

residual toxicity was probably due to emulsified aromatic hydrocarbons from the "inert ingredients" of the formulation and/or to chlorinated products from the reaction of hypochlorite with these ingredients.

Hypochlorite oxidation does degrade diazinon at a rate acceptable for use as a field method for disposal of wastes containing this pesticide. It is a simple and inexpensive approach that uses common reagents and would appear to be ideal for field use. However, this study has shown that hypochlorite does not detoxify all formulations of diazinon and that the diazinon-hypochlorite reaction does yield products (i.e., trichloroacetate and chloroform) that may cause environmental problems if disposed of in the field.

These results demonstrate the need for careful study of any chemical disposal system before its use is recommended. Such studies should follow an approach similar to that used in this effort (Figure 1) and must include bioassay comparisons to assure that the degraded material has been acceptably detoxified. As seen in this study, disappearance of the parent compound and identification of nontoxic products are not sufficient justifications for using a specific disposal method. An otherwise acceptable procedure may be unsafe for use because of toxic impurities, unidentified toxic products (from the pesticide and/or formulation), and/or toxic "inert" ingredients that are not detoxified by the chemical system. Screening bioassay of the material before and after chemical degradation should help to determine if the system has been detoxified. The combination of bioassay and chemical data allows a more accurate assessment of the environmental im-

pact and of the acceptability of field disposal of the product waste.

Literature Cited

- (1) Miller, T. H., USAMEERU Report No. 73-01, AD 757603, Aug 1972.
- (2) Faust, S. D., Gomaa, H. M., *Environ. Lett.*, **3**, 171 (1972).
- (3) Meier, E. P., Warner, M. C., Dennis, W. H., Randall, W. F., Miller, T. A., USAMBRDL Technical Report 7611, AD A036051, Nov 1976.
- (4) Meier, E. P., Dennis, W. H., Jr., Cooper, W. J., Warner, M. C., Rosencrance, A., Randall, W. F., *Bull. Environ. Contam. Toxicol.*, to be published.
- (5) Litchfield, J. T., Wilcoxon, F., *J. Pharmacol. Exp. Ther.*, **96**, 99-133 (1949).
- (6) Snyder, R. E., Tonkin, M. E., McKissick, A. M., Final Report, Contract No. DADA 17-73-C-3112, U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, Md., Sept 1975.
- (7) Epstein, J., Bauer, V. E., Saxe, M., Demek, M. M., *J. Am. Chem. Soc.*, **78**, 4068 (1956).
- (8) Gomaa, H. M., Suffet, I. H., Faust, S. D., *Residue Rev.*, 171 (1972).
- (9) Hsieh, D. P. H., Archer, T. E., Munnecke, D. M., McGowan, F. E., *Environ. Sci. Technol.*, **6**, 826 (1972).
- (10) Rosenblatt, D. H., "Disinfection—Water and Wastewater", Johnson, J. D., Ed., Ann Arbor Science Publishers, Ann Arbor, Mich., 1975, pp 249-276.
- (11) Margot, A., Gysin, H., *Helv. Chim. Acta*, **40**, 1562 (1957).
- (12) Johannes, H., Kemmerling, W., *Wasser Boden*, **24**, 235 (1972).
- (13) Grimme, L. H., *Pharm. Unserer Zeit*, **2**, 51 (1973).

Received for review September 18, 1978. Accepted January 8, 1979.

Elemental Emissions from a Coal-Fired Power Plant. Comparison of a Venturi Wet Scrubber System with a Cold-Side Electrostatic Precipitator

John M. Ondov*, Richard C. Ragaini, and Arthur H. Biermann

Lawrence Livermore Laboratory, University of California, Livermore, Calif. 94550

■ Emissions of elements in total suspended particles and in discrete particle-size intervals are compared for two coal-fired electrical generating units equipped with venturi scrubbers and one unit with a cold-side electrostatic precipitator (ESP). Coal and particulate emission samples were analyzed by instrumental neutron activation analysis, atomic absorption spectroscopy, and X-ray fluorescence. Emissions of Cr, Mn, Zn, Co, Ni, and Cu from the scrubbers were enhanced, probably because of corroded internal metal surfaces. Concentrations of many toxic elements, including Br, As, Se, Sb, U, V, and Cr, in aerosols emitted from the scrubber were up to 170 times greater than in aerosols from the ESP. The scrubber emitted a greater proportion of aerosol mass in particles of respirable sizes. We conclude that the wet scrubbers reduced the potential inhalation hazard from particulate emissions less effectively than an ESP of comparable efficiency.

Coal use for electric power generation in the United States is expected to increase from 3.6 to 5.1×10^{11} kg by 1980 (1, 2). Even now, release of potentially toxic substances to the atmosphere is of concern (3-6), and the possibility of adverse effects of these substances has stimulated considerable interest in the control of particulate emissions.

Electrostatic precipitation and wet scrubbing processes are the two major strategies employed to control particulate

emissions at coal-fired electrical utility stations. Commercial wet scrubbers are very efficient in removing supermicron particles and reduce plume visibility greatly (7, 8). Besides controlling particulate emissions, the units simultaneously reduce SO₂ emissions (7, 9). Thus particulate scrubbers can be used both with and as flue-gas desulfurization systems. However, current commercial wet particulate scrubbers rely principally on impaction and interception mechanisms and theoretically should not remove efficiently the smaller, submicron particles (7, 8, 10, 11). In addition, resuspension of droplets from mist eliminators can augment the emission of fine particles from scrubbers (12). Of the types of scrubbers used on coal utility boilers, high-energy, venturi scrubbers are among the most efficient in removing submicron particles (7, 10).

In view of the greater respirability of fine particles (13) and the well-established concentration of many elements in fine particles from coal combustion (5, 14-20), the emission of substances from wet scrubbers and electrostatic precipitators must be scrutinized. In this work we compare elemental emissions and particle-size distributions from two power units equipped with high-energy, variable-throat, venturi wet scrubbers and a unit equipped with a cold-side ESP. Each of the units was in use at a Western coal-fired power plant at which the same coal was burned in all units. Because fly-ash elutriation and particle-size characteristics of the boilers were

Table I. Design and Operating Parameters of the Coal-Fired Utility Boilers Equipped with a Venturi Wet Scrubber or Electrostatic Precipitator System

parameter	scrubber units ^a		ESP unit
	no. 1	no. 2	
boilers			
type	front-fired	front-fired	front- and rear-fired
efficiency, % ^b	87	87	88.7
excess air, %	15	12.5	16
max steam capacity, kg/s	160	203	654
control devices			
flue gas flow rate at inlet, m ³ /s ^c	254	322	1026
temp, °C ^d	54	54	117
suspended particle concn at inlet, mg/m ³	20.2	20.2	23
SO ₂ concn at inlet, ppm	650	650	800
efficiency of particulate removal, %	99.2 ^e (99.7 ± 0.1) ^g	99.2 ^e	97 ^f

^a Liquid-to-gas ratio, 1.4 L/m³ (actual); make-up water for the system, 6.4 to 7.6 m³/min; liquid delay time in the venturi-cycle loop, about 2 min; liquid temperature leaving the scrubber, 54 °C; pH of liquid in the thickener maintained at 7.5 by the addition of lime; suspended solids in recirculated flow maintained at 6%. ^b At maximum generating capacity. ^c Nominal value at 21 °C. ^d Measured at outlet sampling location. ^e Nominal value. ^f Estimated from elemental penetrations and plant-design data. ^g Measured during February sampling period at a differential venturi pressure of 36.8 mmHg and 95% of maximum electrical generating capacity.

similar, the relative effectiveness of the two types of control devices can be evaluated for trace element removal by comparing their emissions.

Experimental

Power Units. Three separate units, designated as 1, 2, and 3, with respective maximum steam capacities of 160, 203, and 654 kg/s were tested. Blended, pulverized, surface-mined, subbituminous coal from the same source was burned in each of the units. All three boilers operated dry bottom without fly-ash reinjection. Flue gasses from both of the scrubber-equipped units (1 and 2) were fed through an air heater before entering the scrubber. Gasses from the scrubber passed through a mist eliminator, a wet, induced-draft fan, and another mist eliminator. The scrubbing solution was continuously recycled from the cyclone separator to the venturi. Blowdown from the cyclone was sent to a thickener where lime (CaCO₃) was added. The scrubber systems were designed to remove 99.2% of the incident particulate material and also removed 30 to 35% of the SO₂.

