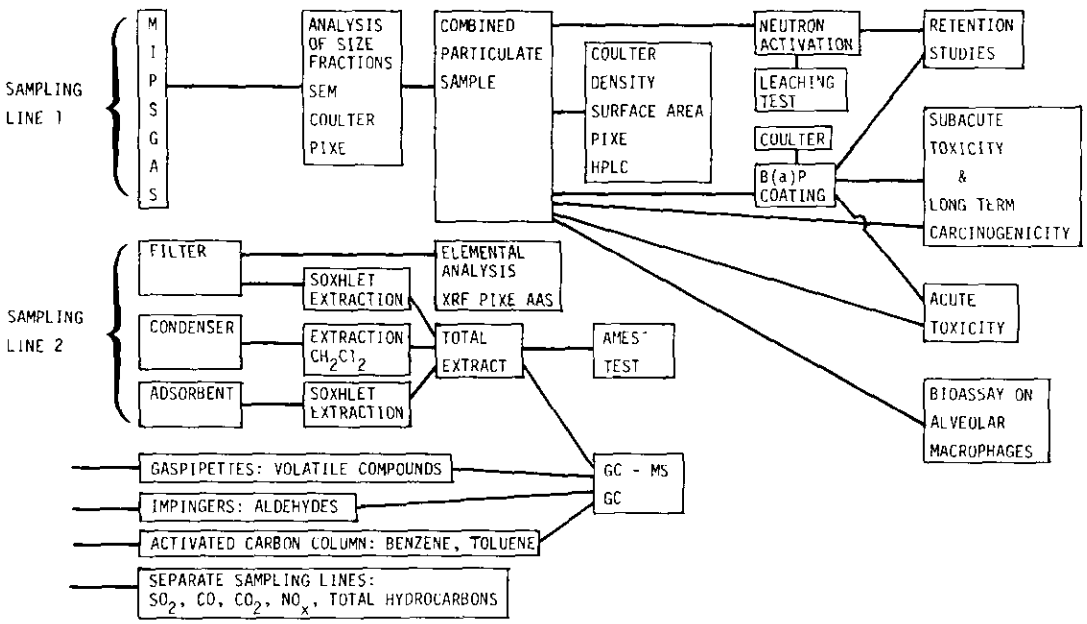

FIGURE 3. Outline of the sampling and the sample processing for the two main sampling lines, SL 1 and SL 2, and for the separate sampling lines.

samples collected in sampling line 2, denoted coal fly ash 2 and oil soot 2, were examined according to Figure 3.

Analyses

Flue Gas Parameters. Flue gas parameters were monitored in separate sampling lines (Fig. 3). The carbon dioxide and the carbon monoxide concentrations were analyzed continuously by infrared absorption measurement (Uras). Nitrogen oxides were analyzed continuously with a chemiluminiscence instrument (Monitor Labs).

To determine the total amounts of hydrocarbons, the flue gases were at first filtered (filter temperature 150–200°C) and thereafter suctioned through heated Teflon tubing (150–200°C) to the total hydrocarbon analyzer (Ratfisch flame ionization detector).

Chemical Analysis. The "total extract" from sampling line 2 was analyzed in the following way. Extractable matter was analyzed by gas chromatography with a flame ionization detector (GC-FID). The quantification (determined as milligrams hexacosane equivalents) was done with a planimeter. The area of the compounds in the region dodecane–dotriacontane was integrated.

Polyaromatic hydrocarbons (PAH) were analyzed by GC-FID according to Alsberg and Stenberg (*6*). For calculation of total amount of PAH, the compounds in the range phenanthrene to coronene were used.

Chlorinated benzenes were analyzed by gas chromatography. For quantification an HP mass spectrometer was used. The fragments M^+ and $(M + 2)^+$ were monitored by the SIM technique. For quantification of the total amount of chlorobenzenes, the following compounds were included: 1,3- and 1,4--dichlorobenzenes, 1,2-dichlorobenzene, 1,3,5-trichlorobenzene, 1,2,4-trichlorobenzene, 1,2,3-trichlorobenzene, 1,2,3,5- and 1,2,4,5-tetrachlorobenzenes, 1,2,3,4-tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene.

The phenols were analyzed by GC-MS on a OV-1 capillary column.

Aldehydes were determined as the hydrazones formed on treatment with 5 mL of hydrazine absorption solution. This solution was extracted with 2 mL of methylene chloride. After concentration on the extract, formaldehyde and acetaldehyde were analyzed by GC-FID.

To determine methane to propane the gas pipet samples were analyzed by GC-FID on a packed alumina oxide column. Benzene and toluene were analyzed by gas chromatography on a Tenax column. To detect the aromatics, specific mass fragments were monitored by a LKB mass spectrometer.

Benzene and toluene which had been enriched on adsorbent columns (Carbopack C/activated carbon) were first thermally desorbed at 300°C and then analyzed by GC-FID on a packed Tenax column.

Elemental analyses were done by atomic absorption spectrometry (AAS) using acid digestion and a conventional flame technique, by x-ray fluorescence (XRF) (Kevex ultra tracer, Scandlab, Sollentuna, Sweden) and by proton-induced x-ray emission (PIXE). The PIXE analysis was performed at Lund Institute of Technology, Sweden. The material from sampling line 1 was mixed with cellulose and pressed into pellets. The cellulose concentration necessary to make stable pellets varied between 20 and 75%, depending on the type and size fraction of the material. The analyses of the thick pellets were performed according to Carlsson and Akselsson (*7*).

Physical Characterization. Physical characterization was performed on the particulate material from sampling line 1. The morphology of the particles was studied with scanning electron microscopy (JEOL 100CX).

Size distributions were measured with a Coulter counter (Model TA II) with samples in 0.9% saline solution. The apertures of the orifice tubes used were 30, 50 and 140 μm, respectively, depending on size fraction.

The density was measured in xylene with a pycnometer according to DIN 51057, 1969.

Specific surface area of the particles was determined by the Technical University of Luleå, Sweden, using conventional nitrogen BET-adsorption methods.

Bioassay

Intratracheal Instillation. Intratracheal instillation was used as a means of administration. To examine the long-term effects, particularly the carcinogenicity of the particles, the Syrian golden hamster was chosen. This animal has been shown to be resistant to infections of the respiratory tract and not to develop tumors of the lungs spontaneously (*8,9*). Furthermore, the Syrian hamster has been demonstrated to be a useful model for studying the carcinogenic effects of various materials on the upper respiratory tract and lung (*10*). The long-term toxicity and carcinogenicity study was performed on outbred male Syrian hamster (Bantin and Kingman, Hull, Quality 2).

The hamsters were housed individually, and the cages were placed in two identical rooms: one room for animals treated with benzo(a)pyrene (BaP)-coated material and one room for animals treated with material not coated with BaP. (The coating procedure is described in the following section.) The hamsters were set on a 12-hr day and night light cycle with light on at 6 A.M. and off at 6 P.M.

The room temperature was 21–24°C. The hamsters were given Astra-Ewos commercial pelleted diet (R3) and water *ad libitum*. The humidity was 50 ± 5%. Cages were changed once a week. The body weight was recorded weekly. Each animal was examined daily and observations on their health recorded. Before treatment, the hamsters were allowed to acclimate for 2–3 weeks. At the beginning of the experiments the hamsters weighed ca. 80–90 g and were ca. 8–13 weeks old. The treatments were completely randomized. No selection was made by weight. Before treatment (instillation) the hamster was anesthetized with methohexital, (Brietal, Eli Lilly), 40–50 mg/kg IP. The anesthetized hamster was placed in special equipment allowing proper fixation before the instillation procedure. The instillations were performed mainly as described by Saffiotti et al. (*10*). We used a device made of Teflon and consisting of a cylinder with a conical end to which a thin (0.75 mm diameter) 100 mm long steel tube, bent at an angle of about 135°, was fixed. The device was attached to a 1 mL disposable syringe. Before use the device was sterilized in an autoclave. Before starting the intratracheal instillations of the hamsters, the volume of the various suspensions of dust delivered from the device was checked. The reproducibility was found to be quite satisfactory for a volume of 0.2 mL.

