new evidence of middle ear disease and probable defective hearing among ancient Egyptians. Histologic study of these temporal bones is under way.

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Toxic Trace Elements: Preferential Concentration in Respirable Particles

Abstract. *The toxic trace elements arsenic, antimony, cadmium, lead, selenium, and thallium were found to be most concentrated in the smallest respirable particles emitted from coal-fired power plants. These elements, or their compounds, are probably volatilized during combustion and preferentially adsorb or condense onto the small particles which can most easily pass through conventional control equipment.*

Possibly one of the most dangerous, and certainly one of the most insidious, forms of pollution arises from the mobilization of toxic trace elements, such as Be, Cd, As, Se, Pb, Sb, Hg, Tl, and V, in our environment (*1, 2*). The majority of living organisms possess little or no tolerance for these elements whose presence in the environment is unseen and often undetected.

It is now well established (*3*) that many trace elements are mobilized in association with airborne particles derived from high-temperature combustion sources such as fossil-fueled power plants, metallurgical smelters and blast furnaces, municipal incinerators, and automobiles. It is also established that many elements, notably Pb, Cd, Zn, Cr, V, Ni, Mn, and Cu, are found at highest concentrations in the smallest particles collected from ambient air (*3–5*).

This finding has considerable significance in terms of environmental health because it is these same small particles from which trace elements are most effectively extracted into the human bloodstream (*1, 6, 7*). Thus, particles less than about 1 μm in equivalent aerodynamic diameter deposit predominantly in the alveolar regions of the lung where the absorption efficiency for most trace elements is 50 to 80 percent. Larger particles, on the other hand, deposit in the nasal, pharyngeal, and bronchial regions of the respiratory system and are removed by cilial action to the stomach where absorption efficiency is commonly only 5 to 15 percent for most trace elements (*1, 7*). The natural size distribution of particles in ambient air ensures that about one-third of the total particulate mass retained during respiration is deposited in the lung (*1*), and it is clear that this organ constitutes the major gateway to the bloodstream for toxic elements that are present in airborne particles.

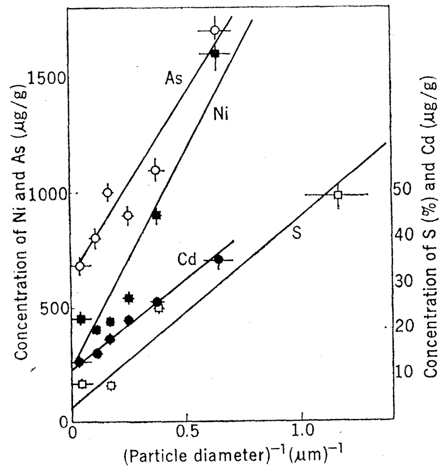

Fig. 1. Dependence of the average concentrations of As, Ni, Cd, and S on airborne particle size in coal fly ash.

Consequently, attention should be focused sharply on the chemical composition and physical form of submicrometer-sized respirable particles. In particular, the reasons why many toxic elements are most concentrated in the smallest ambient airborne particles require elucidation. This could simply be the result of the mixing of particles from a variety of sources, each with its own characteristic particle size distribution. Alternatively, the effect may be determined by combustion characteristics at the particle source. The work reported herein was designed to test this latter suggestion for the case of fly ash derived from coal-fired power plants.

Fly ash samples were collected from eight power plants in the United States. A variety of coal types are represented. The samples can be divided into two classifications which represent (i) fly ash retained in the precipitation system of a plant and (ii) airborne fly ash leaving a plant. The retained material was collected in bulk and differentiated both physically, by sieving, and aerodynamically, with a Roller particle size analyzer (*8*), into a range of particle size fractions. Airborne fly ash samples were collected inside the plant stacks, and the sizes were differentiated aerodynamically in situ with an Anderson stack sampler (*9*).