Gasses leaving the boiler of the ESP-equipped unit flowed through two cold-side precipitators, which were arranged in a chevron design, before exiting through a 91-m stack. The total specific collecting area of the ESP was 4760 cm²/m³. When all sections were operating properly, net removal efficiency of the ESP was typically 97%. Other specifications for the boilers and control devices are listed in Table I.

Sampling. Samples were taken with a modified, EPA-type sampling train as described previously (20). The same filter materials (47-mm, 0.4-μm pore, Nuclepore membranes) and University of Washington Mark III and Mark V source test cascade impactors (21) were used in each of the units. The impactors, respectively, provided 8 and 12 discrete fly-ash size fractions for chemical analysis ranging from ≤0.1 to ≥30 μm.

Table II. Typical Coal Consumption and Efficiencies of Energy Conversion

power unit	load factor, %	coal consumption, g/s × 10 ⁴	energy conversion efficiency, Btu/kW-h
scrubber-equipped units			
1 (Feb 76)	100	2.74	1.00 × 10 ⁴
2 (June 75)	100	3.58	1.02 × 10 ⁴
ESP-equipped units			
(July 75)	94	9.71	9.47 × 10 ³
(July 75)	82	8.57	9.38 × 10 ³

Samples were collected at the outlets of the scrubber mist eliminators and in-stack at the 61-m level of the ESP-equipped unit during two periods in June and July 1975. Scrubber maintenance was performed several months before sampling in June. Additional samples were collected from the first scrubber and the ESP unit along with inlet and outlet testing during a third period in February 1976 shortly after scrubber maintenance.

Records of plant-operating data collected hourly include gross generating load, coal consumption, and proximate analyses. Energy-conversion efficiencies (determined monthly), status of ESP sections, and scrubber venturi pressure (hourly) were obtained from plant personnel. Velocity, temperature, and pressure of the stack gas were monitored continuously during each sampling. Samples of coal, ESP fly ash, bottom ash, and scrubber slurry were also taken during the stack fly-ash collections.

Plant Operation. During the sampling period in June, operation of the scrubber-equipped units remained relatively stable. During the sampling period in July, 4 of the 32 precipitator sections were inoperative but compliance with emission standards (215 ng/J) and precipitator efficiency (97% for total suspended particles) were maintained by operating at reduced loads. In February, failure in the precipitator resulted in a 10- to 20-fold increase in emissions. These data are not reported.

Analyses. Stack-, ESP-, and bottom-ash, scrubber-slurry, scrubber-lime, and coal samples were analyzed for up to 43 elements by instrumental neutron activation analysis (INAA) as previously described (22, 23). Filter, fly-ash, and coal samples were analyzed for Pb, Cd, and Be by atomic absorption spectroscopy (AAS). Nickel, Pb, and Cd were determined in coal and fly-ash samples by energy-dispersive, X-ray fluorescence analysis (XRF) (24). Results from these techniques were verified by analyses of National Bureau of Standards' standard reference materials, coal (SRM 1632) and coal fly-ash (SRM 1633), and through interlaboratory comparisons of SRM samples (25, 26).

Size distributions of particles collected on several individual impactor stages, backup filters, and total filters, i.e., 47-mm filter preceded only by an inlet nozzle, were determined by scanning electron microscopy (SEM). The treatment and results of these data were discussed previously (20).

Data Normalization. Rates of atmospheric discharge of minor and trace element species in each sample were computed from the stack concentrations and gas velocities. Emission rates were further normalized to the boiler heat input to account for differences in coal consumption, electric power production, and efficiency of energy conversion of each unit. The heat input was computed from the gross generating load and energy-conversion efficiency of each unit. Coal consumption rates were computed from the gross generating load (*L*), the known thermal efficiency (a monthly average *E*), and the heat content of the coal (*Q_c*) as follows:

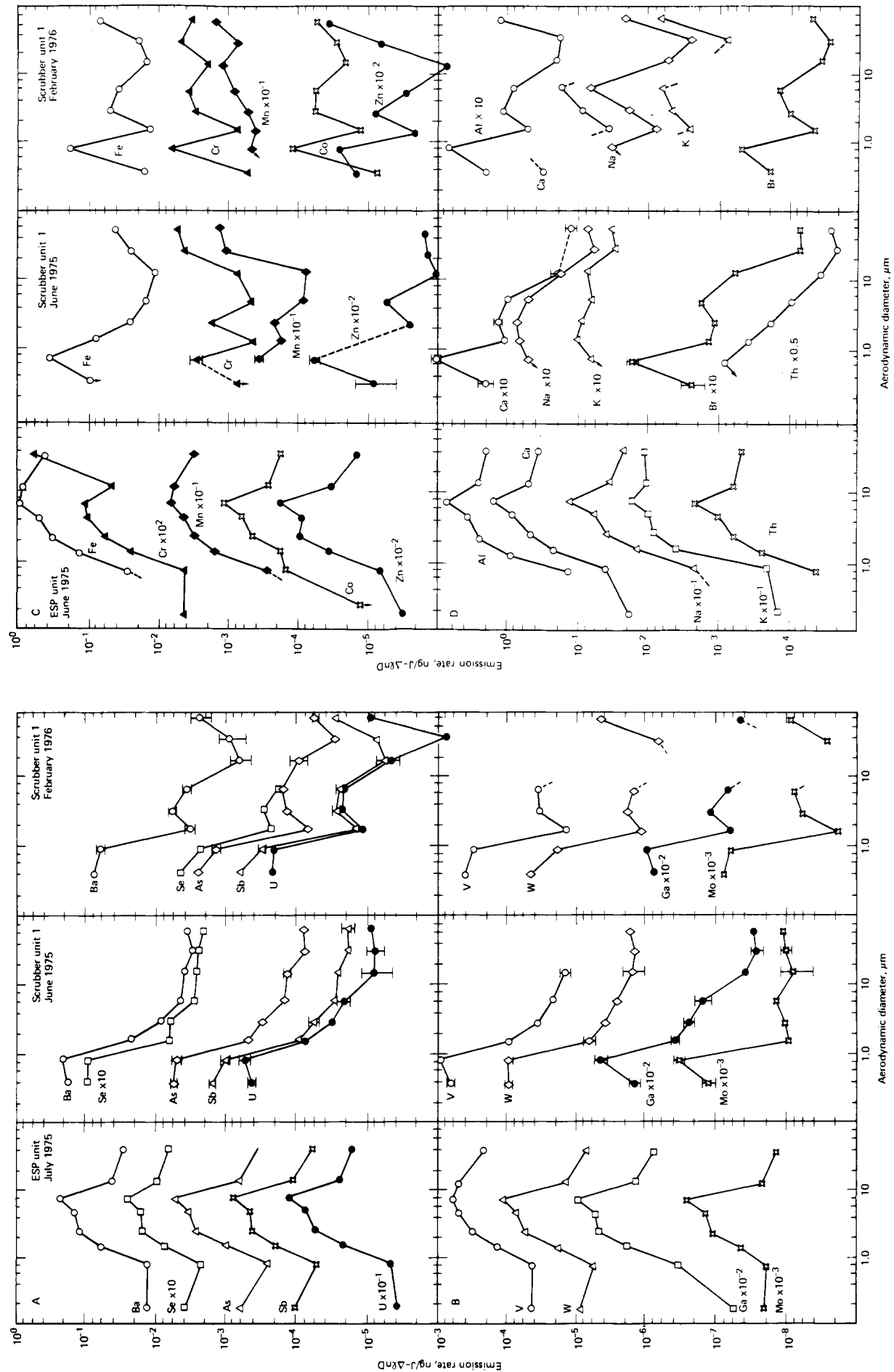


Figure 1. Particle-size distributions of elements emitted from power units equipped with a cold-side ESP and a venturi wet scrubber. The concentration data of individual elements are expressed as emission rate per joule of heat input to the boiler to allow comparison of the two units. The data are normalized to log size intervals (D = particle diameter)