The intratracheal instillation was performed in the following way. Under careful inspection, the tip of the tube was located approximately 5 mm down into the larynx of the anesthetized hamster without touching the inner laryngeal walls. The material, consisting of a 0.2 mL particulate suspension in sterile saline with 0.5% gelatin added, was delivered. In order to obtain a homogeneous suspension, it was necessary to omit the gelatin in the suspensions made of uncoated oil soot. A detailed description of the preparation of the suspensions is found in the following section. After checking the proper delivery of the material to the hamster, the animal was released from the instillation equipment and allowed to wake up from the anesthesia. The hamster was carefully watched under this procedure. Frequently an animal showed apnea, and sometimes it was necessary to help it breathe by gentle massage of the thorax.

Retention, Bioavailability and BaP Coating. The retention and bioavailability of the particulate materials were studied in two ways: by using benzo(a)pyrene-coated particles or by using neutron-activated particles.

The BaP coating was done primarily to study synergistic carcinogenic effects associated with particulate material as a carrier for BaP. This procedure and the coating technique is described by Saffiotti (*11*). The coating is performed by mixing equal amounts of BaP as a 10% solution in acetone and particulate material as a 0.2% suspension in cold water (4°C). When the acetone solution is mixed with the water, BaP crystallizes on the particles which are then filtered off. The mixed material is scraped off the filter and suspended in saline solution for instillation. The hamsters were instilled with doses of 4.5 mg BaP per 0.2 mL saline solution in four groups: pure BaP, BaP + Fe_2O_3; BaP + coal fly ash; and BaP + oil soot (Fe_2O_3, Fisher Scientific Company, ferric oxide Lot 743290). Four animals from each group were sacrificed at 30 min, 180 min, 1 day and 7 days after instillation, and the BaP content of the lungs was measured with high performance liquid chromatography (HPLC) using fluorescence detection.

The neutron activation was performed with 10^{13} n/cm^2-sec for 24 hr at Studsvik Energiteknik AB, Sweden. The leachability of the activated isotopes in the particulate material was studied by repeated washing with saline solution. In the washing, 45 mg of material was suspended in 2 mL saline solution by ultrasonification. After centrifugation at 1500*g* for 15 min the supernatant was suctioned off, and the activity of the sedimented material and the supernatant was determined. Similarly, 4.5 mg of coal fly ash, oil soot or Fe_2O_3 was then instilled as above, and four animals from each group were sacrificed at 1 day, 1 week, 6 weeks and 18 or 21 weeks, respectively. Since preliminary tests showed a slow clearance, the 1-day group for Fe_2O_3 was omitted. The activity of nonleachable isotopes in the lungs was then measured with a high resolution Ge(Li)-spectrometer. The data were evaluated by a computer fitting code of the gamma spectra.

Bioassay on Alveolar Macrophages. Alveolar macrophages were obtained from the hamsters by bronchopulmonary lavage. The technique used was essentially the same as previously described by Kavet and Brain (*12*). The animals were anesthetized as described above and laparatomized. Blood was drawn from the animals through the abdominal aorta by aid of a syringe. The trachea was exposed and cannulated with a fine polyethylene tubing connected to a 5 mL syringe. The lungs were washed six times with Dulbecco's phosphate-buffered saline (PBS) warmed to 37°C. Each wash consisted of 3 mL solution, and the instillate was withdrawn over a period of 45-60 sec. These six PBS washes removed free particles and nonadherent cells (erythrocytes, lymphocytes, granulocytes, monocytes) not firmly attached to the alveolar surface of the pulmonary airways. The lungs were then lavaged 10 additional times with CaMg-free PBS warmed to 37°C. A gentle massage of the chest was performed to increase the yield of cells in the lavage fluids. The cells from the 10 washes using CaMg-free PBS were pooled and centrifuged at room temperature for 10 min at 150*g*. The supernatant was aspirated and discard-

ed, and the cell pellet was resuspended in 1.0 mL Ringerdex (Pharmacia). The total number of cells was determined by counting the cells in a hemocytometer chamber, and the differential distribution of cell types was finally analyzed by differential counts of May Grünewald and Giemsa stained smears of the cell pellet. Cell viability was tested by trypan blue exclusion.

The phagocytic capacity of the alveolar macrophages and their ability to attach particles to the cell surface were tested *in vitro* according to Hed (*13*). In brief, the cells were centrifuged at room temperature for 10 min at 150*g*, washed twice in CaMg-free Ringerdex and then resuspended in Ringerdex containing Ca^{2+} and Mg^{2+} to a concentration of 10^6 cells/mL. A sample of 0.1 mL of the cell suspension was placed on each of three glass slides and the cells were allowed to adhere for 30 min at 37°C. The slides were then rinsed in Ringerdex containing Ca^{2+} and Mg^{2+} at 37°C. Thereafter, 0.1 mL of a suspension of yeast particles (*Saccaromyces cerevisiae*, 10^7 particles/mL) labeled with fluorescein isothiocyanate (FITC) was added, and the preparations were incubated for 45 min at 37°C. Before addition, the yeast particles were opsonized in homologous hamster serum by heating at 37°C for 30 min. The phagocytic reaction was interrupted by placing the slides in cold (+4°C) Ringerdex solution containing Ca^{2+} and Mg^{2+} The preparations were finally stained by adding five drops of a crystal violet solution (0.5 mg/mL) to each slide for 10 sec. The number of intracellular particles per cell (distinguished by their fluorescence) and the number of attached particles per cell (colored dark-blue by the crystal violet) were determined for 50 cells on each slide by using a fluorescence microscope (Leitz Orthoplan).

Studies on the Acute and Subacute Toxicity of Particulate Material. Based on the results of preliminary experiments, the acute toxicity of the particulate suspensions was tested in 21 male Syrian hamsters divided into seven groups with three hamsters per group. Suspensions of oil soot particles were instilled intratracheally with doses of 3, 4.5 or 6 mg/hamster. Suspensions of coal fly ash particles were instilled intratracheally at doses of 3, 6 or 9 mg/hamster. The controls received the vehicle (saline + 0.5% gelatin) by intratracheal instillation.

Subacute toxicity was examined after four repeated intratracheal instillations with an interval of 5–7 days. Suspensions of oil soot particles in three hamsters per dose and three controls (saline + 0.5% gelatin) were instilled at the dose levels of 3 or 4.5 mg/hamster. Suspensions of coal fly ash particles were instilled at a dose of 6 mg/hamster. The doses were chosen with consideration to the results of the acute toxicity studies.

Before the long-term carcinogenicity study, we also found it necessary to examine the toxicity of the particles coated with BaP. Suspensions of particulate material from oil or coal combustion with BaP coating were instilled intratracheally at three different doses (particles + BaP): (3 + 3), (4.5 + 4.5) or (6 + 6) mg/hamster. Each group consisted of five hamsters.

In the long-term carcinogenicity study, 540 male Syrian hamsters were instilled intratracheally once a week for 15 weeks. For practical reasons it was necessary to divide the hamsters into three instillation groups. The treatments with the particle suspensions and with the vehicle control were randomized. The number of various treatments was as equal as possible in the three groups. Hamsters which died before the fourth instillation were replaced by new hamsters.

