Distribution of Hazardous Element in PM10 and PM2.5 Emitted by Coal Combustion in China

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Distribution of Hazardous Element in PM10 and PM2.5 Emitted by Coal Combustion in China

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Abstract - China is one of the largest coal consumer countries in the world. At present more than 70% of total electric power capacity is produced by coal-fired power plants, and about 500 million tons of coal are consumed per year. Coal combustion is the main source of atmospheric pollution. Determination of particles emitted by a coal-fired power plant and hazardous elements in the particles has been investigated first by the authors in this paper. The result obtained is helpful for decreasing hazardous elements in particles from coal combustion and implication of clean coal technology.

I. Introduction

China is one of largest coal producer and coal consumer countries in the world. Coal is the primary energy of production of industry and agriculture and people's living. According to the characteristics of energy development in China, total coal consumption will increase as time goes by with development of national economy for considerable period. Now the coal-fired power plants' output accounts for 75.6% in total power generation, and about 500 million tons of coal have been consumed per year. The coal consumption covers 70% of all energy consumption. The discharge of soot and SO2 in coal-fired power plants is the first in all industries, and pollutants caused by coal combustion cover more than 70% in atmospheric pollutants. Therefore, coal combustion is the main source of atmospheric pollution in China, and it belongs to coal smoke pollution. Electric power industry is the basic industry of Chinese national economy, and the energy policy of "focus on electric power, base on coal" is inevitable choice of energy's development, which resulted in great pressure of electric power on environment [1].

Coal resources distributed in various geological ages in China, from Carboniferous of Paleozoic era to Tertiary of Cenozoic era. Middle -advanced rank coals cover majority in late Paleozoic era, coals are low rank bituminous in Mesozoic era, in Tertiary era coals are mainly lower carbon cohesive, weakly cohesive and lignite. Carboniferous - Permian coals are mainly used as power generation and for coking industry, and become energy bases of the country. Trace elements in coals of various geological eras differ greatly because of different geological environment [2, 3]. Therefore, the amount of hazardous elements in waste residue and fly ash coming from coal combustion differs greatly. Although the efficiency of removing dust is up to 99.95% in most power plants, large amount of fly ash was emitted to ambient atmosphere for a 1000 MW- power plant (about 1 ton per day), which dispersed to vast area as airflow moves, and subsides from several kilometers to dozens, hundreds of kilometers, or even further away from the plant, depended upon the height of chimney and particle size as well as various density.

With strict monitoring of environmental quality for countries over the world, developed countries has made a comprehensive study of respirable particles of PM10 and PM2.5 and established the guideline of controlling the amount of discharge [4]. In 1997, Environmental Protection Agency (EPA) of USA established the standard of PM2.5, and European Union countries strengthened the research on PM10 and PM2.5 [5, 6, 7, 8]. With the rapid development of electric power industry in China, authorities and institutions from local to central government have realized that the atmospheric pollution caused by coal-fired power plants becomes more and more serious, they pay attention to control acid rain and confirm the discharge quantity of SO_2 and NO_X [9, 10], in addition, they have noticed that the soot, which has hazardous elements, coming from coal-fired power plant, can do harm to mankind's health. A series of research of pollution condition of PM10 and PM2.5 have been investigated, including the studies around 8 elementary schools in cities of Guangzhou, Wuhan, Chongqing, Nanzhou, and in Beijing [11,12,13,14]. But in the studies mentioned above trace elements' content of particles in atmosphere were measured only, pollutant sources were not determined.

This is the first time to measure the particles with various dimensions emitted by a coal-fired power plant and the hazardous trace elements in the particles. It's helpful to the power plants and other industrial branches for investigating hazardous elements in particles from the discharge, and implicating clean coal technology.