Solid particulate material was analyzed directly by means of spark-source mass spectrometry, d-c arc emission spectrometry, and wavelength-dispersive x-ray fluorescence spectrometry. The particles were also digested in a mixture of 3.5 parts of aqua regia and 1.5 parts of 48 percent hydrofluoric acid in a Teflon-lined Parr pressure bomb at 120°C for 2 hours. The neutralized solution was then analyzed by atomic absorption spectrometry, differential pulse anodic stripping voltammetry, and colorimetrically, with a Weisz ring oven. Each element was determined by at least two techniques to establish the reliability of the data.

Results representative of our findings are presented in Table 1 for particles derived from a single representative coal-fired power plant equipped with cyclonic particle collectors. For comparative purposes results obtained for the major matrix elements Al, Si, Fe, K, and Ca are listed in Table 2. Raw analytical data are presented for the method considered most reliable for each element. Comparison of the results obtained with different techniques

Table 1. Trace elements in coal fly ash. Analytical methods used: a. atomic absorption; b, spark source mass spectrometry; c, x-ray fluorescence spectrometry; and d, d-c arc emission spectrometry.

Particle diameter (μm)	Concentration (μg/g)									S (% by weight)	Mass fraction (%)
	Pb	Tl	Sb	Cd	Se	As	Ni	Cr	Zn		
Fly ash retained in the plant											
Sieved fractions											
> 74	140 (b)	7 (b)	1.5 (b)	< 10 (b)	< 12 (b)	180 (b)	100 (d)	100 (d)	500 (d)		66.30
44–74	160 (b)	9 (b)	7 (b)	< 10 (b)	< 20 (b)	500 (b)	140 (d)	90 (d)	411 (d)	1.3 (c)	22.89
Aerodynamically sized fractions											
> 40	90 (b)	5 (b)	8 (b)	< 10 (b)	< 15 (b)	120 (b)	300 (d)	70 (d)	730 (d)	< 0.01 (c)	2.50
30–40	300 (b)	5 (b)	9 (b)	< 10 (b)	< 15 (b)	160 (b)	130 (d)	140 (d)	570 (d)	0.01 (c)	3.54
20–30	430 (b)	9 (b)	8 (b)	< 10 (b)	< 15 (b)	200 (b)	160 (d)	150 (d)	480 (d)		3.25
15–20	520 (b)	12 (b)	19 (b)	< 10 (b)	< 30 (b)	300 (b)	200 (d)	170 (d)	720 (d)		0.80
10–15	430 (b)	15 (b)	12 (b)	< 10 (b)	< 30 (b)	400 (b)	210 (d)	170 (d)	770 (d)	4.4 (c)	0.31
5–10	820 (b)	20 (b)	25 (b)	< 10 (b)	< 50 (b)	800 (b)	230 (d)	160 (d)	1,100 (d)	7.8 (c)	0.33
< 5	980 (b)	45 (b)	31 (b)	< 10 (b)	< 50 (b)	370 (b)	260 (d)	130 (d)	1,400 (d)		0.08
Airborne fly ash											
> 11.3	1,100 (a)	29 (b)	17 (b)	13 (a)	13 (a)	680 (a)	460 (a)	740 (d)	8,100 (d)	8.3 (c)	
7.3–11.3	1,200 (a)	40 (b)	27 (b)	15 (a)	11 (a)	800 (a)	400 (a)	290 (d)	9,000 (d)		
4.7–7.3	1,500 (a)	62 (b)	34 (b)	18 (a)	16 (a)	1,000 (a)	440 (a)	460 (d)	6,600 (d)	7.9 (c)	
3.3–4.7	1,550 (a)	67 (b)	34 (b)	22 (a)	16 (a)	900 (a)	540 (a)	470 (d)	3,800 (d)		
2.1–3.3	1,500 (a)	65 (b)	37 (b)	26 (a)	19 (a)	1,200 (a)	900 (a)	1,500 (d)	15,000 (d)	25.0 (c)	
1.1–2.1	1,600 (a)	76 (b)	53 (b)	35 (a)	59 (a)	1,700 (a)	1,600 (a)	3,300 (d)	13,000 (d)		
0.65–1.1										48.8 (c)	

indicates a comparative analytical accuracy of ± 30 percent for the values given; their scatter is attributed to poor sampling statistics.