Table 1 shows the various treatments of the total number of hamsters in the long-term study. The doses were selected with consideration to the results of acute and subacute toxicity tests.

Mutagenicity. Mutagenicity was determined on the material from SL 2 (Fig. 3) by the Ames Salmonella/microsome plate incorporation method with bacterial cultures fully grown overnight (*14–16*).

Table 1. Treatment of hamsters in the long-term study.

Code	Treatment	Level, mg/hamster	Number of animals
A	Vehicle controls (sterile saline + gelatin, 0.5 g/100 ml)		60
Ba	Coal fly ash	4.5	60
Bb	Coal fly ash	6.0	30
Ca	Oil soot in sterile saline without gelatin	4.5	60
Cb	Oil soot in sterile saline without gelatin	3.0	30
D	Fe_2O_3 (inert dust, Fisher Scientific Company)	4.5	60
E	Sterile saline + gelatin (0.5 g/100 ml) + B(a)P	4.5	60
F	Coal fly ash (4.5 mg) + B(a)P	4.5	60
G	Oil soot (4.5 mg) + B(a)P	4.5	60
H	Fe_2O_3 (4.5 mg) + B(a)P	4.5	60
			Total 540

The mutagenicity tests were performed by G. Löfroth, The Wallenberg Laboratory, Stockholm University, Stockholm.

All samples were assayed with the strains TA 98 and TA 100 (obtained from B. N. Ames, University of California, Berkeley, CA) in the absence and the presence of the microsome-containing rat liver supernatant S9 and necessary co-factors. The S9 was prepared from Aroclor 1254-induced male SPD rats, and the assays comprised one level of S9, i.e., 20 μL S9/plate.

The total extracts were tested at appropriate dose levels up to doses corresponding to 0.2 m^3 NTP stack gas per plate.

Results

Operating Conditions

Oil-Fired Boiler. The sampling in line 2 was done when the boiler was operated at 90% (two samples) and at 60% (one sample) of full power. The oxygen content in the flue gases was 0.25–0.5% O_2. The results are summarized in Table 2.

The burning conditions in the boiler were very stable, as indicated by the registration of the amount of carbon monoxide in the flue gas which was about 100 ppm with small variations. The particulate emission was 120 mg/m^3 NTP dry gas normalized to 10% carbon dioxide. The collected particles were black and contained high amounts of unburned substances. The ash content of these particles was 14%.

Boiler Fired with Pulverized Coal. All samples in line 2 were taken at full power of the boiler. The results are summarized in Table 3. Recording of the carbon monoxide and oxygen content of the flue gases showed that the boiler was operated at very stable conditions. The low amount of carbon monoxide in the flue gas (25 ppm CO) and the low amount of unburned substances in the fly ash (ash content 98%) indicate very good outburning conditions in the boiler. The oxygen content in the flue gases was 5% O_2.

The emission of particles as measured was 170, 500 and 760 mg/m^3 dry gas, respectively, related to 10% carbon dioxide. The high particulate emission in two samples was due to failure of one section of the electrostatic precipitator.

Chemical and Physical Characteristics

Sampling Line 1. Figures 4 and 5 show scanning electron micrographs of the coal fly ash and oil soot particles, respectively. The coal fly ash consists of round smooth particles, some of them hollow. The oil soot particles are all round hollow cenospheres with a characteristic perforated surface. Their characteristic morphology as a means of distinguishing them from other particles has been pointed out by others (*17*).

Table 4 shows the weight of the material fraction by fraction as collected with the impactor in sampling line 1. Coulter analyses of the coal fly ash size fractions show a decrease of volume median diameter with smaller aerodynamic diameter except for the back-up filter. This indicates bounce-off of material from the impactor stages to the filter, although one should bear in mind that the Coulter counter analysis of the particles below 1 μm is somewhat uncertain. Bounce-off is to be expected with the heavy loadings we used in this experiment. For the oil soot, 60% of the collected material is found on the back-up filter. These particles are large and have probably bounced off the first stage. Our Coulter counter analysis procedure does not permit the measurement of water-soluble particles or of submicron particles in the same sample as particles around 20 μm. However, electron microscopy of unsuspended oil soot indicates that submicron aerosol particles, if present, constituted a minor weight fraction of the material collected on the back-up filter.

When the fractions were mixed to a blend for biological testing the filter fraction of the coal fly ash had to be omitted, since it was otherwise impossible to avoid contamination with filter material. No such problems arose when the oil soot fractions were mixed. PIXE analysis of the coal fly ash size fractions showed a small increase of V, Cu, Zn, Ga, Se, Sr, Ba and Pb with decreasing particle size. Since for the coal fly ash only 13% of the original material was in the filter fraction, the fact that this fraction was omitted in the composition of the blend did not decrease the concentration of the two elements most affected (Zn and Se) more than 25% in the final blend.

In Table 5 results of PIXE analysis of the material from the electrostatic precipitators and of the blends used for biological tests are shown. The results compare fairly well with the concentrations measured in sampling line 2 and are in agreement with what is usually found in these types of materials (*18,19*).

It is worthy of mention that the elements found to be enriched on small particles (V, Cu, Zn, Ga, Se, Sr, Ba and Pb) are also enriched on the impactor-collected material as compared with the material from the electrostatic precipitator and from sampling line 2. This result and the very high enrichment of Cl and Br on the impactor-collected material show that we really have had a condensation of volatile elements in the dilution and cooling process in sampling line 1. In spite of condensation, the organic material collected in sampling line 1 was

Table 2. Oil-fired boiler.