II. Sample Collection and Analysis

TABLE I

The Concentration Of Trace Elements In Soot Coming From Power Plant ($\mu g/m^3$)

U m	< 1.8	1.8 -3.3	3.3 -4.7	4.7 -6.5	6.5 -8.9	8.9 -13.0	13.0 -20.8
As	0.8833	8.5789	7.4603	2.6198	1.8780	7.7396	0.9854
B	8.6905	4.1260	2.4570	0.6528	5.1791	3.5089	-
Cd	5.7865	0.1923	0.1119	0.0712	0.2132	-	0.1381
Co	9.2157	0.1336	0.0100	0.1927	0.0608	0.0308	0.1007
Cr	4.2456	11.5030	1.9132	2.0107	1.7001	2.3960	1.3770
Cu	1.3246	-	-	-	-	-	-
F	5.2558	125..6511	43.3240	8.5604	118.5751	-	43.3169
Ge	0.1566	0.1757	0.1389	0.0674	0.0224	0.1100	0.2207
Mo	6.8431	-	-	-	-	-	-
Ni	4.2450	9.9261	1.1876	1.6563	0.8815	2.3834	0.7841
Pb	3.4044	1.3986	1.5828	1.5815	1.1241	1.0379	1.1937
Sb	0.1190	0.2673	0.1307	0.1977	0.1633	15.9121	0.5341
Se	0.0125	0.0066	0.1389	0.0179	0.0603	0.0324	0.0774
Zn	33.0749	10.7655	9.9023	9.7927	12.8159	11.7364	14.3685

Notes: - means the contents of elements was not measured;

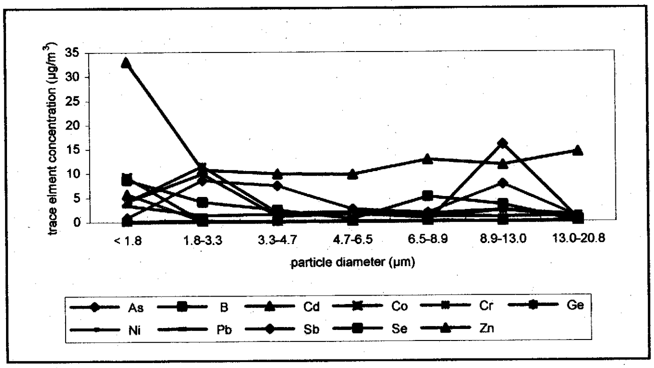

Fig. 1. Relationship between particle diameter and trace element concentration

Using improved Anderson impulsive particles rank sampler to take the rank samples in the chimney behind electrostatic dust catcher. The contents of elements were measured by ICP-MS. The results were shown in table 1.

In table 1, particles with highest density of hazardous elements focused on ≤3.3μm (shown on aerodynamics diameter) except Se, which was rich in 3.3-4.7μm. The concentration of B, Cd, Co, Cu, Mo, Pb, Zn is highest among the smallest particles (smaller than 1.8μm). The relationship between particle aerodynamics diameter and the contents of trace elements in it is shown in figure 1. By calculating the correlation coefficient between elements of different particle size, we found out that the correlation coefficient between Ni and Cr is 0.992, while the correlation coefficient between Zn and Co is 0.980, and the correlation coefficient between Zn and Pb is 0.906, and the correlation coefficient between Co and Pb is 0.996. Studied from the mineralogy and chemical characteristics, it's clear that Zn, Pb, Co, Cr occurred in the form of sulphate and aluminosilicate, and they have common characteristics and belong to volatile elements.

TABLE II

The Correlation Coefficient between Elements of Different Particle Size

	[Zn]	[Cr]	[Co]	[As]	[Sb]	[Se]	[Ge]	[Pb]
[Ni]	.107	.992	.172	.476	-.086	-.578	.347	.197
[Zn]		.025	.980	-.530	-.159	-.325	.241	.906
[Cr]			.085	.492	-.147	-.513	.337	.120
[Co]				-.443	-.182	-.356	.192	.996
[As]					.434	.103	.093	-.383
[Sb]						-.158	-.100	-.323
[Se]							.081	-.285
[Ge]								.200

III. Atmospheric Particles Sampling and Analysis

To study the dispersion and transportation of particles, there were 6 inspection places established around the power plant at 6-12 km under key wind direction where atmospheric particle was collected during chimney particles was taking (see fig. 2).

