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AN INVESTIGATION OF SIZE-DEPENDENT CONCENTRATION OF TRACE ELEMENTS IN AEROSOLS EMITTED FROM THE OIL-FIRED HEATING PLANTS

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16. Abstract

Aerosols emitted from two oil-fired heating plants were aerodynamically separated into eight size groups and were analyzed using the proton-induced X-ray emission (PIXE) technique. It was found that Zn, Mo, Ag, and Pb, and (to a lesser extent) Cd, have a tendency to concentrate preferentially on the smaller aerosols. All of these elements, in certain chemical forms, are known to be toxic. Zinc and molybdenum, although present in low concentrations in the parent fuels, show the strongest tendencies to be concentrated in finer aerosols. Selenium, previously reported to show a very strong tendency to concentrate in finer fly ash from coal-fired power plants, shows little preference for surface residence. Vanadium, which occurs in significant concentration in the oil fuels for both plants, also shows little preference for surface concentration. Even though the absolute concentrations of the toxic elements involved are well below the safety levels established by the National Institute for Occupational Safety and Health (NIOSH), it would be advisable to raise the heights of the heating-plant exhaust chimneys well above the neighborhood buildings to insure more efficient aerosol dispersal.

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AN INVESTIGATION OF SIZE-DEPENDENT CONCENTRATION OF TRACE ELEMENTS IN AEROSOLS EMITTED FROM THE OIL-FIRED HEATING PLANTS

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SUMMARY

Aerosols emitted from two oil-fired heating plants were aerodynamically separated into eight size groups and were analyzed using the proton-induced X-ray emission (PIXE) technique. It was found that Zn, Mo, Ag, and Pb, and (to a lesser extent) Cd, have a tendency to concentrate preferentially on the smaller aerosols. All of these elements, in certain chemical forms, are known to be toxic. Zinc and molybdenum, although present in low concentrations in the parent fuels, show the strongest tendencies to be concentrated in finer aerosols. Selenium, previously reported to show a very strong tendency to concentrate in finer fly ash from coal-fired power plants, shows little preference for surface residence. Vanadium, which occurs in significant concentration in the oil fuels for both plants, also shows little preference for surface concentration. Even though the absolute concentrations of the toxic elements involved are well below the safety levels established by the National Institute for Occupational Safety and Health (NIOSH), it would be advisable to raise the heights of the heating-plant exhaust chimneys well above the neighborhood buildings to insure more efficient aerosol dispersal.

INTRODUCTION

Certain toxic elements have been reported to exhibit a preference for surface residence on aerosols emitted from aircraft engines (refs. 1 and 2). This phenomenon was hypothesized to be the result of recondensation of volatile toxic compound vapors on the surfaces of aerosols formed in the combustion process. Because these aerosols showed a strong tendency to be concentrated in smaller sizes, an excess concentration of toxic elements in smaller size aerosols was implied. Such a concentration of toxic elements is of concern since the smaller particles ($\leq 2~\mu$ m) are not stopped in the nasal (bronchial) passages and have a greater opportunity to react with the bloodstream because of their efficient retention on the lung lining (refs. 3 to 6). These smaller particles also have a higher biologic solubility and reactivity because of their higher surface to volume ratio.

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This investigation was undertaken to confirm whether aerosols emitted from other high temperature combustion sources such as heating plants and municipal incinerators also exhibit similar size-dependent toxic-element concentrations. Several investigators have recently reported these trends in aerosols emitted from such sources as coal-fired power plants and municipal incinerators (refs. 4 to 10). The chemical composition of the fuel used in a plant is expected to play a dominant role in determining which elements, if any, would have a preference for surface residence on the aerosols emitted from such plants. Because of the variability of the chemical composition of the fuels used in various types of combustion-based plants, similar measurements should be made on all representative plants. These measurements can then be used as the basis for future environmental impact assessment of similarly fueled plants. This report discusses the size dependence of trace-element concentration in aerosols emitted from two oil-fired heating plants at Langley Research Center. For the purpose of this paper, these two plants are identified as heating plant 1 (Air Force plant, east area) and heating plant 2 (NASA plant, west area).

Values are given in both SI and U.S. Customary Units. Calculations were made in U.S. Customary Units.

EXPERIMENTAL PROCEDURE

Aerosol Sample Collection

Aerosols emitted from the heating plants were aerodynamically separated into eight size groups, summarized in table I. The aerosols were collected on filter papers for periods ranging from 24 to 48 hours, by using Andersen samplers (ref. 11). The aerosols from heating plant 1 were collected on Mylar substrates; the aerosols from heating plant 2 were collected on nuclepore substrates. During the same time that the size-differentiated aerosols were collected, aerosol size distribution was also measured every hour with a Royco light scattering photometer, model 220 (ref. 12). All meteorological parameters (temperature, humidity, windspeed, and direction) were also continuously recorded during the aerosol collection periods to determine their effects on aerosol characteristics. In the case of aerosol collection from heating plant 1, two identical samplers were located downwind at a distance of 30.48 m (100 ft) from the plant, atop a 4.57-m- (15-ft-) high mobile research laboratory. (See fig. 1.) For aerosol collection from heating plant 2, one sampler was located downwind from the exhaust chimney at a distance of 15.24 m (50 ft), whereas another sampler was similarly located upwind from the chimney. (See fig. 2.)

Target Preparation and Data Analysis

Detailed procedures for aerosol target preparation and data analysis have been previously described in reference 1. Weighed filters with aerosol deposits were placed on a $3.62-\mu m$ Mylar film and dissolved in situ in chloroform predoped with chromium acety-

lacetonate. The chloroform solution was uniformly spread on the Mylar film and allowed to dry under lamp heat in a clean room. Chromium was chosen as the dopant since it was practically absent in the preliminary qualitative analysis of the aerosol samples. The targets thus prepared were then analyzed by using the proton-induced X-ray emission (PIXE) technique at a proton bombarding energy of 3 MeV. Blank filter papers were also analyzed to determine the filter contribution to the measured values of the trace-element concentrations in the aerosols. A typical aerosol X-ray spectrum is shown in figure 3. Heating-oil samples from both plants were also analyzed by using the same technique.