Parameter	Sample 1	Sample 2	Sample 3
Electric power, MW	240	230	165
Heat power, MW	160	190	160
Fuel load, kg/hr	54700	52800	37400
Flue gas flow, m^3/hr			
Wet	7E + 5	6.8E + 5	5.1E + 5
Dry	6.4E + 5	6E + 5	4.4E + 5
Carbon dioxide, vol-%	15	15	15
Range	14-16	14-16	14-16
Carbon monoxide, ppm	100	100	100
Range	25-200	50-150	25-200
Hydrocarbons, ppm CH_4 (range)	< 30	< 30	—
Nitrogen oxides, ppm	—	200	160
Sulfur dioxide, mg/m^3 dry	—	—	—
Sampling volume, m^3 dry	10.1	15.1	18.9
Sampling time, hr	4.0	4.5	5.0
Flue gas temperature at sampling, °C	144	139	136
Particulate matter			
mg/m^3 dry 10% CO_2	120	120	110
mg/kg dry fuel	2100	2100	1900
mg/MJ fuel energy added	51	52	47
Ethene			
mg/m^3 dry 10% CO_2	0.0099	1.0049	1.008
mg/kg dry fuel	0.17	0.083	0.14
mg/MJ fuel energy added	0.0043	0.002	0.0035
Benzene			
mg/m^3 dry 10% CO_2	0.017	0.0066	1.0073
mg/kg dry fuel	0.29	0.11	0.13
mg/MJ fuel energy added	0.0071	0.0028	0.0032
Formaldehyde			
mg/m^3 dry 10% CO_2	< 0.026	< 0.026	< 0.018
mg/kg dry fuel	< 0.47	< 0.45	< 0.31
mg/MJ fuel energy added	< 0.011	< 0.011	< 0.0076
Acetaldehyde			
mg/m^3 dry 10% CO_2	< 0.046	< 0.04	< 0.032
mg/kg dry fuel	< 0.81	< 0.68	<0.56
mg/MJ fuel energy added	< 0.02	< 0.017	<0.014
Extractable matter			
mg/m^3 dry 10% CO_2	1.3	1.3	0.88
mg/kg dry fuel	23	22	15
mg/MJ fuel energy added	0.57	0.55	0.38
Sum of PAH			
µg/m^3 dry 10% CO_2	< 2	< 2	< 2
µg/kg dry fuel	< 40	< 40	< 40
µg/MJ fuel energy added	< 1	< 1	< 1
Benzo(a)pyrene			
µg/m^3 dry 10% CO_2	0.0013	0.00088	0.00071
µg/kg dry fuel	0.023	0.015	0.012
µg/MJ fuel energy added	0.00057	0.00037	0.0003
Chlorobenzenes			
µg/m^3 dry 10% CO_2	< 0.04	< 0.026	< 0.021
µg/kg dry fuel	<0.7	<0.45	< 0.37
µg/MJ fuel energy added	< 0.017	< 0.011	< 0.0091
2,3,7,8-TCDD			
µg/m^3 dry 10% CO_2	< 0.0079	< 0.0053	< 0.0042
µg/kg dry fuel	< 0.14	< 0.091	< 0.075
µg/MJ fuel energy added	< 0.0034	< 0.0022	< 0.0018
2,3,7,8-TCDF			
µg/m^3 dry 10% CO_2	< 0.0013	< 0.00084	< 0.00067
µg/kg dry fuel	< 0.022	< 0.014	< 0.012
µg/MJ fuel energy added	< 0.00054	< 0.00035	< 0.00029
Chlorophenols (Cl_4, Cl_5)			
µg/m^3 dry 10% CO_2	< 0.33	< 0.22	< 0.18
µg/kg dry fuel	< 5.8	< 3.8	< 3.1
µg/MJ fuel energy added	< 0.14	< 0.092	< 0.076
Mutagenicity (highest response in strain and + or –S9)			
Revertants/m^3 dry 10% CO_2	< 200	< 200	< 200
Revertants/kg dry fuel	< 3500	< 3400	< 3500
Revertants/MJ fuel energy added	< 85	< 83	< 86

Table 3. Boiler fired with pulverized coal.

Parameter	Sample 11	Sample 12	Sample 13
Electric power, MW	255	255	255
Fuel load, kg/hr	90000	90000	90000
Fuel temperature, °C	950	950	950
Flue gas flow, m^3/hr			
Wet	8.88E + 5	9.87E + 5	9.31E + 5
Dry	8.35E + 5	9.37E + 5	8.75E + 5
Carbon dioxide, vol-%	13	12	13
Range	12-14	12-13	12-15
Carbon monoxide, ppm	20	30	25
Range	20-25	25-35	20-30
Hydrocarbons, ppm CH_4	—	—	—
Nitrogen oxides, ppm	350	350	350
Sulfur dioxide (dry), mg/m^3	1200	1300	—
Sampling volume (dry), m^3	17	14.8	13.6
Sampling time, hr	5.9	7.1	6.0
Flue gas temperature at sampling, °C	145	135	140
Particulate matter			
mg/m^3 dry 10% CO_2	170	500	760
mg/kg dry fuel	2300	6900	11000
mg/MJ fuel energy added	86	260	400
Ethene			
mg/m^3 dry 10% CO_2	< 0.009	—	< 0.009
mg/kg dry fuel	< 0.12	—	< 0.13
mg/MJ fuel energy added	< 0.0045	—	< 0.0048
Benzene			
mg/m^3 dry 10% CO_2	0.072	—	0.11
mg/kg dry fuel	0.97	—	1.5
mg/MJ fuel energy added	0.036	—	0.057
Formaldehyde			
mg/m^3 dry 10% CO_2	0.045	0.056	—
mg/kg dry fuel	0.61	0.78	—
mg/MJ fuel energy added	0.023	0.029	—
Acetaldehyde			
mg/m^3 dry 10% CO_2	0.14	0.11	—
mg/kg dry fuel	1.8	1.6	—
mg/MJ fuel energy added	0.068	0.059	—
Extractable matter			
mg/m^3 dry 10% CO_2	0.11	0.14	0.14
mg/kg dry fuel	1.5	2	2
mg/MJ fuel energy added	0.057	0.073	0.075
Sum of PAH			
$\mu g/m^3$ dry 10% CO_2	< 2	< 2	< 2
µg/kg dry fuel	< 25	< 25	< 25
µg/MJ fuel energy added	< 1	< 1	< 1
Benzo(a)pyrene			
$\mu g/m^3$ dry 10% CO_2	< 0.0032	< 0.0039	< 0.004
µg/kg dry fuel	< 0.042	< 0.055	< 0.056
µg/MJ fuel energy added	< 0.0016	< 0.0021	< 0.0021
Chlorobenzenes			
$\mu g/m^3$ dry 10% CO_2	< 0.027	< 0.034	< 0.034
µg/kg dry fuel	< 0.36	< 0.47	< 0.48
µg/MJ fuel energy added	< 0.014	< 0.018	< 0.018
2,3,7,8-TCDD			
$\mu g/m^3$ dry 10% CO_2	< 0.0054	< 0.0068	< 0.0068
µg/kg dry fuel	< 0.073	< 0.094	< 0.095
µg/MJ fuel energy added	< 0.0027	< 0.0035	< 0.0036
2,3,7,8-TCDF			
$\mu g/m^3$ dry CO_2 10%	< 0.00086	< 0.0011	< 0.0011
µg/kg dry fuel	< 0.012	< 0.015	< 0.015
µg/MJ fuel energy added	< 0.00043	< 0.00056	< 0.0057
Chlorophenols (Cl_4, Cl_5)			
$\mu g/m^3$ dry 10% CO_2	< 0.23	< 0.28	< 0.28
µg/kg dry fuel	< 3	< 3.9	< 4
µg/MJ fuel energy added	< 0.11	< 0.15	< 0.15
Mutagenicity (highest response in strain and + or –S9)			
Revertants/m^3 dry 10% CO_2	< 260	< 280	< 260
Revertants/kg dry fuel	< 3500	< 3900	< 3700
Revertants/MJ fuel energy added	< 130	< 150	< 140

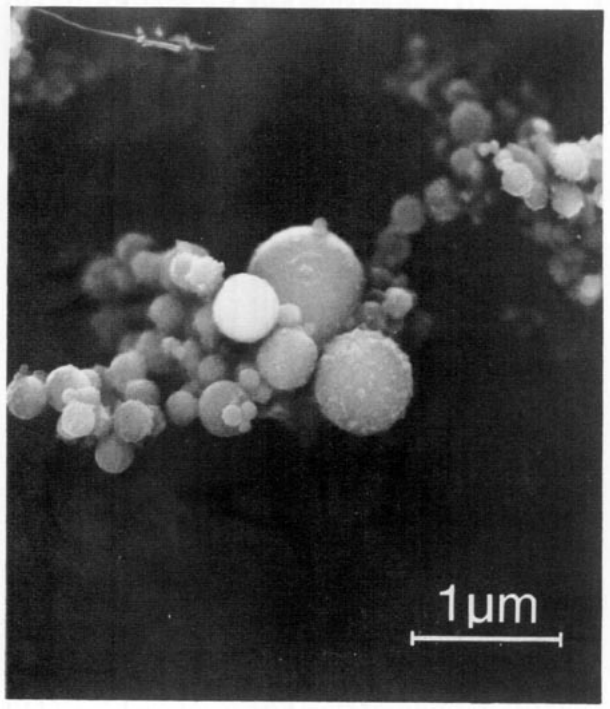

FIGURE 4. Coal fly ash particles from stage 6 in the Sierra high volume impactor in sampling line 1; 0.5–1 μm aerodynamic diameter. SEM magnification 20,000 ×.

