



## Occupational Hygiene around the World

### Current Occupational Exposures in Chinese Iron and Copper Mines

Zhien Wu , Frank J. Heart , Kailiang Peng , Michael A. McCawley , Anluo Chen , John Palassis , Mustafa Dosemeci , Jingqiong Chen , Joseph K. McLaughlin , Suzanne H. Rexing & William J. Blot

**To cite this article:** Zhien Wu , Frank J. Heart , Kailiang Peng , Michael A. McCawley , Anluo Chen , John Palassis , Mustafa Dosemeci , Jingqiong Chen , Joseph K. McLaughlin , Suzanne H. Rexing & William J. Blot (1992) Occupational Hygiene around the World, *Applied Occupational and Environmental Hygiene*, 7:11, 735-743, DOI: [10.1080/1047322X.1992.10388080](https://doi.org/10.1080/1047322X.1992.10388080)

**To link to this article:** <https://doi.org/10.1080/1047322X.1992.10388080>



Published online: 25 Feb 2011.



Submit your article to this journal 



Article views: 17



View related articles 



Citing articles: 7 [View citing articles](#) 

## *Occupational Hygiene Around the World*

# Current Occupational Exposures in Chinese Iron and Copper Mines

Zhien Wu,<sup>A</sup> Frank J. Hearl,<sup>B</sup> Kailiang Peng,<sup>A</sup> Michael A. McCawley,<sup>B</sup> Anluo Chen,<sup>A</sup> John Palassis,<sup>C</sup> Mustafa Dosemeci,<sup>D</sup> Jingqiong Chen,<sup>A</sup> Joseph K. McLaughlin,<sup>D</sup> Suzanne H. Rexing,<sup>E</sup> and William J. Blot<sup>D</sup>

<sup>A</sup>Tongji Medical University, School of Public Health, Department of Labor Health and Industrial Diseases, 13 Hang Kong Lu, Wuhan, Hubei, People's Republic of China    <sup>B</sup>National Institute for Occupational Safety and Health, Division of Respiratory Disease Studies, 944 Chestnut Ridge Road, Morgantown, West Virginia 26505    <sup>C</sup>National Institute for Occupational Safety and Health, Division of Physical Science and Engineering, 4676 Columbia Parkway, Cincinnati, Ohio 45226    <sup>D</sup>National Cancer Institute, Division of Cancer Etiology, Executive Plaza North, Bethesda, Maryland 20892    <sup>E</sup>Westat Inc., Rockville, Maryland 20850

To conduct a retrospective exposure assessment for a study of silica, silicosis, and lung cancer, current exposure measurements and techniques were compared with industrial hygiene data that had been systematically collected in Chinese industries over the past three decades. Historically, sampling was usually confined to total dust evaluation and bulk silica determinations. For comparison, from 1988 through 1989, several special surveys were conducted in Chinese iron and copper mines in the Huangshi region of Hubei Province. In addition to the total dust and silica measurements using the traditional Chinese sampling system, data were collected using standard National Institute for Occupational Safety and Health (NIOSH) sampling equipment for respirable dust, total dust, particle size distribution, selected trace elements, radon, and fibers. Overall, total dust measurement using NIOSH sampling and analytical procedures were correlated to the corresponding Chinese measurement,  $r^2 = 0.77$ . No statistically significant difference was observed between historical data from recent sampling cycles and the current measurements. Some current silica determinations using the Chinese phosphoric acid digestion method, with gravimetric analysis of the residue, were biased by the presence of insoluble oxides in the residues. Exposure to carcinogenic trace metals was limited in the copper and iron mines; however, substantial radon progeny levels were observed, in one case exceeding 40 WL. No installed asbestos was found in any of these mines nor were any fibers detected in the analyzed bulk samples. The completeness of the historical record of exposures in this group of workers makes it particularly well suited for epidemiological study of dust-related diseases. Wu, Z.; Hearl, F.J.; Peng, K.; McCawley, M.A.; Chen, A.; Palassis, J.; Dosemeci, M.; Chen, J.; McLaughlin, J.K.; Rexing, S.H.; Blot, W.J.: Current Occupational Exposures in Chinese Iron and Copper Mines. *Appl. Occup. Environ. Hyg.* 7(11):735-743; 1992.

## Introduction

Silicosis has long been recognized as an illness resulting from exposure to dusts in mining environments and other dusty trades.<sup>1</sup> Recently, debate has been growing about silica being carcinogenic.<sup>2</sup> Several studies have reported a relationship between silicosis and excess risk of developing lung cancer.<sup>3</sup> The International Agency for Research on Cancer (IARC) has concluded that there is limited evidence to establish a causal relationship between crystalline silica exposure and human lung cancer mortality.<sup>4</sup>

Since 1958, the government of the People's Republic of China has enforced dust sampling regulations.<sup>5</sup> These regulations require mines and companies in the dusty trades to measure the total dust level in dusty work areas monthly, to measure size distribution and free silica content if deemed technically necessary, and to report the results to higher administration levels quarterly. Additionally, medical records including chest X-ray films are available for most of those in the dust-exposed workforce. Based on the existence of such information, it was decided to begin epidemiological and industrial hygiene investigations of silica-exposed Chinese workers to explore the relationship among silica exposure, silicosis, and lung cancer.