RESULTS AND DISCUSSION

Aerosol targets prepared from filter papers from each stage of the aerosol samplers were analyzed separately for their trace-element content. The concentrations of all significant elements in aerosols collected at various stages of a sampler are summarized in table II for heating plant 1. Similar data for heating plant 2 are summarized in table III. Because the Langley Research Center is located near natural bodies of water, some of the aerosols collected could be of marine origin. (Marine aerosols are known to contain mainly Na, S, and Cl with traces of P, K, Ca, and Br. Therefore, their contribution to the measured aerosol composition could be allowed for.) However, close proximity of the aerosol collectors to the heating-plant sites insured that the collected aerosols would come primarily from the heating plants.

As previously noted, temperature, humidity, and wind velocity were recorded continuously during the aerosol collection period. The weather conditions were typical of late March with frequent changes in wind direction. Aerosol dispersal in the vicinity of the heating plants was thus insured. For heating plant 2, aerosols were collected both upwind and downwind to allow for the background aerosols. The aerosol data were analyzed as: (1) downwind data alone and (2) downwind-upwind data. Both sets of data behaved similarly and thus confirmed that the aerosols were well-dispersed in the vicinity of the heating plant as a result of frequent changes in wind direction. Figures 4(a) and 4(b) illustrate typical data behavior for downwind and downwind-minus-upwind aerosols. For heating plant 1, it was not possible to locate collectors both upwind and downwind from the plant site. Both of the collectors were located downwind, and the aerosols from each collector were analyzed separately.

The compositions of the heating oils for the two plants are summarized separately in tables IV and V.

The data summarized in tables II and III illustrate that none of the trace elements shows a trend that is wholly consistent with "only surface" residence or "only bulk" residence. Some illustrative results are shown in figures 5 to 7. The experimental trends

suggest that each element has a different surface-bulk concentration. A discussion of the procedure developed to determine surface-bulk concentration of the various trace elements follows.

In the following analysis, it is assumed that:

- (1) The surface-layer thickness t is the same for all aerosols, i.e., independent of aerosol size. (See appendix.)
- (2) Each aerosol consists of a sphere surrounded by a surface layer of constant thickness t.
- (3) The experimentally measured unimodal size-distribution function for the aerosols from heating plant 1 is consistent with that for the aerosols from heating plant 2. This size-distribution function was obtained by measuring aerosol size-distribution spectra (in the size range 0.5 to 6.0 μ m) at hourly intervals during the entire collection period (March 24 to 26, 1975) using a Royco photometer. The spectra were then fitted to a power law function of the form

$$\frac{dN}{d(\log r)} = \frac{A}{r\beta}$$

where r is the particle size (ref. 13). By using the individual values of the distribution parameter β and the corresponding number of total particles N, a statistically weighted average value of $\bar{\beta} = 2.7$ was determined for the duration of the aerosol collection interval.

(4) The sizes of the aerosols collected at any stage lie in the range corresponding to 50-percent impaction efficiency sizes for that stage. (Even though there is a known size overlap in the neighboring stages, the error resulting from this simplification would be small.)

Mathematical Analysis

By use of the experimentally measured aerosol size-distribution function, the volume of the surface-deposition layer $\,V_{\rm Si}\,$ on aerosols collected in stage $\,$ i $\,$ of an Andersen sampler is calculated as

$$V_{Si} = t \int_{r_1}^{r_2} \frac{dN}{dr} 4\pi (r - t)^2 dr = 4\pi At \int_{r_1}^{r_2} \frac{r^2 - 2rt + t^2}{r^{3.7}} dr$$
 (1)

where ${\bf r}_1$ and ${\bf r}_2$ are size limits for stage i and t is the surface-deposit thickness. (It is assumed that t << ${\bf r}_1$.)

The volume of the inner sphere $\,V_{\mbox{\footnotesize{Bi}}}\,\,$ in aerosols collected in stage $\,$ i $\,$ is calculated as

$$V_{Bi} = \int_{r_1}^{r_2} \frac{dN}{dr} \frac{4}{3} \pi (r - t)^3 dr = \frac{4\pi A}{3} \int_{r_1}^{r_2} \frac{r^3 - 3r^2t + 3rt^2 - t^3}{r^{3.7}} dr$$
 (2)

If the surface number density for an element is n_S and the bulk number density is n_V on any given stage i, the total number of atoms of that element on the aerosols in stage i (and hence its mass) is given by

$$n(\text{total})_{i} \approx n_{S}(V_{Si}) + n_{V}(V_{Bi}) = \frac{n_{S} + n_{V}}{n_{S} + n_{V}} \left[n_{S}(V_{Si}) + n_{V}(V_{Bi}) \right] = \text{Constant} \left[x(V_{Si}) + (1 - x)(V_{Bi}) \right]$$

$$(3)$$

where

$$n_s + n_v = Constant$$

$$x = \frac{n_S}{n_S + n_V}$$

$$1 - x = \frac{n_V}{n_S + n_V}$$

Therefore,

(Experimentally measured mass of element)_i = Constant
$$[xV_{si} + (1 - x)V_{Bi}]$$
 (4)

Subject to the assumptions (1) and (2) listed earlier, the values of $p = \frac{x}{1-x}$ were calculated for each element, arbitrarily assuming the aerosol surface-deposit thickness to be 100 Å. (An attempt was made to fit the experimental data to the values computed by using a surface-deposit thickness of 1000 Å. However, the computed values, even for all-surface residence, are always lower for stage 7 than for stage 6. This trend is in contrast to the experimentally observed data. This indirect evidence, coupled with recently reported experimental measurements on the depth profile of several elements in fly ash (ref. 14), indicates that 100 Å is a judicious choice for surface-deposit thickness.) Only those elements which could be fitted with a unique value of p for all stages have been

included in the subsequent analysis. Based on these p values, the fractional surface mass concentration f_{Si} for any given element on any stage i, f_{Si} is calculated

$$f_{Si} = \frac{pV_{Si}}{pV_{Si} + V_{Bi}}$$
 (5)

The values of f_{Si} thus calculated for the last three stages of the collectors (stages 5 to 7) are summarized in table VI. These last three stages correspond to the aerosols in the size range of 0.43 to 2.1 μ m. Figures 8 and 9 show comparisons of the experimentally observed elemental concentrations with those predicted on the basis of $p = \frac{x}{1-x}$ values obtained by using the above surface-bulk model. The agreement between the experimental and the calculated values appears to be reasonably good.