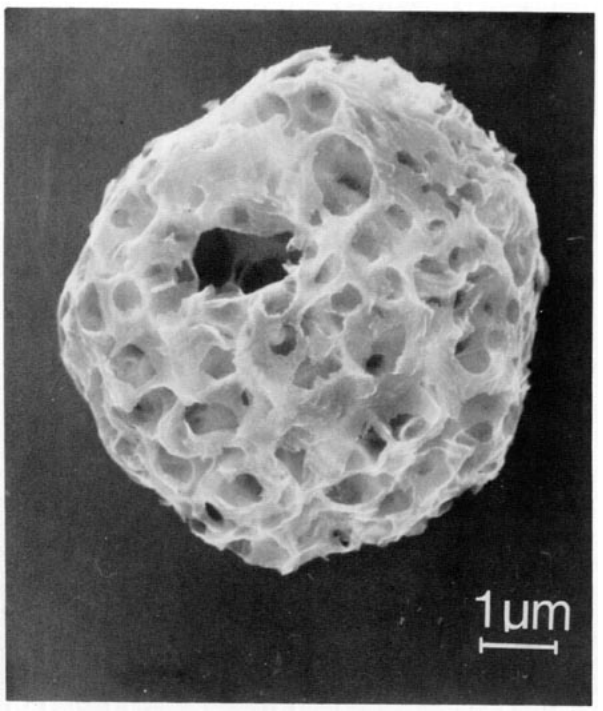

FIGURE 5. Oil soot particle from the Sierra high volume impactor in sampling line 1. SEM magnification 10,000×.

low. This is to be expected from the results of the analysis of the condensates in sampling line 2. The BaP content of the fly ash and soot was below detection limit, 0.1 μg/g.

Table 6 shows the physical parameters of the collected particles. The size of the oil soot particles collected before the electrostatic precipitator was the same as that of those from the precipitator, while the coal fly ash collected after the electrostatic precipitator in sampling line 1, as expected, is much smaller than that from the precipitator. The density and specific surface area of the coal fly ash compare well with that measured by other authors. Notable is the large specific surface area for the large oil soot particles which is due to their high porosity.

The mass median aerodynamic diameter D_a for coal fly ash as determined from the impactor data in Table 4 is 2.9 μm for the blend. Using the equation, $D_a = VMD\sqrt{\rho}$, the data in Table 6 give a value of 4.4 μm. The values from the impactor might be low, since bounce-off decreases the aerodynamic diameter measured. The value from Table 6 can be too high, since hollow particles will decrease the effective density. Since the mass median aerodynamic diameter of the coal fly ash used in the biological tests consequently is less than 5 μm, it will be classified as respirable according to the Johannesburg convention, 1959 *(22)*.

The density of the oil soot particles in Table 6 is not applicable to single particles for calculation of the aerodynamic diameter since these are hollow. From impactor data in Table 4 the mass median aerodynamic diameter is found to be well above 7 μm when bounce-off is taken into account. Thus the oil soot used in the biological tests is not respirable as defined by the Johannesburg convention *(22)*.

Sampling Line 2. The emission of organic compounds was very low (Tables 2 and 3). The concentration of specific organic compounds was in general below the detection limits of the methods. However, analysis of extractable matter, as determined by GC, showed that the oil-fired boiler had a higher emission, (1200 μg/m^3) of unspecified organics than the coal powder-fired boiler, which emitted 400 μg/m^3. The concentrations of individually measured PAH compounds was less than 0.05 μg/m^3 NTP dry gas of each species.

For the oil-fired boiler, the mass transport for the fuel (F) and the fly ash collected in the electrostatic precipitator (EP) was as follows: Hg, F 0.55 g/hr, EP 0.002 g/hr; Pb, F 25 g/hr, EP 21 g/hr; Cd, F 10 g/hr, EP 0.025 g/hr; Ni, F 610 g/hr, EP 580 g/hr. These results indicate that a high fraction of the metals mercury and cadmium will be emitted to the atmosphere. Lead and nickel are mostly particulate bound and are emitted to a lesser extent. The

Table 4. Weight, volume median diameter (VMD) and percent in the final blend for biological testing of the different impactor size fractions of the particulates collected in sampling line 1.

		Coal fly ash			Oil soot		
Impactor stage	Aerodynamic diameter, μm	Weight, g	VMD, μm	Proportion in blend, %	Weight, g	VMD, μm	Proportion in blend, %
1+2	7	1.93	6.8	10.3	6.91	16.5	27.1
3	3–7	7.37	3.8	39.3	2.35	11.0	9.2
4	1.5–3	5.28	2.6	28.2	0.63	12.9	2.5
5	1–1.5	3.21	1.4	17.1	0.05	12.3	0.2
6	0.5–1	0.95	1.4	5.1	0.14	10.1	0.5
Filter	<0.5	2.83	2.3	0	15.46	16.3	60.5
Total		21.57			25.54		

Table 5. Elemental composition of the blended material from sampling line 1 (SL1) and of the material from the electrostatic precipitator (EP) for the two power plants.

	Concentration in coal fly ash, μg/g[a]		Concentration in oil soot, μg/g[a]	
Element	SL	EP	SL	EP
Al	14%	9.0%	0.9%	1%
Si	20%	14%	< 3100	< 1400
P	3900	< 1000	< 2100	< 1200
S	1.2%	0.42%	10.4%	11.6%
Cl	9700	< 240	2500	< 410
K	2.12%	1.5%	300	< 440
Ca	4.2%	3.6%	2700	4500
Ti	7200	4500	100	120
V	800	< 140	1.2%	2.3%
Cr	220	100	< 200	< 200
Mn	1400	790	< 60	< 60
Fe	5.4%	4.0%	4100	5700
Ni	240	80	3200	6000
Cu	260	100	110	60
Zn	990	260	340	780
Ga	70	23	< 6	15
Ge	25	9	< 5	< 5
As	65	18	< 5	14
Se	29	< 3	9	7
Br	72	< 3	28	5
Rb	160	100	< 3	< 3
Sr	1100	640	26	50
Y	60	40	< 4	< 5
Zr	190	140	< 4	< 5
Nb	23	13	< 4	< 4
Mo	20	<8	85	70
Cd	< 20	< 15	< 15	< 15
Ba	4100	1800	210	360
Pb	510	150	90	220
Th	32	< 30	< 15	< 15

[a]Concentrations in μg/g unless otherwise noted.

Table 6. Physical characteristics of the particles used for biological tests, together with some literature data.

	Electrostatic precipitator		Material for biological tests			
Material	VMD, μm	σ_g[c]	VMD, μm	σ_g[c]	Density, g/cm^3	Specific surface area, m^2/g
Oil soot	17	2.2	16.5	2.0	2.08	2.3
Coal fly ash	19	3.0	2.9	1.9	2.33	4.0
Coal fly ash[a]					2.5–2.8	4–8
Coal fly ash[b]					2.4–2.5	

[a]Data of Dlugi et al. (*20*).
[b]Data of Raabe et al. (*21*).
[c]Geometric standard deviation.

analytical data of the elemental analyses are shown in Table 7.

For the boiler fired with pulverized coal, the mass transport for the fuel (F), the fly ash collected in the electrostatic precipitator (EP) and in the flue gas particulates collected after the electrostatic precipitator (FG) was as follows: Hg, F 9 g/hr, EP 2.9 g/hr, FG 0.07 g/hr; Pb, F 990 g/hr, EP 770 g/hr, FG 210 g/hr; Cd, F 17 g/hr, EP 11 g/hr, FG 3.2 g/hr; As, F 240 g/hr, EP 220 g/hr, FG 50 g/hr. These results indicate that the retention for the elements Hg, Pb, Cd and As tend to be lower than the retention of the particles in the electrostatic precipitator which during this sampling period was about 90-95% efficiency. The analytical data of the elemental analyses are shown in Table 8.