Table III. Concentrations of Elements in Coal Burned during Sampling Periods ($\mu\text{g/g}$)^a

elements	June 75	July 75	Feb 76
Al	30 100 \pm 4990 (7)	30 300 \pm 3600 (15)	29 500 \pm 2390 (7)
As	2.03 \pm 0.43 (7)	2.73 \pm 0.71 (11)	2.84 \pm 0.84 (6)
Ba	466 \pm 108 (7)	418 \pm 88 (14)	420 \pm 167 (7)
Be	1.51 \pm 0.17 (7)	1.67 \pm 0.14 (9)	1.2 \pm 0.6 (7)
Br	0.97 \pm 0.20 (6)	0.96 \pm 0.18 (2)	—
Ca	6 300 \pm 1610 (7)	5 360 \pm 730 (15)	5 620 \pm 860 (7)
Cd	0.053 \pm 0.020 (7)	0.061 \pm 0.019 (10)	0.17 \pm 0.02 (7)
Ce	24.9 \pm 2.0 (7)	25.6 \pm 1.7 (15)	27.0 \pm 2.0 (7)
Cl	54.4 \pm 11.5 (2)	71 \pm 20 (4)	48 \pm 17 (1)
Co	1.94 \pm 0.17 (7)	1.98 \pm 0.25 (14)	2.08 \pm 0.22 (7)
Cr	6.12 \pm 0.52 (7)	5.19 \pm 0.29 (15)	7.02 \pm 1.28 (7)
Cs	0.590 \pm 0.084 (6)	0.70 \pm 0.08 (15)	0.72 \pm 0.16 (7)
Cu	14.0 \pm 0.5 (2)	13.4 \pm 1.2 (6)	12.7 \pm 0.6 (7)
Fe	5 940 \pm 740 (7)	5 720 \pm 380 (15)	6 470 \pm 570 (7)
Ga	8.30 \pm 1.72 (2)	8.8 \pm 1.4 (11)	8.48 \pm 1.25 (7)
Hg	0.25 \pm 0.05 (6)	0.065 \pm 0.015 (5)	0.10 \pm 0.02 (5)
In	0.037 \pm 0.007 (4)	0.0415 \pm 0.0046 (13)	0.039 \pm 0.006 (5)
K	1 690 \pm 170 (6)	1 820 \pm 250 (14)	1 730 \pm 260 (7)
La	13.0 \pm 1.0 (7)	14.3 \pm 0.8 (15)	13.4 \pm 0.8 (7)
Mg	1 950 \pm 460 (4)	2 330 \pm 470 (11)	2 240 \pm 753 (6)
Mo	2.4 \pm 0.9 (1)	2.60 \pm 0.54 (15)	2.67 \pm 0.26 (6)
Mn	56 \pm 24 (6)	54.1 \pm 1.6 (15)	60.2 \pm 20.0 (7)
Na	2 970 \pm 370 (7)	2 940 \pm 160 (15)	2 930 \pm 248 (7)
Ni	4.4 \pm 0.5 (2)	—	—
Pb	10.7 \pm 0.5 (2)	10.2 \pm 1.2 (16)	12.1 \pm 0.7 (7)
Rb	9.95 \pm 1.96 (7)	9.05 \pm 0.53 (15)	12.1 \pm 1.8 (7)
S ^b	5 800 \pm 1000 (7)	5 200 \pm 800 (2)	5 800 \pm 600 (12)
Sb	0.656 \pm 0.086 (7)	0.572 \pm 0.049 (15)	0.614 \pm 0.095 (7)
Sc	2.84 \pm 0.20 (7)	2.77 \pm 0.11 (15)	2.98 \pm 0.20 (7)
Se	1.41 \pm 0.11 (7)	1.55 \pm 0.15 (15)	1.74 \pm 0.25 (7)
Sr	88 \pm 13 (7)	87.2 \pm 8.9 (15)	97.7 \pm 8.3 (7)
Ta	0.509 \pm 0.038 (7)	0.492 \pm 0.038 (15)	0.513 \pm 0.056 (7)
Th	5.95 \pm 0.41 (7)	5.73 \pm 0.32 (15)	6.21 \pm 0.67 (7)
Ti	1 120 \pm 222 (6)	1 220 \pm 200 (14)	1 230 \pm 180 (6)
U	2.13 \pm 0.11 (7)	1.85 \pm 0.19 (15)	2.12 \pm 0.25 (7)
V	22.9 \pm 3.0 (4)	22.1 \pm 3.2 (9)	24.9 \pm 3.1 (4)
W	0.99 \pm 0.40 (2)	0.80 \pm 0.24 (5)	<0.13 (1)
Zn	15.8 \pm 1.4 (6)	14.7 \pm 1.7 (15)	16.4 \pm 3.2 (7)
Zr	55.6 \pm 8.7 (7)	52.2 \pm 5.9 (15)	66.7 \pm 9.8 (7)

^a Averages and standard deviations; number of samples given in parentheses. ^b Analyses obtained from power plant.

$$\text{coal flow} = L(\text{kW}) \times E \frac{\text{Btu}}{\text{kW}\cdot\text{h}} \times \frac{1}{Q_c \frac{\text{Btu}}{\text{lb}}} \times 0.126 \frac{\text{g}\cdot\text{h}}{\text{s}\cdot\text{lb}}$$

Rates of coal consumption and the efficiencies of energy conversion are listed in Table II. Consumption rates of individual elements were obtained by multiplying their concentrations in coal (Table III) by the coal consumption rate. Overall penetrations of individual elements were computed by dividing the emission rate by the consumption rate. Penetrations are independent of the concentrations of elements in coal.

Elemental concentrations in particles associated with the observed distributions were determined by INAA of impactor samples. Using SEM analysis, density measurements, and INAA, we corrected elemental mass on impactor backup filters for excess mass resulting from particle bounce-off and reentrainment to provide a more accurate estimate of the small particle component (see ref 20). Particle-size distributions of several elements from both the scrubber-equipped (unit 1) and ESP-equipped units are shown in Figures 1A through D. Normalized emission rates (ng/J) are plotted vs.

the aerodynamic diameters of particles on individual impactor stages and backup filters; aerodynamic diameters were determined from SEM measurements (20).

Results and Discussion

Scrubber Emissions. As shown in Table IV, emissions of most elements from the scrubber units agreed closely during June 1975, despite large differences in steam generating loads (about 160 and 203 kg/s in units 1 and 2, respectively). Thus, normalization to gross heat consumption accounts successfully for differences in coal consumption of these units (see Table II). Number vs. size distributions of fly-ash aerosols collected from each of the units were distributed bimodally, reflecting in part particles derived from vapor condensation and from residual mineral matter (fly ash) that is eluted from the boiler (see Table V). A third peak in aerosol size distribution was often observed in particles collected by impaction from scrubbers (Figure 1) in both the June and July experiments and is attributed to liquid aerosols that penetrate the mist eliminators.

In the scrubber experiment in June, $\geq 90\%$ of the mass of

Table IV. Normalized Emission Rates of Elements in Particulate Emissions from Scrubber- and ESP-Equipped Electrical Generating Units (pg/J) ^a