A comparison of the data in table VI with the respective fuel compositions shows that

- (1) Almost all the trace elements observed exhibit similar trends in aerosols from both heating plants. This result is not surprising since the thermal efficiencies of the two plants are approximately equal (≈ 89 N of steam per 0.004 m³ of heating oil or ≈ 120 lb of steam per gallon).
- (2) Vanadium, which is the most abundant element in both types of fuel oil, shows little surface preference in aerosols from either plant.
- (3) The elements Zn, Mo, Ag, Pb, and Cd show an equally pronounced tendency for surface concentration in aerosols from both heating plants. Barium appears to show a slight tendency for surface concentration in aerosols from heating plant 1 only; tin shows a similar trend in aerosols from heating plant 2 alone.
- (4) The elements Zn and Mo, although present in low concentrations in the parent fuels, show the strongest tendencies for concentration in finer aerosols. Although selenium has been reported to show a very strong tendency to concentrate in finer fly ash from coal-fired power plants (ref. 15), this study shows that it has little preference for surface residence.
- (5) The aerosols from heating plant 1 have comparatively higher concentrations of V, Mn, Ni, and Se; the aerosols from heating plant 2 have higher concentrations of Cu, Zn, and Br. The latter result is surprising since heating plant 1 fuel oil has higher concentrations of Cu and Br whereas Zn concentration is equal in the two types of fuel oil.
- (6) For all the trace elements listed in tables II and III, the absolute concentration levels are well below the safety limits established by the National Institute for Occupational Safety and Health (NIOSH) (ref. 16). However, the trend for surface residence exhibited by

some of the elements does lead to an ''effective'' increase in their concentrations in the air. This increased effective concentration for elements such as Zn, Mo, Ag, Pb, and Cd indicates a need for developing better techniques for dispersal of aerosols from the two heating plants.

CONCLUDING REMARKS

It appears that certain trace elements (Zn, Mo, Ag, Pb, and Cd) have a marked tendency to concentrate preferentially on the smaller aerosols emitted from the two oil-fired heating plants located at the Langley Research Center. The absolute concentrations of the trace elements involved (all of which, in certain chemical forms, are known to be toxic) are well below the safety levels established by the National Institute for Occupational Safety and Health. It would, however, be advisable to raise the heights of the heating plant exhaust chimneys well above the neighboring buildings to insure more efficient diffusion of the exhaust aerosols, particularly for heating plant 1 where aerosols have rather high concentrations of the toxic elements V, Mn, and Ni.

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APPENDIX

CALCULATION OF SURFACE-LAYER THICKNESS ON AEROSOLS OF DIFFERENT SIZES

In the combustion process, all the aerosols are exposed to a certain elemental vapor density $N_{\rm total}$

$$N_{total} = N_a + N_b + N_e + \dots$$
 (A1)

where N_a , N_b , . . . are vapor densities for different elements. The values n_a , n_b , n_c , . . . represent the corresponding bombardment rate (per cm² per sec) on the aerosol surface. These bombardment rates, for any given element, are the same for all aerosols (i.e., independent of aerosol size). Therefore, the total number of vapors of element a striking the aerosol on stage i will be given by

$$n(total)_i = n_a \times Time \times (Surface area of aerosols)_i$$
 (A2)

The vapor deposition-layer thickness t, when a 100-percent sticking probability is assumed, and any mutual interference and surface effects are disregarded, is

$$t = Constant \frac{(Surface area of aerosols)_i \times n_a \times Time}{(Surface area of aerosols)_i} = K(n_a \times Time)$$
 (A3)

where K is a constant. It is obvious from equation (A3) that t is independent of aerosol size.

Of course, the thickness of the layers corresponding to different elements will differ (since n_a , n_b , n_c , . . . are different) even for aerosols of equal size. However, for fixed values of n_a , n_b , n_c , . . . (as expected in a given combustion process), the sum of the elemental partial layers is a constant, independent of the aerosol sizes.

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TABLE I.- AERODYNAMIC DIAMETERS OF AEROSOLS FOR AN IMPACTION EFFICIENCY OF 50 PERCENT FOR A FLOW RATE OF 0.027 $\rm m^3/min~(1~ft^3/min)$

| Stage | Particle diameter, μm |
|-------|-----------------------|
| 0 | 11.0 |
| 1 | 7.0 |
| 2 | 4.7 |
| 3 | 3.3 |
| 4 | 2.1 |
| 5 | 1.1 |
| 6 | .65 |
| 7 | .43 |

TABLE II.- ELEMENTAL CONCENTRATIONS OBSERVED IN AEROSOLS COLLECTED DOWNWIND FROM HEATING PLANT 1 AT LANGLEY RESEARCH CENTER