Bioassay

Retention and Bioavailability. The investigation of retention and bioavailability is in the process of being finished, and data in addition to those presented in this report will be available later on.

The volume median diameters of the pure Fe_2O_3, the pure BaP and the BaP-coated material were measured with the Coulter counter. The results as measured in the suspensions used for instillation are shown in Table 9. The pure Fe_2O_3 particles were too small to be accurately measured.

The BaP retrieved in the lungs from the four groups of animals instilled with BaP-coated material is shown in Figure 6. The amount of BaP decreases rapidly with time from an original dose of about 2.5 mg. The decrease seems to be more rapid the smaller the particle size. This size dependence has also been shown by Saffiotti (*11*).

For the leaching tests, the material was suspended in saline solution in the same concentrations as for the instillations. The sum of the leached isotopes in the supernatants from the repeated centrifugations was calculated and is given in Table 10, together with the pH measured in the first of the repeated suspensions. Of the activated isotopes the bioavailability is high for ^{51}Cr, ^{75}Se and ^{124}Sb in the coal fly ash and for ^{60}Co, ^{65}Zn, ^{110m}Ag and ^{152}Eu in the oil soot. The high buffering capacity of the coal fly ash gives an alkaline suspension which tends to decrease the leaching of the elements from this material. Henry and Knapp (*9*) find leachable elements to be associated with sulfates and nonleachable elements to be associated with oxides in flue gas particulates from coal and oil firing.

When calculating particle retention we use the nonleachable isotopes ^{59}Fe and ^{46}Sc for the coal fly

Table 7. Analysis of metals for oil-fired boiler.

	Metal concentration, μg/g					
	Oil soot collected in the electrostatic precipitator			Fuel oil		Oil soot particulates collected before eletrostatic precipitator (Sampling line 2, AAS)
Metal	AAS	XRF	PIXE	AAS	XRF	
S		75800	146000		57900	
Cl		1800	880		786	
K		217	553		23	
Ca		2000	5470		16	
Ti		985	120		7	
V	16000	10600	26000	69	101	16000
Cr	26	< 3		< 5	< 3	
Mn	56	16		< 2	< 2	
Fe	6300	2300	5970	30	108	5300
Ni	6700	2900	7030	11	31	6300
Cu	39	14	64	< 2	2	
Zn	1100	401	834	3,1	4	
Ga		9	18.2		1	
Ge		< 0.45			< 0.45	
As	12	< 0.42	20.1		< 0.42	
Se		2	9.29		< 0.42	
Br		2	6.52		0.6	
Rb		< 0.45			0.5	
Sr		27	51.8		1	
Y		< 0.5			< 0.5	
Zr		< 0.52			< 0.52	
Mo	170	32	65	< 15	< 0.56	220
Cd	0.29	< 3		< 0.3	3	< 2
Hg	< 0.002	< 1.2		0.01	1.2	1.2
Pb	240	117	217	5	2	

Table 8. Analysis of metals for boiler fired with pulverized coal.

	Metal content, μg/g												
	Coal powder			Bottom ash			Fly ash at electrostatic precipitator			Fly ash (sampling line 2 collected after the electrostatic precipitator)			
Element	AAS	XRF	PIXE	AAS	XRF	PIXE	AAS	XRF	PIXE	AAS[a]	XRF[a]	PIXE[a]	AAS[b]
S		10500	10500		470			2800	6070		4700	7700	
Cl		3100	1810		450			< 70	120		130		
K		2800	3090		4700			9300	18000		11400	19800	
Ca		9900	13900		14800			24900	53800		25100	45000	
Ti		1000	820		1450			3100	5650		3800	6160	
V	13	185		47	44		110	191		260	342	321	220
Cr	7.9	33	37.3	32	13		90	161	136	170	199	167	160
Mn	200	24	288	1000	430		1100	674	1200	1100	747	1200	750
Fe	8700	7100	10800	32000	26000		33000	33500	57400	35000	32200	53300	37000
Ni	14	19	12.4	25	6		53	64	109	120	113	148	120
Cu	12	24	14	46	23		80	69	162	180	126	180	190
Zn	43	14	21.5	61	47		180	177	344	410	381	572	
Ga		4	7.36		7			14	37.1		38	23	
Ge		2			2			5	14.7		17	54	
As	2.7	3			2		22	13	25.6		52	54.6	
Se		1			0.5			2			6	17.7	
Br		22	13.6		2			1			3		
Rb		20	17		42			76	144		97	145	
Sr		176	76.5		260			539	748		780	872	
Y		10			21			38			59		
Zr		32			96			173	204		244	209	
Mo	< 6	0.8		7.6	< 0.7		21	6		48	14		< 30
Cd	0.19	< 3		0.15	< 4		1.1	4		3.3	< 3		2.3
Hg	0.10	< 1.2		0.005	4.8		0.29	< 1.2		0.33	5		
Pb	11	31		10	32		77	96	190	220	183	328	170
Co	5			6			18			39			35

[a]Particulate matter 850 mg/m^3 NTP dry gas at 10% CO_2.
[b]Particulate matter 400 mg/m^3 NTP dry gas at 10% CO_2.

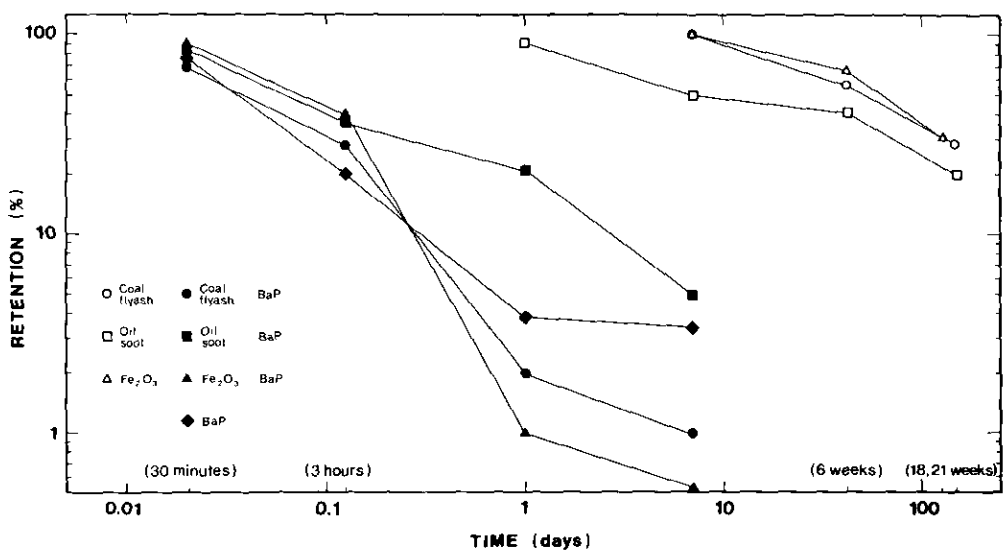

FIGURE 6. Retention in hamster lungs after intratracheal instillation of coal fly ash, oil soot and Fe_2O_3 particles, measured with neutron-activated particles (○,□,△) and the retention of benzo(a)pyrene, BaP, from BaP-coated coal fly ash, oil soot and Fe_2O_3 particles and B(a)P alone, measured by HPLC (●,■,▲,◆). Each point is the average of four animals.

