

VARIABILITY OF COMPOSITIONS OF PARTICLES RELEASED BY
COAL-FIRED POWER PLANTS

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Introduction

Methods are needed for determining contributions of emissions from coal-fired power plants to atmospheric pollution problems ranging from total suspended particulate matter (TSP) on a local scale (10s of km) to sulfates and acid precipitation on a regional scale (100s of km). One of the best approaches is receptor modeling (1), in which unique chemical and other characteristics of emissions are used to identify contributions from various sources. According to the most widely used receptor model, "chemical mass balances" (CMBs), the composition of airborne particles is expressed as a linear combination of the composition patterns for all important sources:

$$C_i = \sum_j m_j x_{ij}, \quad 1)$$

where C_i is the concentration of element (or species) i in an ambient particulate sample, m_j is the mass concentration contributed by source j , and x_{ij} is the concentration of element i in particulate matter from source j . Concentrations of many species, C_i , in the atmosphere and compositions of particles from many sources, the x_{ij} s, are measured and a least-squares fit to the C_i values is performed to obtain the source-strength terms, the m_j s. The CMBs are most successful if the measured elements include some, often called "marker elements", that are contributed mainly by certain sources, e.g., Pb and Br from motor vehicles, V and Ni from oil combustion, As and Se from coal-fired plants (2).

Progress in this field, especially on an urban scale, has been good (3), but to make receptor modeling more precise and to extend it to a regional scale, we need greatly to improve our knowledge of source-composition terms, the x_{ij} s, for use in CMB calculations. For this reason, we have assembled a source-composition library, which includes data from the literature and our group's research on compositions of particles from important types of air-pollution sources. Here we report on 21 studies of compositions of particles released by coal-fired power plants.

Source-Composition Library

We have tried to make the source-composition library as useful as possible for interpretation of existing large data sets. Therefore, whenever size data were available, we entered the compositions of "fine", "coarse", and "total" particles. We define fine particles as those of diam $< 2.5 \mu\text{m}$ and coarse particles as those with diameters from $2.5 \mu\text{m}$ up to the maximum collected in a given experiment, usually 15 to $20 \mu\text{m}$. Most data were taken with different size cuts, so it was necessary to group data in different ways and

interpolate around the 2.5- μ m region. The "total" category (a properly weighted combination of fine and coarse particles) was included for CMB treatments of many otherwise excellent ambient particle data sets containing no size information. The "total" component also contains data from source studies in which no size information was obtained. Some source categories would contain few entries if restricted only to size-segregated data.

Most recent data sets are accompanied by estimates of errors of the measurements or observed sample-to-sample fluctuations, which we have entered into the library, as it is important to weight various data sets by some inverse function of the uncertainty (traditionally $1/\sigma^2$, which we have used) to compute overall averages and their uncertainties. The latter are important, as modern CMB programs use uncertainties of source compositions in weighted least-squares fitting procedures. We excluded fluctuations arising from variations of mass loading of the stacks or errors in the air volume sampled. For receptor modeling, the appropriate errors for weighting are those of the concentrations of the species in the particulate mass (or relative to that of some normalizing element, if mass was not measured). For each source type, we normalized concentrations of all elements to that of a prominent element, e.g., Al for emissions from coal-fired plants. However, when a data set contains reliable information on mass, we enter a value for mass relative to the normalizing element to retain that information. Data for 21 studies of coal-fired plants (including more than one study of some plants) are included in the library.

Compositions of Particles from Coal-Fired Plants

When coal burns, elements present in the carbonaceous phase tend to be liberated to the gas phase, whether or not they are volatile. Aluminosilicate fragments, the "ash" of coal, melt and outgas volatile species, but are only slightly vaporized (4). When the exhaust stream leaves the combustion zone and cools, major portions of the moderately volatile elements condense on pre-existing particle surfaces and, as finer particles present more surface area, these elements become preferentially associated with fine particles (5). Fine particles also tend to be transmitted through pollution-control devices more readily than large particles. Thus, moderately volatile elements tend to be enriched relative to lithophiles such as Al and Si with respect to the input coal.