| 2 | T) cmont | o domination of | | | Elemental concentration, ng/m³ for aerosol collector stage number of | ntration, ng/m ³ | for aerosol colle | ector stage numb | ber of - | | Equivalent backing filter |
|-----|---------------|-----------------|------------------------------|-------------------------|--|--|------------------------|---------------------------------------|----------------------|------------------------|---|
| 2 | Piement | ionii ke | 0 | - | 2 | 3 | 4 | 2 | 9 | 7 | contribution, ng/m ³ (a) |
| | Vanadium | ^ | 97.471 ± 6.939 41.841 | 41.841 ± 10.206 129.319 | ++ | $6.238\ 177.838\ \pm\ 8.649\ 97.886\ \pm\ 12.973\ 105.656\ \pm\ 9.730$ | 97.886 ± 12.973 | | 56.663 ± | 7.977 128.108 ± 10.270 | |
| 7 | Manganese | Mn | 4.919 ± 5.101 | ≦21.321 | 3.742 ± 5.535 | ≦22.057 | ≦15.806 | ≦19.507 | 8.884 ± 3.831 | ≤20.606 | €0.568 |
| က | 3 Iron | Fe | $185.633 \pm 0.995 55.191$ | 55.191 ± 0.931 | 66.261 ± 2.376 | 96.757 ± 1.081 84.324 ± 1.622 | 84.324 ± 1.622 | 57.838 ± 1.081 | 16.405 ± 0.981 | 14.989 ± 1.122 | 1.944 ± 0.126 |
| 4 | 4 Nickel | ž | 16.069 ± 0.412 12.301 | 12.301 ± 0.425 | 17.719 ± 0.382 | 34.205 ± 0.604 | ± 0.604 24.425 ± 0.772 | 20.894 ± 0.470 | 8.832 ± 0.388 | 17.488 ± 0.536 | €0.095 |
| | 5 Copper | Cn | 4.955 ± 0.236 4.240 | 4.240 ± 0.235 | 4.109 ± 0.255 | 5.467 ± 0.339 | 4.488 ± 0.485 | 5.213 ± 0.308 | 4.822 ± 0.298 | 5.436 ± 0.363 | 0.098 ± 0.022 |
| 9 | Zinc | Zn | 14.818 ± 0.218 13.716 | 13.716 ± 0.256 | 13.730 ± 0.290 | 17.919 \pm 0.432 27.694 \pm 0.736 | 27.694 ± 0.736 | $24.671 \pm 0.436 25.182$ | 25.182 ± 1.103 | 33.715 ± 0.550 | 6.320 ± 0.252 |
| 7 | 7 Arsenic | As | ≦0.625 | ≦0.675 | ≦0.782 | ≦1.258 | 1.842 ± 0.692 | 0.862 ± 0.491 | 0.431 ± 0.378 | 0.185 ± 0.436 | 0.066 ± 0.140 |
| 80 | Selenium | Se | ≨2.588 | 1.457 ± 0.505 | ≦3.373 | 0.705 ± 0.162 | ≦0.744 | 0.810 ± 0.160 | 0.904 ± 0.154 | 0.910 ± 0.178 | 0.033 ± 0.009 |
| 6 | Bromine | Br | $2.012 \pm 0.120 \mid 1.765$ | 1.765 ± 0.170 | 2.841 ± 0.215 | 4.411 ± 0.315 | 3.811 ± 0.450 | 3.241 ± 0.286 | 1.543 ± 0.229 | 1.803 ± 0.281 | 0.046 ± 0.010 |
| 10 | 10 Rubidium | Rb | ≦0.458 | €0.508 | ≦0.591 | €0.789 | ≦1.237 | 50.687 | ≤0.562 | €0.670 | €0.039 |
| Ξ | 11 Strontium | Sr | 1.070 ± 0.171 0.471 | 0.471 ± 0.175 | 0.606 ± 0.199 | 0.537 ± 0.207 | €0.936 | 1.025 ± 0.232 | 0.436 ± 0.178 | ≦0.692 | 0.110 ± 0.018 |
| 112 | 12 Molybdenum | Мо | 0.481 ± 0.288 | ≦0.904 | 0.736 ± 0.355 | 0.705 ± 0.339 | ≤1.823 | ≦1.012 | 1.234 ± 0.384 | 1.739 ± 0.501 | ≦0.100 |
| 13 | 13 Silver | Ag | 1.631 ± 0.865 1.819 | 1.819 ± 0.965 | ≦2.944 | 2.144 ± 0.989 | 4.103 ± 1.892 | 2.364 ± 1.146 | 3.538 ± 1.205 | 4.224 ± 1.523 | 0.408 ± 0.121 |
| 14 | 14 Cadmium | Cq | €3.659 | €3.590 | ≦3.850 | 2.684 ± 1.257 | 4.103 ± 2.213 | ≦4.186 | 3.864 ± 1.501 | ≦4.528 | ≦0.395 |
| 15 | 15 Tin | Sn | 24.655 ± 2.234 20.040 | 20.040 ± 2.803 | 25.721 ± 3.516 | 27.034 ± 4.793 | 4.793 15.890 ± 5.577 | 17.792 ± 3.746 | 3.746 27.452 ± 4.208 | 24.662 ± 4.835 | 0.765 ± 0.266 |
| 16 | 16 Iodine | - | ≦14.958 | ≨16.128 | ≦18.470 | $11.445 \pm 6.693 10.781$ | 10.781 ± 8.736 | 24.630 ± 7.384 | ≨15.987 | ≦20.096 | 1.367 ± 0.523 |
| 17 | 17 Barium | Ba | 18.685 ± 7.242 | €19.689 | ≦21.202 | 12.297 ± 7.796 | 37.554 ± 18.175 | ≦23.512 | ≦29.308 | ≦32.575 | ≦3.038 |
| 18 | 18 Lead | Pb | 7.572 ± 0.395 | 5.410 ± 0.443 | 9.022 ± 0.541 | $19.136 \pm 0.992 18.135$ | 18.135 ± 1.692 | $28.015 \pm 1.232 17.581 \pm 0.967$ | 17.581 ± 0.967 | 16.516 ± 1.088 | 0.129 ± 0.032 |
| 19 | Bismuth | Bi | ≦1.072 | ≦1.172 | ≦1.282 | ≨1.630 | ≦2.521 | ≦1.814 | 1.317 ± 0.521 | ≦1.748 | 1.541 ± 0.030 |
| | | | | | | | | | | | |

a...Equivalent" backing filter contribution calculated as:

Concentration × Filter area cm² Vol. air

The filter contributions to trace element concentrations are very small except for zinc. Filter contributions were subtracted before data were analyzed to determine surface-volume ratio.