Table 9. Volume median diameter (VMD) and σ_g of the particulate material used for instillation in the biological tests.

Material	VMD, μm	σg
Fe_2O_3	1	—
BaP	3.7	1.6
BaP + Fe_2O_3	1.8	1.6
BaP + coal fly ash	3.3	2.0
BaP + oil soot	17	2.0

Table 10. Percent of isotopes leached

Material	Number of washings	pH of first washing	Isotope	% leached (sum of washings)
Fe_2O_3	1	6.3	^{59}Fe	<1
Coal fly ash	2	8.3	^{46}Sc	<1
			^{51}Cr	40
			^{59}Fe	<1
			^{60}Co	<1
			^{75}Se	100
			^{124}Sb	10
			^{152}Eu	<1
Oil soot	6	4.1	^{46}Sc	<1
			^{51}Cr	1.5
			^{59}Fe	<1
			^{60}Co	44
			^{65}Zn	59
			^{110m}Ag	50
			^{152}Eu	20

[a]A 45-g portion of material was leached with 2 mL of saline solution, pH 6.3.

ash and ^{59}Fe for the oil soot, since we assume these isotopes to be associated with the matrix of the particles. The decrease between 6 and 21 weeks for the oil soot, however, was also calculated from ^{60}Co, since the leaching of this isotope was negligible after 6 weeks. For iron oxide the only radioactive isotope available, ^{59}Fe, was used.

The agreement between particle retention calculated from ^{59}Fe and ^{46}Sc for coal fly ash and between ^{59}Fe and ^{60}Co for oil soot after 6 weeks are within 20%. This agreement supports the assumption that iron and scandium are associated with the matrix of the coal fly ash particles and that iron and the cobalt not leached at 6 weeks are also associated with the matrix of the oil soot particles.

The retention of the particulate material is plotted in Figure 6, together with the results for the BaP-coated particles. The most interesting result is the very long retention time of the particles after intratracheal instillation. No fast clearance seems to occur.

Effects on Alveolar Macrophages. The total number of cells recovered from each animal by bronchopulmonary lavage varied between 2 and 5 $\times 10^6$ cells. Differential counts of cell smears (200 cells) revealed that 50-70% of the cells consisted of alveolar macrophages. According to trypan blue exclusion tests, about 50% of the macrophages were viable. The percentages of lymphocytes and granulocytes were 10-20 and 25-35, respectively. The distribution of different cell types was not significantly different for the groups of experimental animals and the controls.

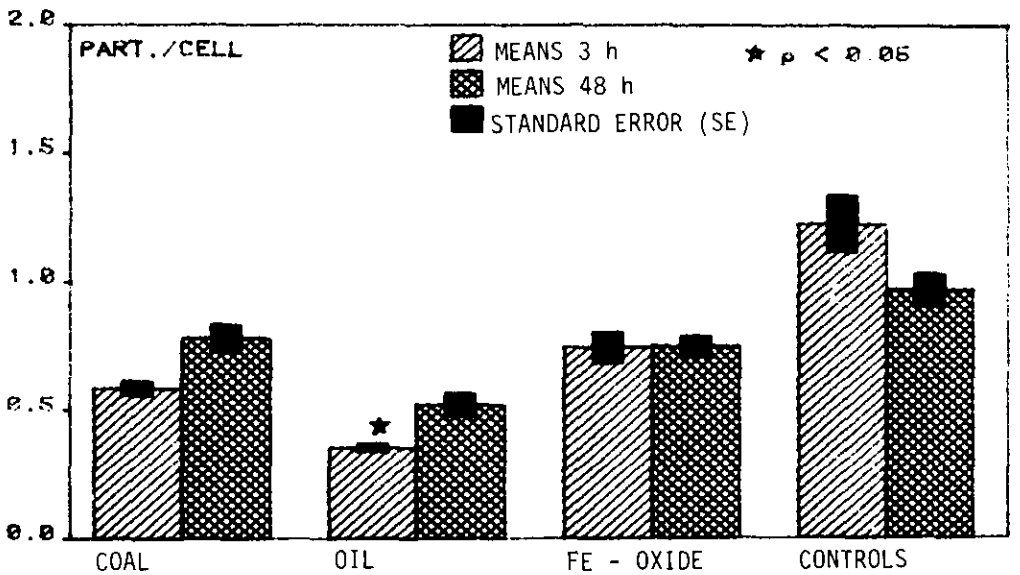

FIGURE 7. Phagocytic function of alveolar macrophages tested *in vitro* from experimental animals at 3 and 48 hr after intratracheal instillation of different kind of particles.

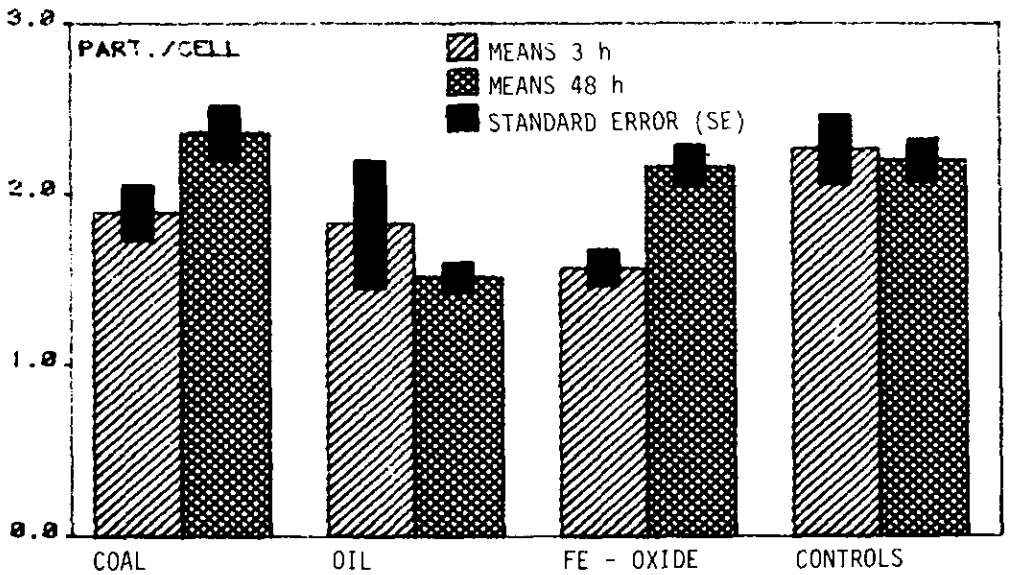

FIGURE 8. Attachment of particles to the cell surface of alveolar macrophages tested *in vitro* from experimental animals at 3 and 48 hr after intratracheal instillation of different kinds of particles.

Figure 7 shows the phagocytic function of the alveolar macrophages tested *in vitro* for the different groups of animals. Tested by analysis of variance, there was a statistically significant decrease ($p<0.05$) in phagocytic capacity of the group of animals instillated with particles from the oil-fired power plant at 3 hr before pulmonary lavage in comparison with the control group. The other groups showed no significant differences. The ability of the alveolar macrophages to adhere particles to the cell surface *in vitro* for the different groups of animals is presented in Figure 8. No statistically significant differences were noticed compared to controls.

Results of the Studies on Acute and Subacute Toxicity. In the studies on the acute toxicity of uncoated particle suspensions, we found that two hamsters out of three died in the group instilled intratracheally with suspensions of oil soot particles 3 mg. At the same dose level, only one hamster of three died in the group instilled with suspensions of coal fly ash particles. Apnea was observed in the majority of the hamsters. Some animals also had general seizures. In the experiments designed to study the acute toxicity of BaP-coated particle suspensions, no hamsters died, but several hamsters showed apnea and only one general seizures. Results very similar to those in the acute experiments were found after the four repeated intratracheal instillations of hamsters in the studies of subacute toxicity.