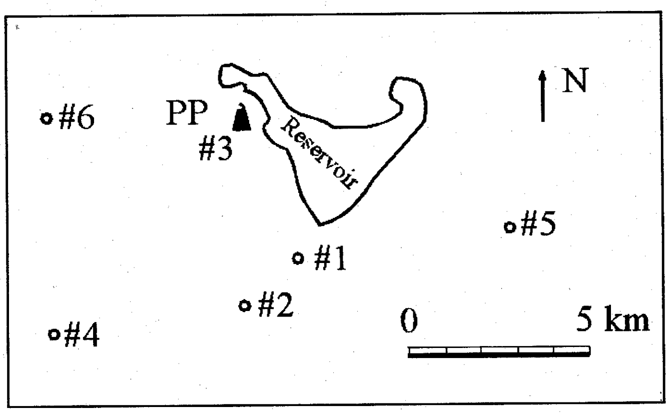

Fig. 2. Sample locations

The concentration of particles of inspection point #1, which lay 6 km away in the southeast of the power plant, was shown in table 3. The concentration of Pb, Cu, Zn, Mo, Co in the particles, whose dimension was smaller than 2μm, was higher than that in other particles.

We systematically measured the concentration of hazardous elements in the atmospheric aerosol near the power plant (see table 4). From table 4, it was given that the concentrations of As, Se, Sb and Cu in the particles of the inspection point #1, located at 6 km in the southeast of the plant, are very high, which are 1.3-208 times than the average in other inspection places. There are few pollutants sources in this area, which lay in the downwind of the plant, and it's obvious that the power plant made more contribution in respect to the hazardous elements in the atmosphere.

TABLE III
Concentration Distribution of Hazardous Elements in Different Size Particles in Atmosphere (μg/m^3)

Size (μm)	Pb	Cu	Zn	Mo	Co	As	Sb	Se	F
>15	0.0093	0.0959	0.0441	0.0003	0.0017	0.0142	0.0071	0.0004	0.0135
2-15	0.0011	0.0485	0.0093	0.0014	0.0008	0.0232	0.0055	0.0003	0.1207
<2	0.0517	0.4651	0.1633	0.0063	0.0048	0.0020	0.0007	0.0001	0.058

TABLE IV
Concentration Distribution of Hazardous Elements in Aerosol of Inspection Places near Power Plant (μg/m^3).

	1	2	3	4	5	6
Pb	0.0627	0.7976	0.5995	0.9989	0.6104	0.2344
Cu	0.1432	0.0931	0.0941	0.0766	0.0126	0.0698
Ni	0.0047	0.0287	0.0157	0.0214	0.0159	0.0467
Zn	0.1093	1.2269	1.4744	1.0095	0.3078	0.2318
Cd	0.0003	0.0058	0.0063	0.0075	0.0022	0.002
Mo	0.0056	0.0271	0.0253	0.0255	0.0494	0.0088
Cr	0.0724	0.0916	0.0182	0.0634	0.0178	0.0174
Co	0.002	0.0115	0.0067	0.0111	0.0039	0.0042
As	0.0417	0.0141	0.0015	0.0309	0.0002	0.0022
Se	0.0078	0.0002	0.0006	0.00002	0.00001	0.0001
Sb	0.0088	0.0034	0.001	0.0044	0.0006	0.0033
Ge	0.0001	0.0012	0.0006	0.0013	0.0004	<0.0002
F	0.2109	22.8784	8.1395	10.7655	1.9479	1.427

The correlation coefficient of hazardous elements in the atmospheric aerosol near the power plant was shown in table 5. From table 5, we will see that the correlation coefficient between Zn and Cd is 0.789, and the correlation coefficient between Cd and Co is 0.784, the correlation coefficient between Cd and Ge is 0.866, and the correlation coefficient between Co and Ge is 0.871, and the correlation coefficient between Zn and Ge is 0.726, while the correlation coefficient between Cd and Pb is 0.711. In other words, the inner correlation coefficient of the particles is 0.7-0.9 in the atmosphere near the plant.

TABLE V
Summary of Correlation Coefficient of Hazardous Elements in Atmospheric Aerosol near Power Plant (N=13)

	Ni	Zn	Cd	Mo	Cr	Co	As	Sb	Ge	Pb
Cu	-.159	-.174	-.013	-.372	.373	.014	.069	.334	.034	-.271
Ni		.230	.315	-.099	.122	.422	-.002	-.019	.238	.279
Zn			.789	.278	.216	.632	.142	-.076	.726	.569
Cd				.118	.550	.784	.444	-.006	.866	.711
Mo					-.131	.182	-.129	-.389	.202	-.021
Cr						.587	.393	.658	.594	.308
Co							.294	.164	.871	.477
As								.381	.230	.230
Sb									.066	-.128
Ge										.720