Instead of considering raw compositions of particles from coal combustion, we use enrichment factors, EF, which are easier to interpret:

$$EF_{\text{crust}} = (C_X/C_{\text{Al}})_{\text{partic}} / (C_X/C_{\text{Al}})_{\text{crust}}, \quad 2)$$

where C_s are concentrations of element X and Al, respectively, in the particles and average crustal material of the earth (6). (Note that Al is not a unique choice of normalizing element; others such as Si or Fe can and have been used.)

The EF_{crust} values are plotted in Fig. 1 for the "total" category for all elements for which there are significant data. We assume that distributions are log-normal and have plotted logs of the (unweighted) geometric means plus

and minus the log of the geometric standard deviations to show the variability of compositions.

In Fig. 1, many elements (mostly lithophile) are only slightly, if at all, enriched with respect to the crust: the alkaline earths, the higher alkali metals, the rare earths, Sc, Ti, Fe, Zr, Hf and Th. That is, these elements occur in the same relative concentrations in coal emissions as in soil or rocks, so they are of little value in distinguishing between coal emissions and airborne soil in CMB calculations. Some elements are depleted relative to the crust because they were washed out of the forming coal in the ground: Na, K and Mn. (Tantalum is probably not depleted; rather, the crustal abundance is incorrectly large.) Many elements are enriched up to ten-fold, especially transition elements V, Cr, Co, Ni, Cu and Zn. The highest EFs, up to 10,000, are for elements that are volatile or have volatile compounds: B, P, S, Cl, As, Se, Br, Mo, Ag, Cd, In, Sb, I, Hg and Pb. In general, the elements of this group will be the most useful for tracing emissions from coal-fired plants unless greater amounts are released by other sources: Pb, Br and Cl from combustion of leaded gasoline; Mo from oil in eastern U.S. cities; Ag, Cd, In and Sb from incinerators, if they are in use; halogens from sea salt in marine areas.

A major problem with these highly volatile elements is that appreciable fractions remain in the gas phase beyond the pollution-control devices, but portions of the vapor may condense when the stack gases are cooled and diluted by ambient air. Thus, concentrations of many of these elements on particles may be greater at the ambient sampling site than in the hot stack. Major portions of S, Cl, Se, Br and Hg are known to be in the gas phase in stacks (7); Se (8) and, of course, S are known to become more strongly associated with particles in ambient air. New sampling methods are needed to obtain particles more similar to those that exist after some time spent in ambient air. Dilution source sampling, in which stack gases are mixed with filtered ambient air before sampling (9), is a step in the right direction, but studies far downwind in plumes are more satisfactory, e.g., the collection of particles from the Four Corners plant on a mesa 8 km from the stack by Wangen (10). Although the gas-phase problem is a nuisance for determining appropriate particle compositions, vapor-phase species could serve as useful tracers if more work were done on them.

Concentrations of some of the most highly enriched elements in Fig. 1 also have some of the highest variabilities, the EF values often covering more than an order of magnitude. In part, the variability may result from fluctuations in the amount of vapor-phase species collected by the particles before they are sampled. However, much of the variation arises because the library contains data for a wide range of plants, some burning eastern (mostly bituminous) coal, some burning western (subbituminous and lignite) coal, some equipped with electrostatic precipitators (ESPs), others with scrubbers. We can attempt to eliminate variations caused by fluctuations of composition of the input coal by considering enrichment factors with respect to input coal, EF_{coal} , the same as Eq. 2, except with $(C_x/C_{A1})_{\text{coal}}$ in the denominator. (Note that the population of plants drops to about half, as coal was not analyzed in the others.) We have listed EF data for several of the enriched elements in Table 1. The key measure of variability, independent of the magnitude of the mean value, is σ_n . Much as in our earlier investigation with

fewer data (11), we see that the use of EF_{coal} instead of EF_{crust} reduces fluctuations for some elements (V, I, W, U and, especially, Se and Mo), but increases them for the others, so this technique is not a complete solution to the problem of variability.