TABLE III.- ELEMENTAL CONCENTRATIONS OBSERVED IN AEROSOLS COLLECTED DOWNWIND FROM HEATING PLANT 2 AT LANGLEY RESEARCH CENTER

| Equivalent backing filter | contribution, ng/m³ (a) | 81 | | 6 ≦0.829 | 7 0.969 ± 0.373 | 4 0.058 ± 0.040 | 8 2.391 ± 0.549 | 8 3.296 ± 0.757 | 1 0.134 ± 0.121 | 5 0.026 ± 0.011 | 0 1.095 ± 0.252 | 9 0.075 ± 0.025 | 4 0.052 ± 0.018 | 5 0.095 ± 0.035 | 5 1.287 ± 0.457 | 1 0.427 ± 0.150 | 0 9.461 ± 2.217 | 1.378 ± 0.648 | 43 \$2.131 | 1 0.295 ± 0.076 | SO 092 |
|--|-------------------------|---|--------------------|-------------------|--|-------------------|--------------------|--------------------|-------------------|-----------------|-----------------|-------------------|-------------------|-------------------|-------------------|-----------------|-----------------|-------------------|--------------------|--------------------|------------|
| | 7 | 252.308 ± 81.9 | 30.333 ± 10.089 | 2.698 ± 3.016 | 40.223 ± 4.297 | 4.428 ± 0.524 | 23.098 ± 0.978 | 91.063 ± 3.468 | 4.428 ± 1.851 | 0.764 ± 0.145 | 13.218 ± 0.640 | 0.671 ± 0.289 | 0.749 ± 0.214 | 1.322 ± 0.385 | 5.638 ± 1.325 | 5.326 ± 1.551 | 45.659 ± 5.240 | ≦17.663 | 27.196 ± 10.343 | 53.548 ± 2.491 | ≦2.023 |
| 1 | 9 | 228.121 ± 27.983 | 12.777 ± 7.137 | ₹6.000 | 40.868 ± 1.398 | 2.207 ± 0.337 | 16.851 ± 0.543 | 77.299 ± 1.939 | 2.939 ± 1.575 | ≦0.343 | 8.996 ± 0.407 | 0.522 ± 0.255 | ≦0.546 | ≦0.923 | ≦3.318 | ≦4.400 | 29.691 ± 4.363 | ≦17.612 | ≦22.788 | 24.654 ± 1.214 | ≤1.707 |
| stage number of | 2 | 358.800 ± 47.262 | 24.301 ± 8.387 | 1.709 ± 3.285 | 58.254 ± 5.800 | 4.139 ± 0.542 | 19.077 ± 1.626 | 102.000 ± 8.000 | 1.811 ± 0.451 | 0.376 ± 0.116 | 10.722 ± 0.948 | 0.812 ± 0.263 | 0.887 ± 0.214 | 1.368 ± 0.394 | 4.812 ± 1.330 | ≦4.079 | 32.078 ± 4.829 | 12.993 ± 6.111 | .23.903 ± 9.760 | 31.674 ± 2.831 | ≦1.673 |
| Elemental concentration, ng/m³ for aerosol collector stage number of | 4 | 193.440 ± 63.708 | 23.162 ± 7.612 | 1.897 ± 3.059 | 71.189 ± 5.221 | 4.262 ± 0.491 | 22.418 ± 1.647 | 36.310 ± 2.627 | 2.783 ± 1.391 | ≦0.277 | 9.988 ± 0.776 | 0.846 ± 0.239 | 0.642 ± 0.175 | 0.793 ± 0.309 | 2.432 ± 0.952 | ≦3.338 | 35.479 ± 4.578 | 11.839 ± 5.483 | 31.029 ± 9.438 | 20.917 ± 1.659 | ≦1.398 |
| ation, ng/m3 for | 3 | 243.427 ± 66.268 | 27.235 ± 8.542 | 2.155 ± 3.061 | 112.000 ± 7.000 | 5.538 ± 0.551 | 18.667 ± 1.367 | 38.209 ± 2.727 | 4.349 ± 1.483 | ≦4.919 | 10.119 ± 0.780 | 1.029 ± 0.251 | 1.209 ± 0.214 | ≦0.975 | ≦3.016 | 3.406 ± 1.401 | 33.554 ± 4.617 | ≦14.60 | ≦23.00 | 21.017 ± 1.710 | ≦1.532 |
| emental concentr | 2 | 227.359 ± 81.036 | 33.687 ± 9.951 | 1.899 ± 3.819 | $147.000 \pm 12.000 112.000 \pm 7.000$ | 5.665 ± 0.680 | 25.407 ± 2.261 | 42.546 ± 3.742 | 2.862 ± 1.618 | ≨0.397 | 9.817 ± 0.925 | 0.717 ± 0.275 | 1.437 ± 0.271 | ≦1.072 | 2.780 ± 1.231 | ≦4.081 | 48.844 ± 6.651 | ≦19.640 | ≦22.929 | 17.931 ± 1.808 | ≤1.587 |
| [9] | 1 | 191,803 ± 58.028 | 13.913 ± 7.187 | 2.276 ± 2.524 | 75.631 ± 4.467 | 3.762 ± 0.381 | 19.977 ± 1.195 | 28.256 ± 1.662 | 1.230 ± 1.129 | ≦2.842 | 6.238 ± 0.436 | 0.597 ± 0.180 | 1.033 ± 0.172 | 0.799 ± 0.292 | 3.328 ± 0.996 | 3.656 ± 1.233 | 23.221 ± 3.369 | ≦13.363 | ≦20.840 | 8.961 ± 0.702 | ±1.037 |
| | 0 | 183.942 ± 51.599 191.803 ± 58.028 227.359 ± 81.036 243.427 ± 66.268 193.440 ± 63.708 358.800 ± 47.262 228.121 ± 27.983 252.308 ± 81.981 | 28.061 ± 6.601 | 1.571 ± 2.148 | 120.000 ± 6.000 | 5.053 ± 0.399 | 20.674 ± 1.075 | 27.105 ± 1.385 | 0.340 t 0.183 | 0.185 ± 0.074 | 7.066 ± 0.407 | 0.520 ± 0.154 | 1.075 ± 0.148 | 0.640 1 0.261 | 3.084 ± 0.821 | 3.679 ± 1.043 | 27.149 ± 3.060 | ≨11.233 | 19.560 ± 6.703 | 9.796 ± 0.650 | ≥0.987 |
| 2 | o di li | రే | > | | Fe | ž | ບຶ | Zn | As | Š | Br | RF0 | Sı | Мо | Αg | р | Si | | Ba | og. | Bi |
| 3 | no. | 1 Calcium | 2 Vanadium | 3 ; Manganese | 4 Iron | 5 Nickel | 6 Copper | 7 Zinc | 8 Arsenic | 9 Selenium | 10 Bromine | 11 Rubidium | 12 -Strontium | 13 - Molybdenum | 14 Silver | 15 Cadmium | 16 Tin | 17 :Todine | 18 Barium | 19 Lead | 20 Bismuth |
| 2 | 2 | Ĺ | . 5 | _د | | · c | 9 | 7 | ∞ | 6 | 01 | Ξ. | 12 . | 13 | 14 | 15 | 16 | 17 | 3 | 13 | 20 |

a"Equivalent" backing filter contribution calculated as:

 $\frac{\text{Concentration}}{\text{cm}^2} \times \frac{\text{Filter area}}{\text{Vol. air}}$

The filter contributions to trace element concentrations are small except for Cu, Zn, Br, and Sn. Filter contributions were subtracted before data were analyzed to determine surface-volume ratio.