IV. Enrichment Factor Analysis

Enrichment factor is often used to describe the distribution, transportation and enrichment of trace elements in the atmosphere, thus to elucidate the origin of the element and analyze the pollution condition. When calculating enrichment factor, following formula was used to present relationship of elements between aerosol and crust [15,16,17]:

$$\mathrm{EF} = \frac{(x / Fe)_A}{(x / Fe)_{Ec}}$$

Where: EF means enrichment factor

x means element in the atmospheric aerosol

$(x/Fe)_A$ means relative concentration of element x

$(x/Fe)_{EC}$ means relative average concentration of corresponding element x in the earth's crust, usually taking Mason's data[18] as relative average concentration of element x in the earth's crust.

Enrichment factor of various crustal elements, corresponding to the elements in the atmospheric aerosol, was shown in the table 6.

From table 6 we can see that the enrichment factor of elements such as As, Se, Sb, Cr in the inspection point #1, which lay in the downwind of the electric power plant, is far higher than that of the power plant, which indicated small particles coming from the electric power plant can flow far away by the wind. All the elements above belong to volatile elements, when the smoke vent from the electric power plant, these elements condensed on the small particles because of cooling, which leads to the higher enrichment factor in the small particles. The enrichment factor of Pb, Zn, Cd, Mo is larger than 10 in all inspection points near the electric power plant, which shows that it is not natural results but manmade pollution, which testified that hazardous elements do harm to the atmospheric environment.

TABLE VI
Enrichment Factor of Various Elements in Atmospheric Aerosol near Power Plant Contrasting to Elements of Crust

	1	2	3	4	5	6
Pb	175.38	182.15	256.48	155.02	547.49	204.77
Cu	94.64	5.03	9.52	2.81	2.67	14.42
Zn	56.71	52.07	117.15	29.10	51.27	37.61
Cd	50.00	85.00	175.25	75.65	128.25	113.50
Mo	136.67	53.67	93.80	34.30	384.00	66.63
Cr	26.30	2.70	1.01	1.28	2.08	1.98
Co	2.90	1.36	1.49	0.90	1.82	1.91
As	297.22	23.33	4.64	34.64	1.30	13.88
Se	5700.00	10.00	6.67	0.81	2.33	22.72
Sb	160.00	5.00	2.78	4.44	3.50	18.74
F	0.0056	108.69	72.43	34.75	36.34	25.93
Ni	2.28	1.13	1.17	0.58	2.47	7.07

V. Main Results

(1) When coal of Carbonic- Permian era burns, hazardous elements in particles dispersed in the environment enriched in PM2.5 particles. So it's necessary to arrange different coals during coal's combustion and minimize hazardous material's harm to the environment.

(2) Among the soot particles vented from the large coal-fired power plant, hazardous elements mainly enrich in the small particles whose diameter is smaller than 3.3um. The concentration of hazardous elements in small particles whose size is smaller than 3.3um is the highest in the atmospheric aerosol near the power plant. Particles containing these hazardous elements can pass through the routine dust catcher freely and enter into the atmosphere, comprising the hazardous pollutants along the atmosphere's transportation and dispersion, and do harm to mankind's health.

(3) It's requisite to design and develop better dust catcher to absorb the PM2.5 particles and reduce the quantity of particles dispersing into the environment.

(4) The correlation coefficient between Ni, Cr, Zn, Co, Pb contained in the soot particles vented from the electric power plant's chimney is 0.906-0.992. For these elements are volatile elements and whose occurrence are in the forms of sulfate and aluminosilicate in the fly ash.

(5) The correlation coefficient between Ni, Zn, Ge, Co, Pb is 0.711-0.871 in the atmospheric aerosol near the electric power plant.

(6) Enrichment factor of hazardous elements in fly ash is larger than that of hazardous elements in slag, which means EFFA>EFS. In other words, the enrichment factor of hazardous elements such as Pb, Zn, Cd, Co, Mo in small aerosol particles is larger than in bigger particles (EFS>EFB). The particles containing hazardous elements flow with the wind and subside in the cities, villages, rivers, lakes, earth, forests and the surface of crops, and do harm to the environment depended on by the mankind, animals and plants. Therefore, it's great significance to make a study of its movement and transformation for the environment and mankind's health.

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