Another approach involves the realization that, for receptor modeling in a given region, the component should not include data from all plants investigated, but from those most representative of the types of plants present in the region. For example, for study of eastern U.S. cities or the acid rain problem in the northeast U.S., the component should be made up mainly from data for eastern plants equipped with ESPs. Note in Table 1 that, except for Br, Mo and Pb, there are reductions in σ_g , some quite significant, when we consider only this group of plants. The removal of plants with scrubbers helps especially in the case of Se, as scrubbers greatly increase the EF of Se (and S) on released particles.

Another possible source of fluctuation is the efficiency of the ESP as a function of particle size. Some of this variability should be removed if we consider only fine particles. Data in Table 2 show that there are further reductions of σ_g in most cases that can be tested (along with expected increases in mean EF) when we consider only fine particles. In the final columns, we show the arithmetic average and standard deviation for the fine particles, in this case, properly weighted by $1/\sigma^2$ of the individual measurements. By thus restricting the data, we have obtained rather small variations; however, very few data sets are included in this group, so more studies are needed to establish reliable composition patterns. Some of the remaining fluctuation, e.g., for Se, surely results from variation in the amount of vapor-phase species that condensed before particles were collected.

Recommendations

More data on compositions of particles and vapors from coal-fired plants are needed for receptor-modeling calculations. Special efforts should be made to analyze for the highly enriched elements, which provide the best tracers of emissions from coal-fired plants. Particles should be collected in at least two size fractions and samples of the input coal should be analyzed. More effort is needed to collect particles representative of those collected at receptor sites, e.g., by dilution source sampling or, preferably, sampling as far as possible downwind in plumes.

References

1. Glen E. Gordon, *Environ. Sci. Technol.* 14, 792 (1980).
2. G. S. Kowalczyk, G. E. Gordon and S. W. Rheingrover, *Environ. Sci. Technol.* 16, 79 (1982).
3. R. K. Stevens and T. G. Pace, *Atmos. Environ.* 18, 1499 (1984) and following five papers of that issue report on the Quail Roost II Workshop on Mathematical and Empirical Receptor Models.
4. B. S. Haynes, M. Neville, R. J. Quann and A. F. Sarofim, *J. Colloid Interface Sci.* 87, 266 (1982).
5. R. D. Smith, *Prog. Energy Combust. Sci.* 6, 53 (1980).
6. K. H. Wedepohl, in Origin and Distribution of the Elements, L. H. Ahrens, ed. (Pergamon Press, London, 1968) pp. 999-1016.
7. M. S. Germani, Ph.D. Thesis, Dept. of Chemistry, Univ. of Maryland, College Park, MD, 1980.
8. K. K. S. Pillay and C. C. Thomas, *J. Radioanal. Chem.* 7, 107 (1971).
9. R. J. Heinsohn, J. W. Davis and K. T. Knapp, *Environ. Sci. Technol.* 14, 1205 (1980).
10. L. E. Wangen, *Environ. Sci. Technol.* 15, 1080 (1981).
11. G. E. Gordon, W. H. Zoller, G. S. Kowalczyk and S. W. Rheingrover, in Atmospheric Aerosol: Source/Air Quality Relationships, E. S. Macias and P. K. Hopke, eds., Amer. Chem. Soc. Symp. Series No. 167 (ACS, Washington, D. C., 1981).

Table 1. Enrichment Factors for Selected Elements Borne by Total Particles from Coal-Fired Power Plants.

Element	All Plants						Eastern Plants with ESPs		
	EF_{crust}			EF_{coal}			EF_{crust}		
	x_g	σ_g	n	x_g	σ_g	n	x_g	σ_g	n
V	3.6	2.8	15	2.5	2.0	8	2.8	1.8	8
Ni	3.5	2.8	16	2.8	3.6	9	2.45	1.6	7
Zn	8.3	3.1	20	7.0	2.5	12	7.0	3.4	8
As	90	4.4	18	2.8	5.6	8	135	2.1	8
Se	1400	6.3	18	8.4	3.1	9	950	3.4	8
Br	27	6.7	6	1.4	8.3	2	13	7.2	3
Mo	76	4.5	9	4.6	4.6	10	34	-	1
Cd	64	3.5	7	7.4	3.8	4	520	-	1
I	190	6.8	3	4.0	2.2	2	570	1.4	2
W	4.0	1.2	4	2.7	1.02	2	4.1	1.0	2
Pb	9.7	3.2	18	4.0	4.0	9	5.7	4.0	7
U	2.6	2.7	5	1.7	2.2	4	-	-	-

Table 2. Enrichment Factors for Selected Elements Borne by Fine Particles from Eastern Coal-Fired Power Plants with Electrostatic Precipitators.