TABLE IV.- MAJOR CONSTITUENTS OF HEATING PLANT 1 FUEL OIL

| Element | Symbol | Concentration, ppm |
|------------|--------|--------------------|
| Vanadium | v | 351 ± 23 |
| Iodine | I | 206 ± 22 |
| Cadmium | Cd | 109 ± 7 |
| Nickel | Ni | 48.7 ± 3 |
| Tin | Sn | 8.0 ± 3 |
| Iron | Fe | 7.4 ± 1 |
| Bromine | Br | 2.5 ± 0.3 |
| Manganese | Mn | 2.1 ± 1.7 |
| Mercury | Hg | 1.3 ± 0.4 |
| Molybdenum | Mo | 1.0 ± 0.4 |
| Copper | Cu | 1.0 ± 0.3 |
| Zinc | Zn | 0.8 ± 0.2 |
| Selenium | Se | 0.6 ± 0.1 |
| Arsenic | As | 0.3 ± 0.2 |
| Barium | Ва | ≦61 |
| Lanthanum | La | ≦39 |
| Cesium | Cs | ≦26 · |
| Tellurium | Te | ≦12 |
| Chromium | Cr | ≦11 |
| Silver | Ag | ≦3.4 |
| Cobalt | Со | ≦1.6 |
| Lead | Pb | ≦1.3 |
| Bismuth | Bi | ≦1.1 |
| Rubidium | Rb | ≦0.6 |
| Strontium | Sr | ≦0.6 |

TABLE V.- MAJOR CONSTITUENTS OF HEATING PLANT 2 FUEL OIL

| Element | Symbol | Concentration, ppm |
|------------|--------|--------------------|
| Vanadium | v | 248 ± 15 |
| Cadmium | Cd | 118 ± 4 |
| Iodine | I | 97 ± 9 |
| Nickel | Ni | 39 ± 2 |
| Iron | Fe | 8 ± 1 |
| Bromine | Br | 1.3 ± 0.1 |
| Zinc | Zn | 0.8 ± 0.1 |
| Lead | Pb | $0.8~\pm~0.2$ |
| Molybdenum | Mo | $0.7~\pm~0.2$ |
| Strontium | Sr | 0.3 ± 0.1 |
| Copper | Cu | 0.3 ± 0.2 |
| Selenium | Se | 0.2 ± 0.1 |
| Barium | Ва | ≦27 |
| Chromium | Cr | ≦16 |
| Cesium | Cs | ≦10 |
| Tellurium | Те | '≦6 |
| Tin | Sn | <u>≤</u> 4 |
| Manganese | Mn | ≦3 |
| Silver | Ag | ≦2 |
| Cobalt | Co | ≦1 |
| Bismuth | Bi | ≦0.6 |
| Rubidium | Rb | ≦0.3 |
| Arsenic | As | · ≤0.3 |

TABLE VI.- FRACTIONAL SURFACE MASS CONCENTRATIONS^a OF TRACE ELEMENTS IN SMALLER AEROSOLS FROM TWO HEATING PLANTS AT LANGLEY RESEARCH CENTER

| | | Surface fract | ional concentration | n, percent of tota | al concentration | |
|--------|----------------------------|-----------------------------|------------------------------|-------------------------|-------------------------------|------------------------------|
| Symbol | | Heating plant 1 | | | Heating plant 2 | |
| | Stage 5 (1.1 to 2.1 μm) | Stage 6 (0.65 to 1.1 μm) | Stage 7 (0.43 to 0.65 μm) | Stage 5 (1.1 to 2.1 μm) | Stage 6 (0.65 to 1.1 μ m) | Stage 7 (0.43 to 0.65 μm) |
| Ca | | · - | | 39 | 53 | 65 |
| v | 11 | 18 | 26 | 11 | 18 | 26 |
| Br | 28 | 42 | 54 | 28 | 42 | 54 |
| Cu | 30 | 44 | 56 | 32 | 46 | 58 |
| Se | 30 | 44 | 56 | 28 | 42 | 54 |
| Ni | 37 | 52 | 64 | 36 | 50 | 62 |
| Sn | 42 | 56 | 68 | 44 | 59 | 70 |
| Te | 43 | 58 | 69 | 39 | 53 | 65 |
| Ba | 50 | 64 | 74 | 43 | 58 | 69 |
| Cd | 47 | 61 | 72 | 44 | 59 | 70 |
| Pb | 50 | 64 | 74 | 51 | 65 | 75 |
| Ag | 54 | 68 | 77 | 54 | 68 | 77 |
| Mo | 61 | 74 | 83 | 61 | 74 | 83 |
| Zn | 75 | 85 | 90 | 69 | 80 | 87 |

^aThe only inference that can be drawn from the listed values is that different elements behave differently in their preference for surface or bulk residence. If vanadium represents one extreme, then zinc represents the other. Figure 10 illustrates this point.

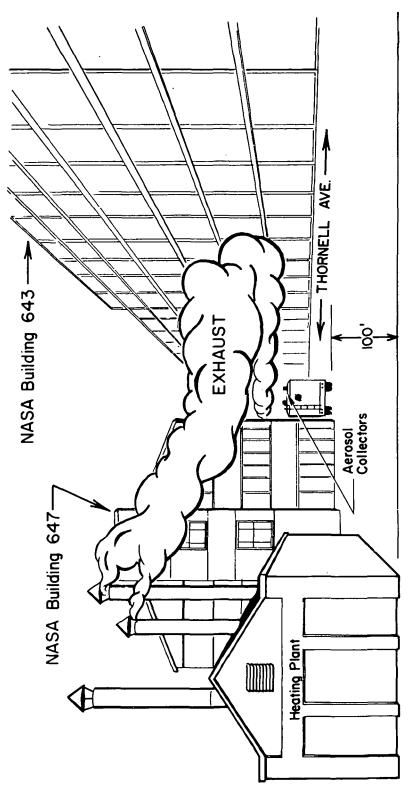


Figure 1.- Aerosol collection stations for heating plant 1.