The ten elements listed in Table 1 show pronounced dependences of concentration on particle size. Much less well defined trends could also be discerned for the eight elements Be, C, Mg, Al, Si, V, Mn, and Fe in some samples. In particular, Be and Mn exhibited sharp concentration increases in the smallest size range (1.1 to 2.1 μm) analyzed. A third set of seven elements (K, Ca, Ti, Co, Cu, Sn, and Bi) showed no convincing evidence of concentration dependence on particle size.

These results clearly demonstrate the following environmentally significant points:

1) The size distribution of certain trace elements in ambient air can be influenced, at least in part, by their particle size distribution in the source emission.

2) The highest concentrations of many very toxic elements are emitted in the smallest, lung-depositing particles.

3) Existing particle-collection devices, although highly efficient for the removal of large particles and thus for the reduction of bulk emissions, preferentially allow the emission of the smallest, most toxic particles.

4) Estimates of toxic element emissions, based on analyses of undifferentiated fly ash collected from particle precipitators, grossly underestimate the actual emissions.

These points take on even more importance when one recognizes that $\sim$ 91 percent of the material retained in the power plant investigated here (Table 1) had particle diameters greater than 40 μm so that average toxic element concentrations in the retained fly ash are essentially the same as for the > 75-μm fraction. More pronounced dependences of element concentration on particle size have been found for ambient urban aerosols (*4*); in this case the samplers had better size-differentiating ability than the multijet Anderson stack sampler employed here. Consequently, the actual dependences for fly ash may be more pronounced than those shown in Table 1.

Table 2. Major matrix elements in coal fly ash; the analytical method used in each case was x-ray fluorescence spectrometry.

Particle diameter (μm)	Concentration (% by weight)				
	Al	Si	Fe	K	Ca
Fly ash retained in the plant					
Sieved fractions					
44–74	9.4	18	18	1.2	5.4
Aerodynamically sized fractions					
> 40	1.3	3.0	50	2.5	2.5
30–40	5.9	14	18	6.3	6.3
15–20				4.5	4.5
10–15	9.8	19	6.6	4.0	4.0
5–10	13	26	8.6		
Airborne fly ash					
> 11.3	19.7	34	13	4.9	4.9
4.7–7.3	16.2	27	12	4.2	4.2
2.06–3.3	21	35	17	5.0	5.0
0.65–1.1	9.8	23	15	2.6	2.6

The reasons why certain trace elements are most concentrated in the smallest fly ash particles are not clear. One attractive explanation is that the element (or one of its compounds) volatilizes in the high-temperature coal combustion zone and then either recondenses preferentially or is adsorbed preferentially onto the large available surface area per unit mass provided by the small particles.

In support of this idea it is noteworthy that all the elements listed in Table 1, with the exception of Ni and Cr, have boiling points comparable to or below the temperature (1300° to 1600°C) of the coal combustion zone. This statement implies that the original, probably pyritic, compounds are reduced to the elements during the coal combustion process. However, although such smelting is undoubtedly feasible in the reducing region of the combustion bed, its occurrence is not strictly necessary to our hypothesis. Both Ni and Cr have access to the vapor phase as their sulfides, or possibly as their carbonyls whose formation (*1*) during and after coal combustion could provide volatile, although highly transient, species. Mercury, of course, undoubtedly volatilizes as the element and, although not studied here, would be expected to exhibit a dependence of concentration on particle size if the proposed mechanism is valid.

Simple models based on this volatilization-adsorption (or condensation) concept predict that the average concentration, $\overline{C}_X$, of an element X should depend on the particle diameter, d, according to an equation of the form (*10*)

$$\overline{C}_X = \overline{C}_0 + \overline{C}_A d^{-1}$$

where $\overline{C}_0$ is related to the average concentration of the element which is intrinsic to the particle and $\overline{C}_A$ is related to the average surface concentration added by adsorption or condensation. This equation relies on the poor assumption that particles of different sizes have the same bulk density. However, within the sampling and analytical errors reported, the model does predict the observed trends as illustrated in Fig. 1.