Element	EF_{crust}				
	Geometric			Weighted Arithmetic	
	x_g	σ_g	n	$x \pm \sigma$	
V	3.1	1.6	6	1.7±0.9	
Ni	4.2	1.2	5	4.0±1.0	
Zn	5.5	1.7	6	4.1±1.1	
As	280	2.0	6	205±80	
Se	1440	2.5	6	990±690	
Br	41	10	3	6.8±2.9	
Mo	97	-	1	97±35	
Cd	-	-	0	-	
I	1180	1.0	2	1180±45	
W	9.1	1.1	2	9.2±0.6	
Pb	9.9	1.9	4	14±5	

ENRICHMENT FACTORS — WEDEPOHL

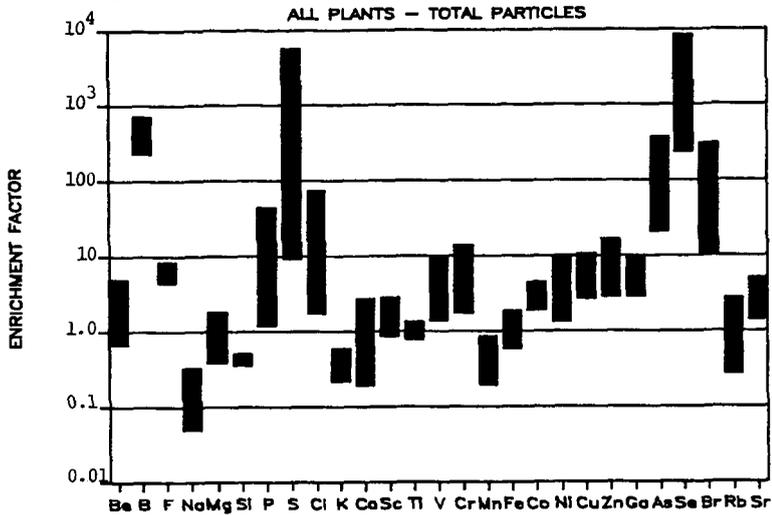


Fig. 1. (a) Enrichment factors for total suspended particles from coal-fired power plants of all types with respect to Wedepohl's crustal abundances (6): Be-Sr.

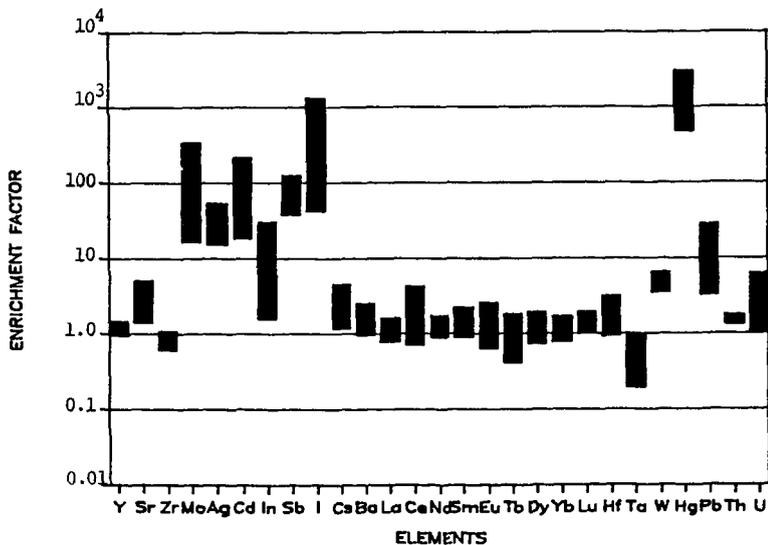


Fig. 1. (b) Same for Y-U.