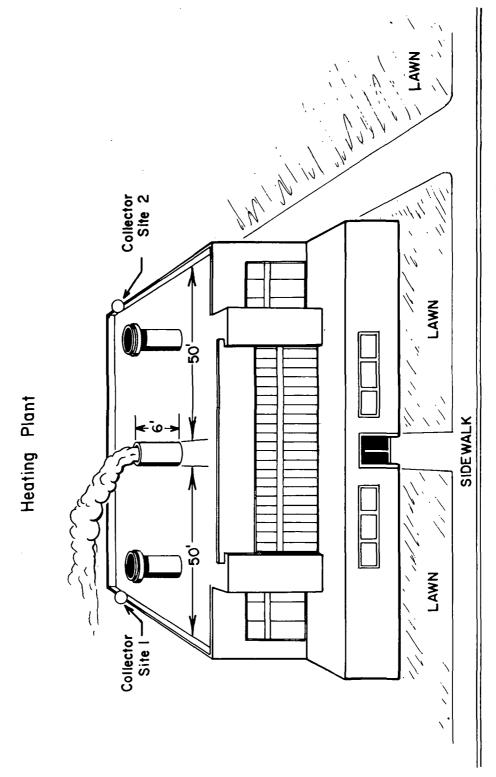


Figure 2.- Aerosol collection stations for heating plant 2.

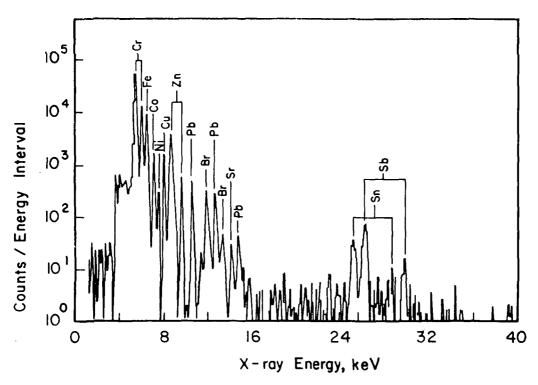
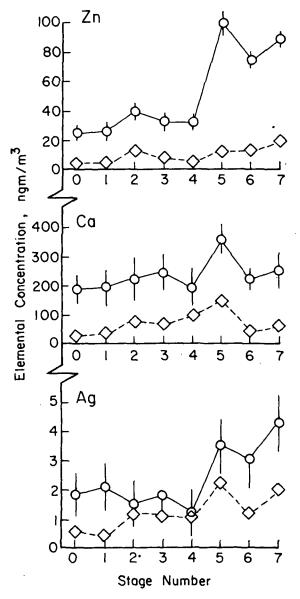


Figure 3.- Typical proton-induced X-ray spectrum from aerosol sample.

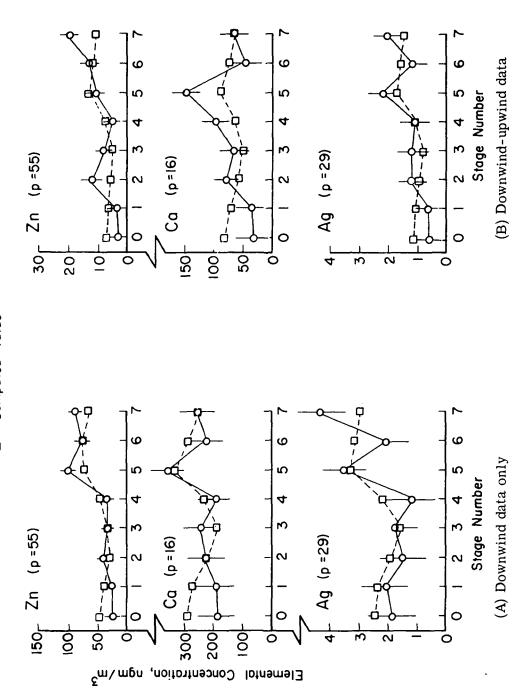
♦- (DOWNWIND-UPWIND) DATA

THE ERRORS ON THE DIFFERENCE DATA ARE NECESSARILY LARGER THAN THE DOWNWIND DATA ERRORS.



(a) Comparison of downwind data with downwind-upwind data for heating plant 2. (Notice general similarity of data trends.)

Figure 4.- Heating plant 2 data.



(b) Comparison of computed values and experimental values based on (A) downwind data only, and (B) downwind-upwind data at heating plant 2. Computed p-values for each element are given.

Figure 4.- Concluded.

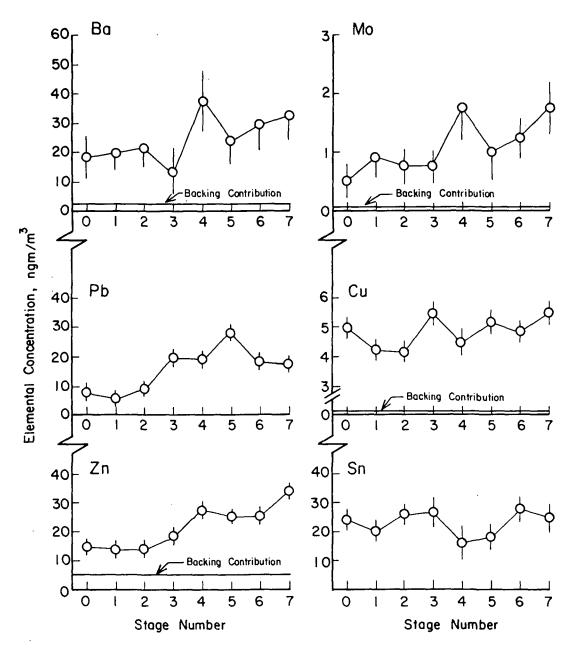


Figure 5.- Concentration of several elements found in aerosol samples from heating plant 1, plotted as function of Andersen sampler stage number.

The backing contribution was too low to be plotted for Sn and Pb.