Element	Scrubber, June 1975 ^b		ESP unit, July 1975 ^c		Scrubber unit 1, February 1976 ^d			
	Unit 1	Unit 2	Sample at 82% Load	Range ^e	Median	Range		
Al	1320 ± 60	1130 ± 60	15,600 ± 500	3860 - 21,700	680 ± 20	367 - 1290	(22)	
As	13.5 ± 0.2	9.2 ± 0.2	15.3 ± 0.3	5.77 - 15.3	5.24 ± 0.08	3.53 - 10.6	(23)	
Ba	450 ± 20	580 ± 30	807 ± 10	243 - 807	97.9 ± 0.8	50.1 - 240	(23)	
Be	—	—	0.72 ± 0.24	0.42 - 0.72	(3)	—		
Br	2.00 ± 0.03	0.53 ± 0.04	6.6 ± 3.5	(1)	0.98 ± 0.02	0.355 - 4.16	(21)	
Ca	—	—	3400 ± 100	1590 - 3940	782 ± 47	525 - 1150	(15)	
Cd	—	0.84 ± 0.34	0.26 ± 0.03	0.097 - 0.26	(4)	—		
Ce	0.93 ± 0.05	0.45 ± 0.09	16.0 ± 0.5	8.25 - 21.3	0.48 ± 0.03	0.35 - 0.83	(18)	
Cl	63 ± 3	49 ± 3	—	—	37.0 ± 6.1	12.8 - 159	(13)	
Co	0.57 ± 0.02	0.30 ± 0.01	2.38 ± 0.04	1.12 - 3.05	0.165 ± 0.005	0.0065 - 2.13	(22)	
Cr	20.7 ± 0.2	3.4 ± 0.1	9.58 ± 0.36	3.1 - 30.5	13.4 ± 0.2	1.96 - 124	(22)	
Cs	—	—	0.410 ± 0.031	0.209 - 0.615	0.014 ± 0.005	—	(1)	
Cu	—	8.8 ± 1.0	—	—	11.6 ± 2.3	4.36 - 23.2	(4)	
Fe	455 ± 20	425 ± 7	3670 ± 40	1980 - 5350	239 ± 14	160 - 1200	(21)	
Ga	5.3 ± 0.2	2.9 ± 0.1	18.7 ± 1.0	9.74 - 19.8	2.01 ± 0.06	1.18 - 4.03	(20)	
I	1.21 ± 0.04	0.82 ± 0.08	—	—	—	—		
In	0.019 ± 0.001	0.014 ± 0.001	0.108 ± 0.008	0.0339 - 0.108	0.0140 ± 0.0009	0.00820 - 0.0203	(17)	
K	41 ± 6	49 ± 5	905 ± 200	441 - 1130	27.7 ± 5.0	13.6 - 72.9	(17)	
La	0.46 ± 0.02	0.45 ± 0.01	8.96 ± 0.09	4.75 - 12.0	0.275 ± 0.009	0.124 - 0.524	(21)	
Mg	230 ± 50	290 ± 110	1360 ± 380	1170 - 3240	112 ± 9	57 ± 11 - 570 ± 320	(15)	
Mo	4.3 ± 0.2	2.7 ± 0.2	6.48 ± 0.76	2.26 - 8.61	2.07 ± 0.12	1.20 - 2.87	(20)	
Mn	38 ± 1	15.7 ± 0.3	41.2 ± 0.5	9.07 - 41.2	23.0 ± 0.4	1.99 - 137	(22)	
Na	230 ± 10	219 ± 6	2210 ± 10	1120 - 2810	170 ± 4	72.5 - 310	(22)	
Ni	15 ± 4	—	—	—	13.3 ± 1.1	5.30 - 40.4	(9)	
Rb	—	—	5.52 ± 0.57	2.52 - 7.52	—	—		
Sb	3.26 ± 0.06	1.7 ± 0.2	2.15 ± 0.04	0.863 - 2.15	1.38 ± 0.02	0.901 - 1.99	(21)	
Sc	0.127 ± 0.005	0.097 ± 0.004	1.96 ± 0.02	1.03 - 2.72	0.0552 ± 0.0009	0.0391 - 0.107	(21)	
Se	20.5 ± 0.5	21.0 ± 0.6	5.82 ± 0.16	2.83 - 6.07	12.9 ± 0.2	8.81 - 18.0	(21)	
Sr	18.4 ± 0.8	20 ± 1	85.4 ± 8.0	32.2 - 111	9.44 ± 3.6	5.11 - 15.7 ± 3.8	(12)	
Ta	0.056 ± 0.005	0.022 ± 0.008	0.323 ± 0.013	0.158 - 0.441	0.017 ± 0.003	0.00898 - 0.288	(11)	
Th	0.22 ± 0.01	0.195 ± 0.007	3.67 ± 0.06	1.96 - 5.09	0.102 ± 0.004	0.0603 - 0.203	(19)	
Ti	76 ± 9	77 ± 9	892 ± 90	338 - 1150	43.1 ± 9.0	27.2 - 86.8	(10)	
U	1.08 ± 0.04	0.58 ± 0.04	3.29 ± 0.15	1.39 - 3.29	0.527 ± 0.008	0.254 - 0.751	(22)	
V	16.6 ± 0.4	19.9 ± 0.6	39.7 ± 3.2	17.3 - 39.5	(5)	9.39 ± 0.53	5.84 - 13.9	(20)
W	2.26 ± 0.04	1.72 ± 0.04	2.78 ± 0.18	1.20 - 2.78	1.04 ± 0.03	0.690 - 1.37	(23)	
Zn	8.8 ± 0.9	4.6 ± 0.3	44.8 ± 2.4	16.5 - 44.8	5.83 ± 0.52	2.51 - 69.4	(21)	
Zr	—	6.6 ± 2.5	34.6 ± 7.1	13.1 - 41.1	2.46 ± 1.00	1.54 - 4.70	(5)	
TSP ^f	—	—	123,000 ± 2000	65,000 - 123,000	10,900 ± 2200	10,100 - 16,100	(16)	

^a Uncertainty given is that of counting statistics of samples and blanks; variation among successive samples is generally less than 20% for the ESP unit, but somewhat larger for scrubber units. Uncertainties in the absolute emission rates from the ESP are estimated to be on the order of 30%. ^b Units 1 and 2 were operated at 97 to 100 and 89 to 100% of full generating capacity, respectively. Differential venturi pressure (ΔP_v) for both scrubber units ranged from 34 to 37 mmHg. ^c Unit operating at 83% capacity with four precipitator sections inoperative. Data are from up to eight samples unless indicated by number in parentheses. Wall and interstage losses were severe in impactor samples from ESP units and these samples are not included; data on scrubber units were derived from both filter and cascade impactor samples (see ref 20). ^d Unit operated at 86 to 100% of full generating capacity with ΔP_v of 23 to 56 mmHg. ^e Unit operated at 69 to 95% of full generating capacity. ^f Total suspended particulates.

most emitted elements occurred in particles of diameters $\leq 1 \mu\text{m}$. Several elements, however, including Co, Cr, Fe, Mn, Cl, Br, Na, K, and Ca, often had appreciable or even major portions of their mass in aerosols of large sizes. Therefore, these elements are most probably contained in the liquid droplets. Scanning electron microscope analyses of dried impactor substrates collected in June revealed only submicron fly-ash particles on the uppermost (large particle) stages. However, on filter and impactor substrates collected in February, fly-ash particles with physical diameters as large as $6 \mu\text{m}$ were present. These larger particles suggest that the scrubber (unit 1) was less efficient in removing supermicron particles of the fly ash in February than in June. Despite this apparent decrease in collection efficiency of supermicron particles, the normalized elemental emission rates (Table IV) of the scrubber-equipped unit in June were 1.5 to 5 times higher than in February. As shown in Figure 1, the increased emission rates in June were generally confined to submicron-size particles. Evaporation of the liquid in entrained droplets can lead to the formation of submicron particles. Hence, the greater emissions in June may have resulted from entrainment problems with the mist eliminators and the high content of dissolved solids in the recycled scrubbing solution. All of the scrubber units were, however, operating within compliance (TSP emission ≤ 21.5

ng/J) during both sampling periods.

ESP and Scrubber Efficiency. Curves of particle collection efficiency vs. particle size for the ESP and unit 1 scrubber were constructed from the data from concurrent inlet-outlet sampling during February. As shown in Figure 2, the collection efficiency of the scrubber unit for supermicron particles is $>99\%$, but below $1 \mu\text{m}$ drops off rapidly with decreasing particle size. The aerodynamic 50% cut-off diameter for the scrubber was about $0.75 \mu\text{m}$, and its efficiency for TSP's was $99.7 \pm 0.1\%$ (see Table I). The negative efficiency for the collection of very small particles is attributed to mist entrainment and flash volatilization of liquid droplets that contain dissolved and suspended solids.

Unfortunately, the mechanical failures noted above prevented measuring optimum ESP performance. The ESP efficiency curve, however, agreed qualitatively with that typical of a cold-side ESP shown in Figure 3 (27). These curves are characterized by high collection efficiencies of both supermicron and submicron particles, with a shallow minimum for particles in the 0.1- to $1.0 \mu\text{m}$ range. Thus, we would expect submicron particles to penetrate the scrubber more effectively than the ESP. As noted above, the relative effectiveness of the two types of control devices may be inferred from particulate emission rates from each, if the particle size distributions of

Table V. Mass Median Aerodynamic Diameters (MMAD) of Elements in Aerosols Emitted from Two Coal-Fired Electrical Generating Units (μm)

ESP unit, July 1975		scrubber unit, Feb 1976	
elements	MMAD, ^a μm	elements	MMAD, ^a μm
Cr, Cs, Rb, Zr	10.7–12.3	Co, Cr, Ni	7.1–12
Al, Br, Ce, Co, Dy, Eu, Fe, Hf, K, La, Lu, Mg, Nd, Sc, Sm, Ta, Tb, Th, Ti	9.1–10.0	Fe, K, Mg, Na, Zn	3.0–4.0
Ca, Mn, Na, Se	7.9–8.6	Al, Br, Ce, Dy, Hf, Lu, Sc, Sm, Th, La	1.4–2.1
As, Ba, Ga, In, Mo, Sb, U, V, W, Zn	4.4–6.3	Ca, Ga, In, Mo	1.69–0.81
total suspended particles ^b		As, Ba, Sb, Se, U, V, W	0.49–0.59
small mode	0.13 ($\sigma_g^c = 1.42$)		0.33 ($\sigma_g^c = 1.57$) ^d
large mode	8.1 ($\sigma_g^c = 2.2$)		0.80 ($\sigma_g^c = 1.20$) ^d

^a Range of median values of MMADs from distributions of up to six impactor samples. ^b Determined from SEM particle counting techniques (20). ^c Geometric standard deviation. ^d Data from SEM analyses of filter sample collected in June 1975.