The results obtained in the test of the acute toxicity, may to a large extent reflect the problem in selection of an optimal dose of the barbiturate anesthetic and lack of training of the technicians at the beginning of the intratracheal instillations.

Table 11 gives the survival rates of the hamsters up to 30 weeks after starting the intratracheal instillations. The data strongly suggest that hamsters treated with oil soot particles had a lower survival, particularly obvious 30 weeks after beginning the test. These data are probably a rather good estimation of the subacute toxicity of the various particle materials.

Mutagenicity (SL 2). The mutagenicity as detected by the Salmonella assay was in all samples below the detection limit ≤5000 revertants/kg fuel.

Table 11. Survivors in the various groups after 15, 20 and 30 weeks (intratracheal instillations were finished after 15 weeks).

Treatments[a]	No. survivors at various times after intratracheal instillation			
	3 weeks[b]	15 weeks	20 weeks	30 weeks
A	60	53	52	51
Ba	58	55	53	49
Bb	30	27	25	24
Ca	59	40	39	35
Cb	29	25	23	23
D	58	52	51	48
E	59	56	56	50
F	59	49	48	46
G	58	36	31	26
H	60	53	50	47

[a]See Table 1.

[b]All hamsters that died before the fourth instillation were replaced. Due to an insufficient number of hamsters, there were fewer hamsters in some groups than originally planned.

However, compared to other emission sources, automobiles and residential burning of wood, the mutagenicity of the samples in this investigation are 10^2-10^3 times lower (revertants/kg fuel).

Discussion

Through the dual sampling-line design of the present studies, it was possible: to obtain samples of particles (SL 1 - MIPSGAS) that had been subject to a cooling and dilution process similar to the one taking place in the plume and simultaneously to characterize the total emissions (SL 2) from the plants. Such samples were obtained from each of two medium-sized plants fired with oil and coal, respectively. Recording of operation conditions indicated that both boilers were run under realistic conditions, and the results from the chemical and biological characterization of the emissions can thus be regarded as representative of the respective fuels and plant types. This is further supported by an additional series of similar sets of chemical and mutagenesis data from a number of other coal-and oil-burning boilers (*23*).

Since most oil-fired boilers in Sweden operate without any particle emissions control device, it was considered most representative of this type of emission to study the flue gases before the EP. For coal-burning plants, EP or other types of particle emission control will always be required, and flue gases after the EP were considered most representative of the actual discharges to the atmosphere.

The two different fuel types in combination with the difference in emission control equipment gave rise to particles with different shape and physical characteristics. Oil burning gave rise to round hollow cenospheres with an aerodynamic diameter well above 7 μm, while the coal-burning device emitted smaller particles (aerodynamic diameter less than 4.4 μm) which were round, smooth and in some cases hollow. These findings are in accord with previous observations on oil soot and coal fly ash (*17,24*).

The difference in aerodynamic diameter between coal fly ash and oil soot will have obvious implications with regard to their atmospheric distribution and deposition pattern in the human respiratory tract, if inhaled, as discussed by the Task Group on Lung Dynamics (*25*).

The chemical analyses of the total emissions (SL 2) indicated that the oil-burning facility emitted more unspecified organic compounds than the coal-burning plant. Analyses of specific components, however, demonstrated that for both plants discharges of PAHs were lower than the detection limit for most specific PAHs analyzed. It may be of interest to mention, in this context, that the concentration of PAH in emissions from residential wood burning and in exhausts from diesel and gasoline-driven automobiles is much higher, sometimes more than 1000 times higher, than in those from the stationary sources of this study. Benzo(a)pyrene concentrations in urban air often exceed those detected in the emissions from these power plants.

The mutagenicity (tested on total extracts - SL 2) of the emissions from both the oil-fired and the coal-fired power plants was below the detection limit of the Ames mutagenicity test as performed in this study. The mutagenicity is lower (by a factor of 100 or more) than that of samples obtained from emission sources such as automobiles and residential wood burning. Since some of the PAHs are particularly active mutagens, the low mutagenicity is in accord with the low concentration of PAH in the presently studied samples.

The particles used for the biological testing in the test of phagocytosis, retention, bioavailability and in the long-term test in hamsters were obtained from the MIPSGAS (SL 1). This sampler simulates the dilution process which takes place in the plume, where the stack gases are simultaneously cooled and diluted by the ambient air. That a condensation of gaseous materials on the particles has taken place is indicated, for example, by the higher chloride content in the particles sampled by the MIPSGAS compared to the particles obtained from the electrostatic precipitators (EP). This condensation has been found in the MIPSGAS in earlier studies (*5*). Possible compounds are HCl and metal chlorides as, for example, $AlCl_3$, which sublimates at 178°C.

The present studies, like those performed recently by others (*23*) on medium-sized plants burning oil or pulverized coal, do not show any important emissions of benzo(a)pyrene. It is well known that such substances can be emitted from combustion processes and it is thus possible that particulate emissions from these plants may occur in the atmosphere together with BaP and other PAHs. It is known, particularly from the studies by Saffiotti et al. (*10,11*), that the carcinogenicity of BaP to the respiratory tract may be enhanced if the BaP administered adhered to certain types of particles (e.g., Fe_2O_3 particles). This enhancement of respiratory carcinogenicity has been related to changes in BaP retention in the respiratory tract.

Particles were coated with BaP in the present studies and administered in the long-term experiment for studies of their possible influence on respiratory carcinogenicity. Retention studies were also performed both to study the BaP component and the matrix of the particles. For the latter type of study the matrix of the particle was made radioactive by neutron activation. The retention times

measured with the neutron-activated particles were much longer than those measured for the BaP or BaP-coated particles. This indicates that the BaP is not cleared from the lungs physically but rather by metabolization or dissolution.

The results from the neutron-activated particles showed that the marker elements used for the oil soot particles were initially cleared faster than those in the small coal fly ash and iron oxide particles. For all types of particles studied, however, the lung clearance was lower than would be expected if the particles would have been deposited predominantly on a functionally intact tracheobronchial mucosa. The results may indicate, therefore, either that the particle suspensions used exerted a ciliotoxic action, or that the predominant deposition occurred in the alveolar region of the lung.

When the particles are coated with BaP, the lung retention of BaP in animals instilled with the bigger BaP-coated oil soot particles is higher at 1 and 7 days after installation than that in the animals instilled with the smaller BaP-coated coal fly ash and iron oxide particles and with BaP alone. Apart from the obvious fact that it would take a longer time to metabolize or dissolve a larger amount of BaP, the negative influence of the oil soot particles on the ability of the macrophages to phagocytize, as documented in the phagocytosis test of these studies, may influence the retention time of unmetabolized BaP.

In summary, these studies have confirmed the basic chemical and physical differences between particles emitted from coal and oil burning. The marked differences in particle size, configuration and chemical composition are reflected in their biological characteristics. Since the combustion was efficient in both types of plants, the concentrations of various PAHs were extremely low or undetectable. The mutagenicity as tested by the Ames test was also negative.

On the other hand, the particulate material from the oil-fired plant exhibited a marked toxicity to the phagocytosis ability of alveolar macrophages; a greater retention of benzo(a)pyrene coated on the oil particles was also demonstrated in relation to other particles. In a long-term experiment on hamsters which were given the respective particles by intratracheal instillation, the oil particles tended to be more toxic. Carcinogenicity data are not yet available.

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