The model further predicts that trace metal concentrations should increase continuously with inverse particle diameter and that the surface concentration of the trace element should be greater than that in the particle interior. These predictions have been confirmed. Thus, Sparks (*11*) has shown that concentrations of the low-boiling (< 1600°C) elements Pb, Ba, Y, Sr, Rb, As, and Zn can be several orders of magnitude higher, in fly ash particles collected on a Millipore backup filter following a cascade impactor, than in those collected on the last impactor stage. The high-boiling elements Fe, Cu, and Ga did not show this effect. Scanning electron microscopic analyses by Hulett (*12*) of individual fly ash particles, which had been etched with a beam of argon ions, confirm that at least Ni, Cr, and Zn (the most concentrated elements listed in Table 1) are considerably more concentrated on particle surfaces than in their interiors.

In the case of sulfur, of course, it is hardly realistic to invoke a surface adsorption in view of the very high concentrations found in the small particle size fractions. These concentrations would suggest that some sulfur may be present as the element or as sulfide. This is contrary to the results of electron spectroscopy (*12*) which indicate the presence of sulfate. However, our sulfur analyses may be high owing to the possibility of preferential surface sampling by x-ray fluorescence and the associated calibration problems.

These results illustrate the importance of determining toxic trace element concentrations as a function of particle size if their full environmental impact is to be assessed. Furthermore, if the proposed volatilization-adsorption mechanism is basically correct, one would expect any high-temperature combustion source to produce concentration trends, similar to those reported here, for volatilizable species. Consequently, control technology designed to reduce the emission of toxic elements to the atmosphere should concentrate on the removal, or detoxification, of submicrometer-sized particles. In the latter context, preferential adsorption of volatile species onto large, easily collected particles of a heat-stable molecular sieve entrained with the feed air may provide an interesting and novel approach to the control of toxic element emissions.

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Postseismic Viscoelastic Rebound

Abstract. *The sudden appearance of a dislocation, representing an earthquake, in an elastic layer (the lithosphere) overriding a viscoelastic half space (the asthenosphere) is followed by time-dependent surface deformation, which is very similar to in situ postseismic deformation. The spectacular postseismic deformation following the large Nankaido earthquake of 1946 yields for the asthenosphere a viscosity of* 5×10^{19} *poise and a 50 percent relaxation of the shear modulus. Large thrust type earthquakes may provide, in the future, a new method for exploring the rheology of the earth's upper mantle.*

A simple, widely accepted model for the mechanical behavior of the earth's crust and upper mantle consists of a relatively elastic, brittle lithosphere overlying a viscous, ductile asthenosphere. Evidence for the existence of the asthenosphere comes from the viscous rebound of the crust upon removal of surface loads, such as the postglacial uplift of Fennoscandia and the rebound of Lake Bonneville which followed the disappearance of the water load. The brittleness and elasticity of the lithosphere are implied by the abundance of crustal earthquakes and the associated elastic rebound.

In a strictly elastic earth, complete elastic rebound would take place in a few seconds and the only slow deformation would be the accumulation of tectonic strain. In contrast, in an earth with a viscous element, a large earthquake would consist of an initial elastic rebound followed by a transient element of deformation controlled by the viscosity.

In order to determine the characteristics of time-dependent deformation which follows the sudden slip on large earthquake faults, we consider the lithosphere-asthenosphere composite as an elastic layer overlying a viscoelastic half space (Fig. 1). Assuming that at time $t = 0$ sufficient tectonic stress has accumulated to cause sudden faulting, we obtain the solution to the elastic-viscoelastic model in two steps: first we solve for the static displacements and stresses due to a fault in an elastic layer welded to an elastic half space. We then make use of the correpondence principle and the Laplace transform to obtain the time-dependent solution.

Consider a two-dimensional elastic layer with shear modulus μ_1, bulk modulus K_1, and thickness H over an elastic half space with shear modulus μ_2 and modulus K_2. The surface $y_3 = 0$ is the free surface. In Fig. 1a we show the two types of faults that we consider here and for which we first determine the elastic solution. In the first case a strike slip fault is modeled by introducing at depth $y_3 = -D$ a screw dislocation with slip Δu (as shown in