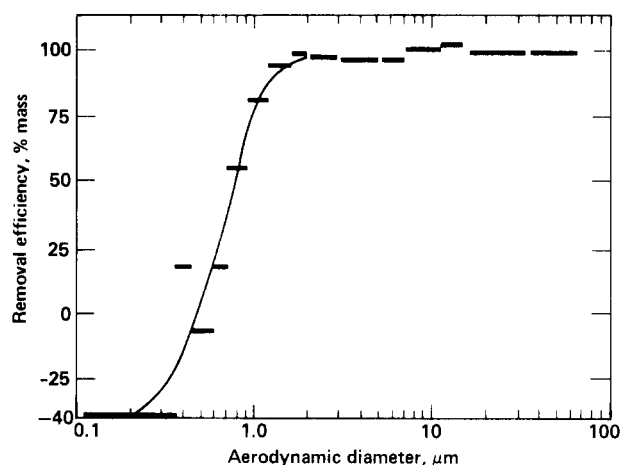


Figure 2. The venturi wet scrubber system is inefficient in removing particles of submicron diameters

aerosols entering the two devices are known.

Size distributions of particles entering both a scrubber system (unit 1) and the ESP were measured with cascade impactors during the February experiment. The distributions of Sc (Figure 4), an element which is independent of particle size, indicate that normalized rates of mass flow (mass/unit heat input) and particle-size distributions are nearly the same for particles $<2 \mu\text{m}$. The considerable discrepancy in the curves at larger particle sizes probably results from problems associated with turbulence and severe losses on walls of the impactor. The data reflect single-point sampling in turbulent inlet ducts and, hence, difficulties in obtaining truly isokinetic and representative sampling. As shown in Figure 4, the results of successive measurements at the inlet of particles $\geq 5 \mu\text{m}$ in both control devices generally agreed poorly. Based on the engineering parameters, the normalized fly-ash input (mass/gross boiler heat input) should be equal to that of the ESP. Because the composition of the coal burned during each sampling period was essentially identical (see Table III), emissions normalized to gross boiler heat input may be compared directly.

Neglecting small differences in elemental concentrations in coal ($\leq 7\%$ for Sb), we can estimate the relative efficiencies of the two devices for collecting particles in the submicron and supermicron size ranges from the normalized curves of emission rate vs. particle size (Figure 1). Based on elements such as As and Sb for which concentrations in small particles can be determined most accurately (see ref 20), scrubber emissions

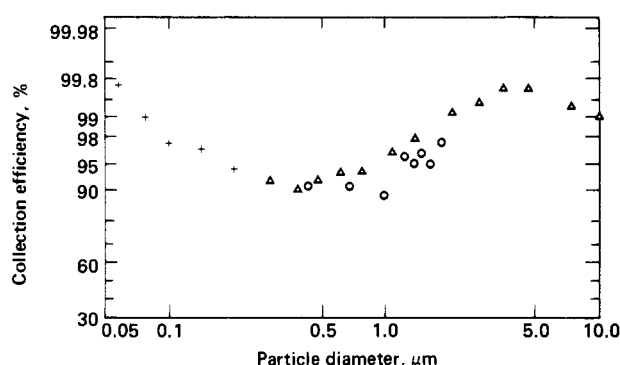


Figure 3. Particle removal efficiency of a cold-side ESP is relatively uniform over the entire range of particle sizes. Reprinted with permission from ref 27. Copyright 1975 Air Pollution Control Association

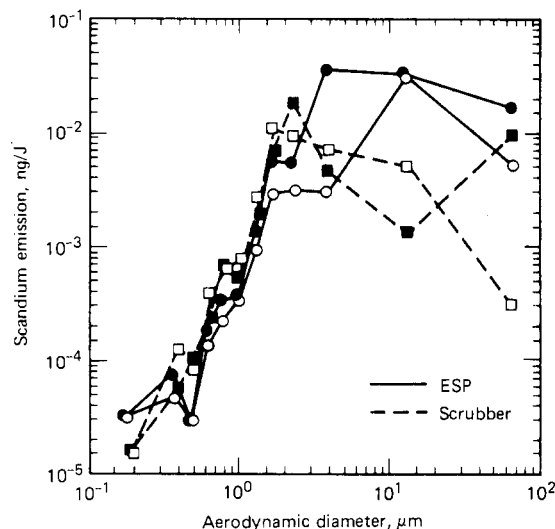


Figure 4. Emission rate of Sc in aerosols collected at the inlet of the precipitator and wet scrubber

(February data) of submicron particles collected on the backup filter are about six times greater than ESP emissions. Scrubber emissions of these elements in the supermicron particles, however, are only about 1/11 of those in the ESP emissions after accounting for losses on the walls in ESP impactor samples, which were as high as 40% (see ref 20). Thus, because normalized mass inputs to both devices were the

Table VI. Penetration of Elements Contained in Particles Emitted from a Venturi Wet Scrubber and an ESP-Equipped Coal-Fired Generating Unit (%)

element	ESP unit, July 1975		scrubber unit, Feb 1976	
	sample at 82% load	range ^a	median ^a	range
Al	1.1 ± 0.1	0.26–1.5	0.047 ± 0.004	0.025–0.088
As	11.5 ± 3.0	4.3–11.5	3.7 ± 1.1	2.5–7.5
Ba	4.0 ± 0.8	1.2–4.0	0.47 ± 0.19	0.24–1.2
Be	0.9 ± 0.3	0.5–0.9 (2)	—	—
Br	0.14 ± 0.08	—	(2.1 ± 0.4) ^b	0.75–8.8
Ca	1.3 ± 0.2	0.61–1.5	0.28 ± 0.05	0.19–0.41
Cd	8.8 ± 3.0	3.3–8.8 (4)	—	—
Ce	1.29 ± 0.09	0.67–1.7	0.036 ± 0.003	0.026–0.062
Cl	—	—	1.6 ± 0.6	0.54–6.7
Co	2.5 ± 0.3	1.2–3.2	0.16 ± 0.02	0.063–2.1
Cr	3.8 ± 0.3	1.23–12.1	3.9 ± 0.7	0.56–36
Cs	1.2 ± 0.2	0.61–1.8	0.040 ± 0.017 (1)	—
Fe	1.32 ± 0.09	0.71–1.9	0.075 ± 0.008	0.050–0.38
Ga	4.4 ± 0.7	2.3–4.6	0.48 ± 0.07	0.28–0.96
In	5.4 ± 0.7	1.7–5.4	0.73 ± 0.12	0.43–1.1
K	1.0 ± 0.3	0.50–1.3	0.032 ± 0.008	0.016–0.085
La	1.29 ± 0.07	0.68–1.7	0.042 ± 0.003	0.019–0.079
Mg	1.2 ± 0.4	1.0–2.9	0.10 ± 0.03	0.051 ^c –0.51 ^d
Mo	5.1 ± 1.2	1.8–6.8	1.6 ± 0.2	0.91–2.2
Mn	1.6 ± 0.5	0.35–1.6	0.77 ± 0.26	0.067–4.6
Na	1.55 ± 0.09	0.78–2.0	0.12 ± 0.01	0.050–0.21
Pb	5.5 ± 1.1	2.2–5.5 (4)	—	—
Rb	1.3 ± 0.1	0.57–1.7	—	—
Sb	7.7 ± 0.7	3.1–7.7	4.5 ± 0.7	3.0–6.6
Sc	1.46 ± 0.06	0.77–2.03	0.037 ± 0.003	0.027–0.073
Se	7.7 ± 0.8	3.8–8.1	15 ± 2	10–21
Sr	2.0 ± 0.3	0.76–2.6	0.20 ± 0.08	0.11–0.32
Ta	1.3 ± 0.1	0.66–1.9	0.067 ± 0.014	0.035–1.1
Th	1.32 ± 0.08	0.70–1.8	0.033 ± 0.004	0.020–0.066
Ti	1.51 ± 0.03	0.57–1.9	0.071 ± 0.018	0.045–0.14
U	3.7 ± 0.4	1.6–3.7	0.50 ± 0.06	0.24–0.72
V	3.7 ± 0.6	1.6–3.7	0.76 ± 0.10	0.47–1.1
W	7.2 ± 2.2	3.1–7.2	(2.6 ± 0.8) ^b	1.7–3.5
Zn	6.3 ± 0.8	2.3–6.3	0.72 ± 0.15	0.31–8.6
Zr	1.4 ± 0.3	0.52–1.6	0.075 ± 0.032	0.047–0.14

^a Number of samples was eight unless otherwise indicated. ^b Data based on elemental concentration in coal collected during July 1975. ^c Unusually high uncertainty of ±0.020. ^d Unusually high uncertainty of ±0.34.

same, the scrubber must be much less efficient than the ESP in removing submicron particles. Furthermore, as shown in Table VI, the overall penetration of As (3.7%) in scrubber aerosols of MMAD of 0.51 μm (Table V) is about 80 times larger than the overall penetration of Al (0.047%), which is associated with aerosols with an MMAD of 1.7 μm . Thus, as one would expect, the overall penetration of a specific element is dependent on its concentration in small particles.