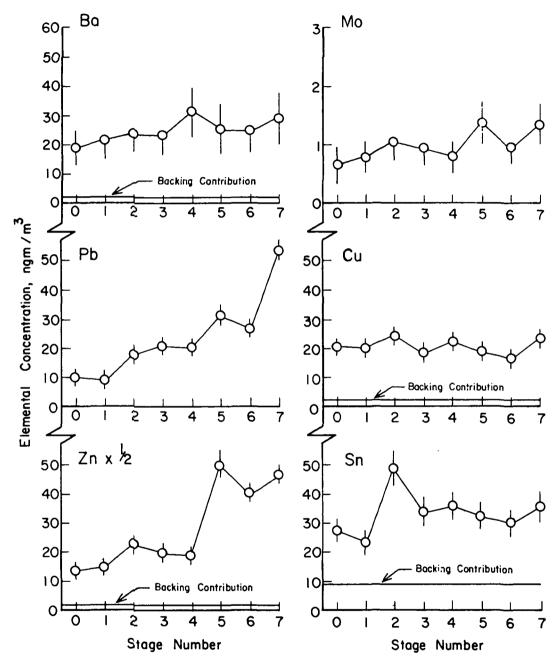


Figure 6.- Concentration of several elements found in aerosol samples from heating plant 2, plotted as function of Andersen sampler stage number.

The backing contribution was too low to be plotted for Mo and Pb.

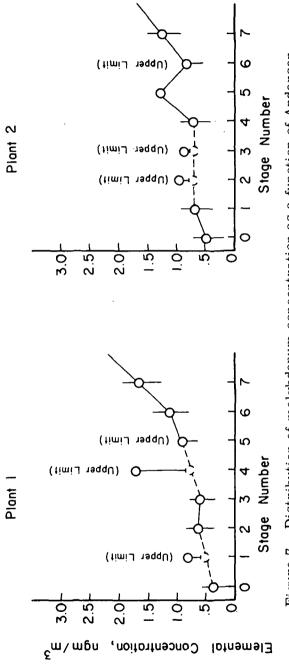


Figure 7.- Distribution of molybdenum concentration as a function of Andersen sampler stage number at heating plants 1 and 2.

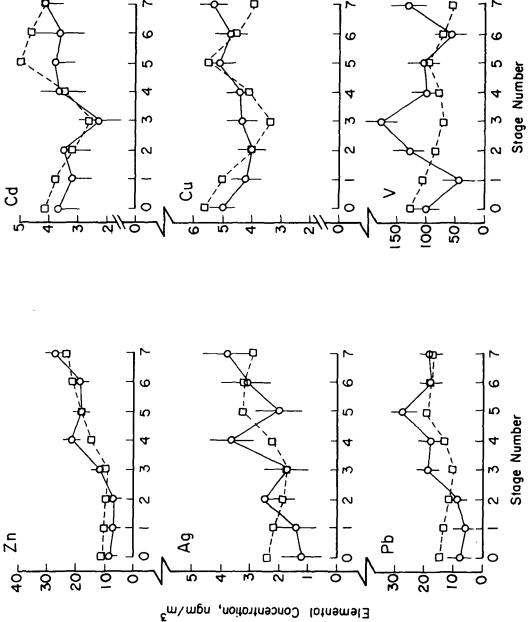


Figure 8.- Comparison of experimentally observed concentration with computed values of concentration for several elements in aerosols from heating plant 1, as a function of Andersen sampler stage number.

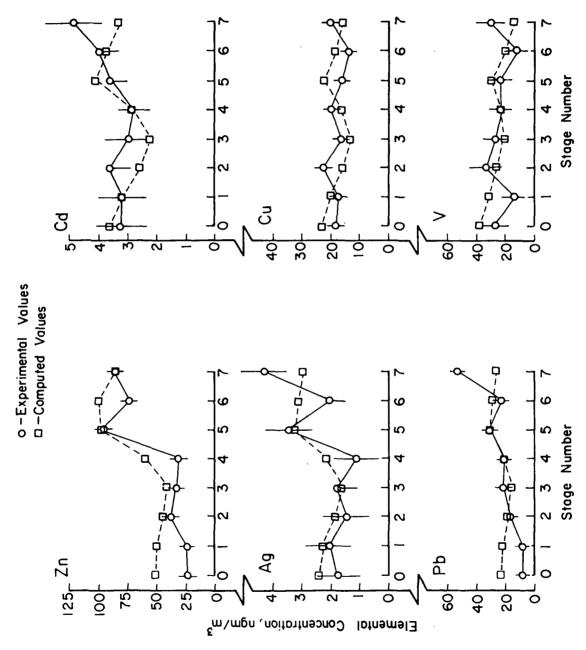


Figure 9.- Comparison of experimentally observed concentration with computed values of concentration for several elements in aerosols from heating plant 2 as a function of Andersen sampler stage number.

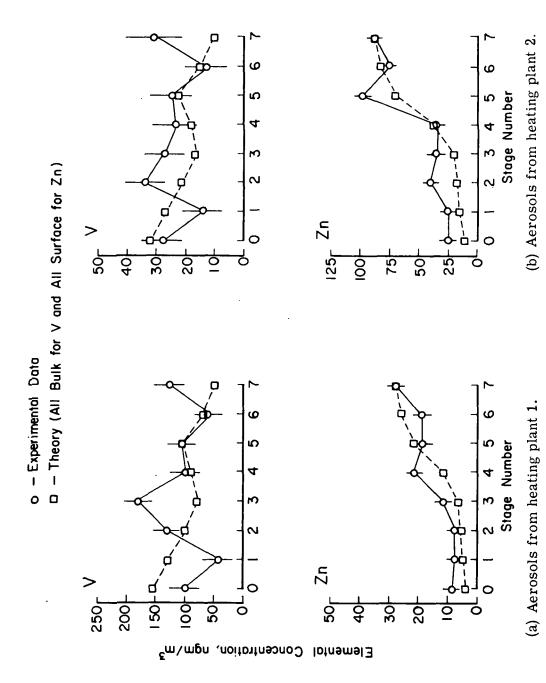


Figure 10.- Comparison of experimental data and theoretical predictions assuming all bulk (for V) or all surface (for Zn) residence.

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