Penetrations of Elements. In Table VII, we compare penetrations of elements through the ESP-equipped unit (July data) to those from the scrubber-equipped unit (February data) measured over the entire particle-size range. The penetration ratios are nearly identical with the normalized emission rates except that they account for the small differences in elemental concentrations in coal.

As shown in Table VII, despite an 11-fold greater efficiency in TSP removal, i.e., $1/0.087$ or $((1 - 0.997)/(1 - 0.97))$, the penetration of elements in the first group through the scrubber was as much as 58% (for Sb) of that through the ESP-equipped unit. Substantial fractions of Br and Se apparently occur in the vapor phase at stack temperatures (10). Thus, the very large relative emission of Se and Br probably results from both scrubbing and condensation occurring at the lower gas temperature at the scrubber sampling location (54 vs. 110 °C

in the ESP stack).

Most of the elements in group 1 of Table VII are associated with ESP and scrubber aerosols of smaller MMADs (see Table V) on which their concentrations are typically highly enriched (5, 14, 16–20). This might be attributed to their presence in coal partly as volatile inorganic or organic species or as fine mineral grains. Considerable evidence of augmented emission via mechanisms of entrainment and droplet evaporation exists (10, 28, 29) and suggests that high penetrations of several elements including S, Na, and K, which may be leached into the recycled scrubbing solution, result from the evaporation of droplets to form fine particles. It is likely, therefore, that the emission of lime-associated elements, i.e., Ca, Al, Mg, K, and Fe, present in limestone at 68, 2.4, 0.87, 0.13, and 0.11%, respectively, is especially augmented by these processes and might account to some extent for their presence in fine particles and their enhanced emission from the scrubber-equipped unit.

Scrubber emissions of Cr and Mn, and to some extent Zn and Co (group 2), were also enhanced relative to the TSP. Emission of these elements seems to be enhanced by corrosion of metal surfaces inside the scrubbers. Although independent evidence (30) supports this conclusion, the magnitude of the enhancement might be in error because of possible contami-

Table VII. Ratios of Emissions Rates and Estimated Potential Pulmonary Deposition of Elements from a Venturi Wet Scrubber and an Electrostatic Precipitator (February Scrubber Data; July ESP Data)

Element	Penetration ratio ^a		Pulmonary deposition ratio ^b		Concentration ratio ^c	
	Median	Range	Median	Range	Median	Range
Group 1						
Br	15 ± 0.04	5.4 - 63	27 ± 7	10 - 1100	170 ± 0.5	66 - 250
Se	1.9 ± 0.1	1.2 - 5.5	3.9 ± 0.5	2.7 - 12	22 ± 3	15 - 22
Sb	0.58 ± 0.02	0.39 - 2.1	0.93 ± 0.21	0.63 - 3.5	6.7 ± 0.7	4.8 - 8.4
W	0.36 ± 0.03	0.25 - 1.1	0.61 ± 0.14	0.40 - 1.8	4.1 ± 0.6	3.0 - 4.4
As	0.32 ± 0.01	0.22 - 1.7	0.57 ± 0.07	0.39 - 3.1	3.7 ± 0.4	2.7 - 6.8
Mo	0.31 ± 0.04	0.13 - 1.2	0.65 ± 0.20	0.28 - 2.6	3.6 ± 0.6	1.6 - 4.8
V	0.21 ± 0.02	0.13 - 0.69	0.44 ± 0.04	0.27 - 1.4	2.4 ± 0.4	1.6 - 2.8
Ca	0.22 ± 0.015	0.13 - 0.67	0.41 ± 0.04	0.23 - 1.3	2.5 ± 0.3	1.6 - 2.7
U	0.14 ± 0.01	0.065 - 0.45	0.35 ± 0.05	0.17 - 1.2	1.6 ± 0.2	0.79 - 1.8
In	0.14 ± 0.01	0.080 - 0.65	0.25 ± 0.04	0.14 - 1.1	1.6 ± 0.2	0.98 - 2.6
Ba	0.12 ± 0.005	0.060 - 1.0	0.22 ± 0.03	0.12 - 1.9	1.4 ± 0.2	0.73 - 4.0
Ga	0.11 ± 0.01	0.061 - 0.42	0.24 ± 0.03	0.13 - 0.90	1.3 ± 0.2	0.74 - 1.7
Sr	0.10 ± 0.04	0.042 - 0.42	d--	--	1.1 ± 0.4	0.51 - 1.7
Group 2						
Cr	1.03 ± 0.06	0.046 - 29	2.8 ± 0.2	0.12 - 80	12 ± 2	0.56 - 120
Mn	0.48 ± 0.02	0.042 - 13	1.0 ± 0.04	0.086 - 27	5.5 ± 0.6	0.51 - 52
Zn	0.11 ± 0.01	0.049 - 3.7	0.30 ± 0.07	0.13 - 9.7	1.3 ± 0.2	0.060 - 15
Co	0.064 ± 0.003	0.020 - 1.8	0.11 ± 0.01	0.034 - 3.0	0.74 ± 0.08	0.24 - 7.2
TSP	0.087 ± 0.009	0.082 - 0.25	--	--	±1.0 ± 0.1	±1.0 - 1.0
Group 3 ^e						
Mg	0.08 ± 0.03	0.02 - 0.5	0.15 ± 0.07	0.04 - 1.0	0.9 ± 0.2	0.2 - 2.0
Na	0.077 ± 0.003	0.025 - 0.27	0.13 ± 0.01	0.044 - 0.5	0.89 ± 0.10	0.30 - 1.1
Zr	0.05 ± 0.02	0.03 - 0.3	d--	--	0.6 ± 0.2	0.4 - 1.2
Fe	0.057 ± 0.004	0.030 - 0.54	0.13 ± 0.03	0.060 - 1.2	0.66 ± 0.09	0.37 - 2.2
Ti	0.047 ± 0.011	0.024 - 0.25	0.080 ± 0.025	0.03 - 0.44	0.54 ± 0.14	0.29 - 1.0
Al	0.043 ± 0.001	0.017 - 0.34	0.082 ± 0.008	0.032 - 0.63	0.49 ± 0.05	0.21 - 1.4
La	0.033 ± 0.003	0.010 - 0.11	0.061 ± 0.006	0.020 - 0.22	0.38 ± 0.05	0.12 - 0.44
K	0.031 ± 0.009	0.012 - 0.17	0.067 ± 0.019	0.026 - 0.37	0.36 ± 0.11	0.15 - 0.68
Ce	0.028 ± 0.002	0.016 - 0.092	0.043 ± 0.004	0.022 - 0.14	0.32 ± 0.04	0.20 - 0.37
Th	0.025 ± 0.001	0.011 - 0.094	0.055 ± 0.004	0.024 - 0.20	0.29 ± 0.03	0.13 - 0.38
Sc	0.025 ± 0.001	0.013 - 0.95	0.054 ± 0.004	0.027 - 0.19	0.29 ± 0.03	0.16 - 0.38

^a Based on data in Table VI. Uncertainties are derived from analytical uncertainties only. ^b Predicted pulmonary deposition ratio at stack conditions (see ref. 13 and 31). ^c Emission ratio normalized to mass emission rates. ^d Element not determined in cascade impactor samples from both units. ^e Group 3 also includes the elements Nd, Eu, Yb, Sm, Dy, and Lu.

nation by corrosion of the stainless steel samplers.

Matrix elements such as Fe, Al, and Sc (group 3), as well as total particulate mass, are emitted in greater quantities per unit heat input from the ESP unit than from the scrubber unit because of their predominant association with large (MMADs of about 10 μ m) silicate fly-ash particles, which are not as efficiently removed by the ESP as by the scrubber.

Lung Deposition. Particles greater than 10 μ m are generally not considered respirable and, as indicated by the curve in Figure 5, pulmonary deposition of the smallest sizes is greatest (13). Because the MMADs of aerosols emitted from the scrubber-equipped unit (~1.7 μ m for group 3 elements; see Table V) are much smaller than those from the ESP-equipped unit (10 μ m for group 3 elements), we used the ICRP pulmonary deposition model (13) to estimate the relative alveolar deposition of aerosols emitted from the two units.

The predicted deposition (mass/unit heat input) from elemental emissions from both units was computed by numerical integration of the product of the mass vs. size distributions from the cascade impactor and the ICRP deposition data as described in Biermann and Ondov (31). Because the data reflect air at stack concentrations, only relative depositions are meaningful; these are listed in Table VII (pulmonary deposition ratios). We note that the ratios listed may change with distance from the plant because of the effects of coagulation and sedimentation. Therefore, the comparison is only qualitative.

Depending on their mass vs. particle-size distributions, the

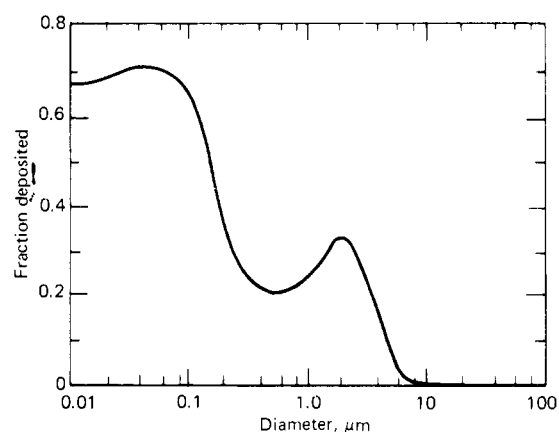


Figure 5. ICRP lung deposition curve (13)

relative depositions of individual elements (pulmonary deposition ratios, Table VII) are about twice the corresponding values of the actual relative emissions (penetration ratios). Thus, the model predicts that the scrubber aerosols are deposited in the lungs to about twice the extent of those from the ESP, because of the smaller particle sizes in the aerosol. Neglecting Se, the median values of the pulmonary deposition of scrubber emissions of group 1 elements ranged from about 20 to 2700% of the ESP emissions; the maximum values were 90 to 11 000% of the ESP emission. The corresponding values

for group 2 elements ranged from a low of 3.4%, the minimum value of Co, to a high of 8000% for Cr. The relative potential pulmonary deposition of group 3 elements from scrubber emissions was generally less than 15% of the ESP emissions, but ranged from about 1.6 to 120%. Thus, considering both overall efficiency (relative emission rates) and the distribution of particle sizes (relative potential pulmonary deposition), the venturi scrubber unit when operating properly was typically as effective or better, i.e., at least 50% of the time, in controlling the emissions of most elements associated with fine particles, including both group 1 and 2 elements. The scrubber was also generally much more effective in reducing emissions of the elements in group 3 on large particles. Notable exceptions were Cr, Mn, Ni, and Cu, which were frequently emitted in much greater quantities from the scrubber. During the June experiment (not shown in Table VII), the relative emission and relative potential depositions (pulmonary deposition ratios) of group 1 elements were from 2 to 5 times greater than those listed; and the corresponding values of group 3 elements were from 1.5 to 3 times greater than the listed values. In June, the scrubber was not operating optimally, probably because of mist entrainment problems discussed above, but was, however, operating in compliance with state emission standards (21.5 ng/J). Under these conditions, the scrubber was less effective than the ESP in controlling the emissions of most group 1 and 2 elements.

Specific Concentrations. As noted above, the ESP that was tested was somewhat undersized ($4760 \text{ cm}^2/\text{m}^3$) and is not nearly as efficient (97 vs. 99.8%) as larger ($12\,100 \text{ cm}^2/\text{m}^3$), more modern units in use at plants burning low-sulfur coal (32). Further normalization of the penetration ratios (Table VII) to the respective TSP ratios yields ratios of the specific concentrations of elements (μg of element/g of fly ash). The ratios of the specific concentrations indicate the relative emission of the two devices operating at equal efficiencies (concentration ratios, Table VII). Given equal efficiencies (for TSP), the penetration of group 1 elements through the scrubber would then range from 1.1 to 6.7 times that of the elements through the ESP (median values), neglecting Se and Br for reasons discussed above. The corresponding factors for group 2 elements ranged from 0.74 to 12. Penetrations of group 3 elements are, however, smaller through the scrubber unit.

Elements in group 3 tend to be distributed throughout the volume of the particle, while the available evidence shows that many of the group 1 elements are deposited on the surface of particles (14, 33–35) and might therefore have greater biologic availability. Based on the penetrations of Be, Cd, and Pb through the ESP-equipped unit (Table VI), we predict both Cd and Pb to behave as group 1 elements, and Be as a group 3 element. The concentration of Si, a major component of fly ash, shows no dependence on particle size (26), and should display group 3 behavior. Elements that are toxic to humans are included in each of the groups (36). However, most of the elements for which we have evidence of group 3 behavior, e.g., Si, Al, Fe, Na, K, lanthanides, and Sc, are generally considered less toxic than those in groups 1 and 2, e.g., As, Se, Sb, U, Cd, Pb, V, and Cr (36, 37). Thus, compared with an ESP of equal efficiency of TSP removal, the scrubber's enhanced emission of particulate species with greater potential toxicity may offset its advantage of greater efficiency in removing large particles because the latter contain potentially less toxic elements.

Summary and Conclusion

The efficiency of a venturi scrubber system was as high as 99.8% in removing TSP, but was severely reduced for particles $<1 \mu\text{m}$, and in fact the venturi wet scrubber emitted as much as 40% more submicron particles than entered the system. Comparison of scrubber emissions with those from an ESP-equipped coal utility unit indicates that despite a factor of 11

lower efficiency in TSP removal, the ESP unit was still significantly more efficient in removing submicron particles. Because of concentration enhancements on small particles and the difference in the removal efficiency of small particles, concentrations of many potentially toxic elements in particulate material emitted from the scrubber systems were as much as 250 times greater than those in emissions from the ESP unit. In addition, the particle sizes in emissions from the scrubber units (submicron size) are more efficiently deposited in the lungs of humans. Furthermore, the emission of several metals, as well as elements associated with the scrubbing liquid, seems to be enhanced because of corrosion of metal surfaces inside the scrubbers. Therefore, we conclude that the wet scrubber system tested was less effective in reducing the potential inhalation hazard of those particulate emissions discussed above than an ESP of comparable overall efficiency.

Acknowledgments

The authors gratefully acknowledge the assistance of R. E. Heft, R. W. Wikkerink, D. G. Garvis, and K. O. Hamby in the collection and analysis of samples; W. H. Martin and R. K. Tandy for assistance in data reduction; and B. K. Ishida and H. R. Ralston for assistance in preparing the manuscript.

Literature Cited

- (1) U.S. Bureau of Mines, "Minerals Yearbook Vol. 1, Metals Minerals and Fuels", U.S. Government Printing Office, Washington, D.C., 1974.
- (2) Interagency Task Force on Coal, "Project Independence", Federal Energy Administration, Task Force Report, 1975.
- (3) Bertine, K. K., Goldberg, E. D., *Science*, **173**, 233–5 (1971).
- (4) Hamilton, L. D., Ed., "The Health and Environmental Effects of Electricity Generation—A Preliminary Report", Brookhaven National Laboratory, July 1974.
- (5) Klein, D. H., Andren, A. W., Carter, J. A., Emery, J. F., Feldman, C., Fulkerson, W., Lyon, W. S., Ogle, J. C., Talm, Y., Van Hook, R. I., Bolton, N., *Environ. Sci. Technol.*, **9**, 973–9 (1975).
- (6) Morris, S. C., Novak, K. M., "Handbook for the Quantification of Health Effects from Coal Energy Systems", Draft Report, Brookhaven National Laboratory, Dec 15, 1976.
- (7) "McIlvaine Scrubber Manual", Vol. II, McIlvaine Co., Northbrook, Ill., 1974, pp 5–11.
- (8) Stern, A. C., "Air Pollution", Vol. III, Academic Press, New York, 1968, pp 437–95.
- (9) Statnick, P. M., Drehmel, D. C., 67th Meeting of the Air Pollution Control Association, Denver, Colo., Paper No. 7-4-231, June 1974.
- (10) Calvert, S., Goldsmith, J., Leith D., Mehta, D., in "Wet Scrubber System Study", Scrubber Handbook, Vol. I, Environmental Protection Agency, Report R2-118a, 1975, pp 5–81.
- (11) Hesketh, H. E., 68th Annual Meeting of the Air Pollution Control Association, Boston, Paper No. 75-50.6, 1975, pp 1–21.
- (12) Johnson, L. D., Statnick, R. M., "Measurement of Entrained Liquid Levels in Effluent Gases From Scrubber Demisters", Environmental Protection Agency, Report 650/2-74-050, 1974.
- (13) Task Group on Lung Dynamics, *Health Phys.*, **12**, 173–208 (1966).
- (14) Natusch, D. F. S., Wallace, J. R., *Science*, **186**, 695–9 (1974).
- (15) Davison, R. L., Natusch, D. F. S., Wallace, J. R., Evans, E. A., Jr., *Environ. Sci. Technol.*, **8**, 1107–13 (1974).
- (16) Kaakinen, J. W., Jorden, R. M., Lawasani, M. H., West, R. E., *Environ. Sci. Technol.*, **9**, 862–9 (1975).
- (17) Ragaini, R. C., Ondov, J. M., Proceedings of the International Conference on Environmental Sensing and Assessment, Vol. 1, Las Vegas, Nev., Institute of Electrical and Electronics Engineers, Inc., New York, 1976, p 17–2.
- (18) Gladney, E. S., Small, J. A., Gordon, G. E., Zoller, W. H., *Atmos. Environ.*, **10**, 1071–7 (1976).
- (19) Block, C., Dams, R., *Environ. Sci. Technol.*, **10**, 1011–17 (1976).
- (20) Ondov, J. M., Ragaini, R. C., Biermann, A. H., *Atmos. Environ.*, **12**, 1175–85 (1978).
- (21) Pilat, M. J., Ensor, D. S., Bosch, J. C., *Atmos. Environ.*, **4**, 671–9 (1970).
- (22) Ragaini, R. C., Heft, R. E., Garvis, D., "Neutron Activation Analysis at the Livermore Pool-Type Reactor for the Environmental Research Program", Report No. UCRL-52092, Lawrence Livermore Laboratory, 1976.

- (23) Heft, R. E., presented at the Third International Conference on Nuclear Methods in Environmental and Energy Research, Columbia, Mo., Oct 10-13, 1977.
- (24) Bonner, N. A., Bazan, F., Camp, D. C., *Chem. Instrum.*, **6**, 1-36 (1975).
- (25) Ondov, J. M., Zoller, W. H., Olmez, K., Aras, N. K., Gordon, G. E., Ranticelli, L. A., Able, K. H., Filby, R. H., Shah, K. R., Ragaini, R. C., *Anal. Chem.*, **47**, 1102-9 (1975).
- (26) Ondov, J. M., Ragaini, R. C., Heft, R. E., Fisher, G. L., Silberman, D., Prentice, B. A., Proceedings of the 8th Materials Research Symposium, Methods and Standards for Environmental Measurement, Gaithersburg, Md., Sept 20-24, in press; Lawrence Livermore Laboratory, Preprint UCRL-78194, 1976.
- (27) McCain, J. D., Gooch, J. P., Smith, W. B., *J. Air Pollut. Control Assoc.*, **25**, 117-21 (1975).
- (28) Ensor, D. S., Cahill, T. A., Sparks, L. E., presented at the 68th Annual Meeting of the Air Pollution Control Association, Boston, June 2-15, Paper No. MRI 75 Pa-1317, 1975.
- (29) Ensor, D. S., Jackson, B. S., Calvert, S., Lake, C., Wallon, D. V., Nilan, R. E., Campbell, K. S., Cahill, T. A., Flocchini, R. G., "Evaluation of a Particulate Scrubber on a Coal-Fired Utility Boiler", prepared for U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C., EPA-600/2-75-074, 1975.
- (30) Ondov, J. M., Ragaini, R. C., Biermann, A. H., Choquette, C. E., Gordon, G. E., Zoller, W. H., presented at the 173rd National Meeting of the American Chemical Society, New Orleans, March 25, 1977, Abstract ENV-124; Lawrence Livermore Laboratory, Preprint UCRL-78825, 1977.
- (31) Biermann, A. H., Ondov, J. M., "Respiratory Retention Function Applied to Particle Size Distribution", Lawrence Livermore Laboratory, Report UCRL-52135, 1976.
- (32) Ondov, J. M., Ragaini, R. C., Biermann, A. H., submitted for publication in *Atmos. Environ.*, 1978; Lawrence Livermore Laboratory, Preprint UCRL-80254, 1978.
- (33) Biermann, A. H., in *Metals and Ceramics Division, Quarterly Reports*, Lawrence Livermore Laboratory, 1977.
- (34) Natusch, D. F. S., Wallace, J. R., Evans, C. A., *Science*, **183**, 202-4 (1974).
- (35) Linton, R. W., Loh, A., Natusch, D. F. S., Evans, C. A., Jr., Williams, P., *Science*, **191**, 852-4 (1976).
- (36) Schroeder, H. A., *Environment*, **13**, 18-24, 29-32 (1971).
- (37) *Fed. Regist.*, **No. 1910.93** (20-098-74-9), 121-127 (July 1974).

Received for review March 13, 1978. Accepted January 12, 1979. Preliminary accounts of the work described in this paper were presented at the 172nd National Meeting of the American Chemical Society, Division of Environmental Chemistry, San Francisco, Calif., Aug 29-Sept 3, 1976, and at the 71st Annual Meeting of the Air Pollution Control Association in Houston, Tex., June 25-30, 1978. Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under Contract No. W-7405-ENG-48. Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that are suitable.

NOTES

Tritium Oxidation in Surface Soils. A Survey of Soils Near Five Nuclear Fuel Reprocessing Plants

James C. McFarlane*, Robert D. Rogers, and Donald V. Bradley, Jr.

Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, P.O. Box 15027, Las Vegas, Nev. 89114

■ The oxidation of elemental tritium into tritiated water by soil microorganisms represents a previously unsuspected pathway for tritium contamination of food. Soils from around potential point source emissions of tritium were tested and all were found to have the capacity of rapidly oxidizing tritium.

Our previous work (1, 2) showed that soil microorganisms are responsible for a rapid oxidation of elemental tritium to tritiated water. This laboratory work pointed to a possible hazard and a pathway of food contamination previously unsuspected. Our work also showed that plants rapidly incorporated tritium (3) when exposed in a growth chamber and that the route of contamination depended on the oxidation of HT in the soil. In past accidental releases of elemental tritium, very little attention has been given to evaluating soil and plant contamination. However, the present data indicate that soil and plants would be the primary accumulation sites and, therefore, the most sensitive media for sampling.

Elemental tritium is produced in nuclear power reactors and is released during reprocessing of the fuel elements. Currently there are nuclear fuel reprocessing facilities operating near Aiken, S.C., Arco, Idaho, Hanford, Wash., and a small experimental unit near Oak Ridge, Tenn., and a new facility is constructed, but inoperative, at Barnwell, S.C. We undertook the project reported here to determine if the soil microorganisms capable of tritium oxidation existed near

these facilities and, if so, to find out if their activity was sufficient to be considered important in the event of a tritium release.

Methods

Tritium oxidation was determined in the following manner. Representative soils were collected from the vicinity of each of these facilities and analyzed for their tritium oxidation potential. The physical and chemical properties of these soils are found in Table I.

The soils (200 g, dry weight basis) were incubated for 7 days at 30 °C in 15-cm petri dishes; daily additions of water were made to maintain them at 50% of their water-holding capacity. The incubation period ensured that the microbial populations in each culture were active and at a stable level of activity. Field conditions were not maintained during the incubation period in order to create optimal conditions for tritium oxidation.

After the incubation period, moist soil equivalent to 20 g on a dry weight basis was removed. The 20-g samples were placed in 1-L round-bottomed flasks and enough water was added to bring each sample to 140% of its water-holding capacity. The flasks were closed with rubber stoppers and the resultant soil slurry was spread over the inner surface by shaking. After the flasks had been flushed with air, 1.5 μ Ci of elemental tritium was injected through the rubber stopper with a gas-tight syringe (5-cm³ injection of HT in N₂). These bottles were then stored at 30 °C for various periods of time before analysis.