Workers included in these investigations were employed in copper and iron mines near Wuhan, PRC, in and around the city of Huangshi. To include these sites in an epidemiologic investigation studying the relationship between silica exposure and lung cancer, comprehensive occupational exposure assessments were performed. The overall approach to the investigation was threefold. First, it was necessary to examine the consistency of the historical dust exposure data. Data from special current sampling surveys could be compared with historical dust exposure data

searching for gross anomalies. Second, because the Chinese method of dust sampling and silica analysis is based on total dust sampling with acid digestion of bulk samples for silica content analysis, it was necessary to evaluate this method through modern X-ray analyses. Finally, it was necessary to catalog and measure exposures to agents known to be related to lung cancer risk, including asbestos, radon, arsenic, cadmium, nickel, and polynuclear aromatic hydrocarbons (PNAs). This article describes the results of the exposure assessments made at the Chinese iron and copper mines.

### Description of Mining Operations

The iron and copper mines in the Huangshi area of Hubei Province are very similar in the type of ore being mined and the mining processes used to extract the minerals. Some iron ore from this region is so copper-rich it is sent for copper refining. Consequently the mining and processing procedures are similar. Figure 1 diagrams the mining and milling process. The first step in mining is to drill holes for the charges in the working face. One or two workers, known as drillers, operate hydraulic or pneumatic drills that usually include a water injection line for dust suppression. Once the prescribed pattern of bore holes has been drilled, the worker described as the blaster enters the area and inserts appropriate charges into the holes. Usually at the end of the shift after all the workers are out of the mine, the charges are set off electronically. On the next shift the broken ore is moved from the freshly blasted face to a fixed loading point. This is accomplished either with a pneumatic front-end loader, known as the T-4 machine, a modern diesel scoop, or an electric dragline. The broken ore is loaded onto either rail cars or conveyor belts at the loading point and is transported to the surface via rail car, shaft elevator, or conveyor. There, the material is unloaded and taken for the first phase of milling and separation. Large material is broken in crushers, washed, and separated by a variety of methods. In iron ore processing a magnetic separator is used to remove the iron-bearing material from the waste. Typically, the ore is processed wet after it passes the primary crushing areas, and so dust levels in the processes beyond the crushers are typically low.

### Sampling Stations

Each of the three sampling stations was chosen to be representative of a distinct exposure zone. The second criterion for selecting a sampling site was that it should be a location that had been historically sampled under the Chinese national dust monitoring program. The result of these selection criteria was that few of our studies' samples were collected at the surface processing areas of the mines, for these areas had not been aggressively sampled in the past. Exposures at some surface areas were assumed or certified by the local occupational health officials to be negligible. Table I lists the jobs associated with each of this project's

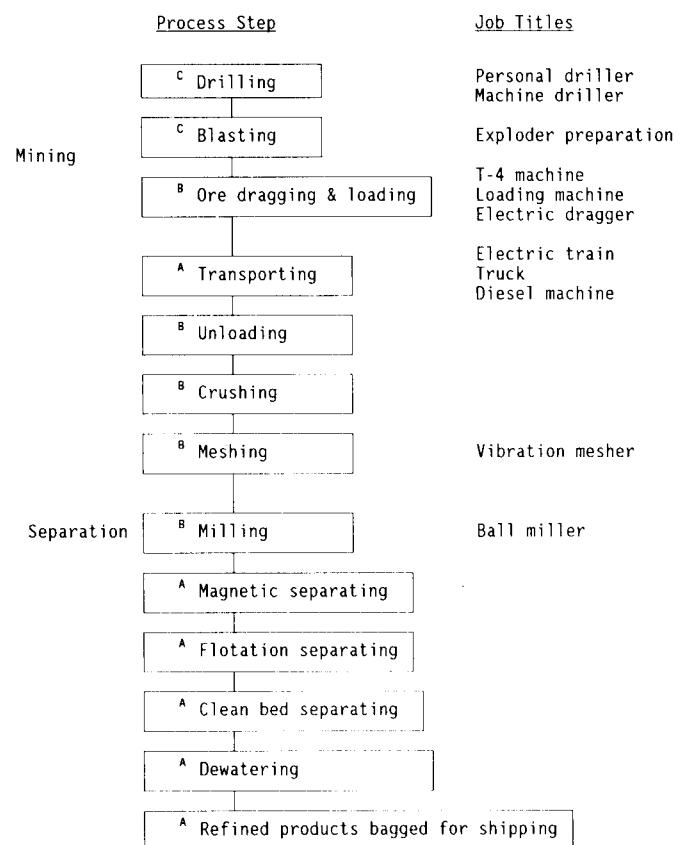


FIGURE 1. The mining and milling process. KEY: A = usually low dust; B = usually average dust; C = usually high dust.

sampling stations, along with a general description of the station's function. The driller stations usually included the jobs for the driller operator, the blaster, the manual miner, roof control, and maintenance. Although all these types of workers do work near or at the driller's station, their work usually is separately sequenced. That is, after the driller has drilled an appropriate pattern of blast holes in the working face, the blaster enters the area to set the explosive charges. Occasionally the blaster may work next to the driller as his assistant during drilling, and the driller provides assistance to the blaster in setting the charges. At the end of the shift the rock is blasted. Roof control workers, followed by manual miners or loader machine operators, will enter the area to remove the broken rock and secure the area. Loader stations may describe loader and unloader workers as well as transportation workers because these operations of dumping and loading are transfer points between the working face area and the main mine haulage. Table I provides some insight into the layout and workings of each mine studied.

### Methods

The sampling strategy employed was to select three exposure-monitoring stations in each mine. The three sampling stations were chosen at locations for which historical

**TABLE I. Jobs Associated with Each Sampling Station**

Mine	Station 1	Station 2	Station 3
31 Iron	Unloader: 21-loader 22-unloader 24-diesel transport operator	Driller: 11-driller 12-blaster 13-excavator 14-ore sampler 16-roof control	Transportation: 33-maintenance 23-train driver 26-drill rod supplier 32-cement sprayer
32 Iron	Driller: 11-driller 12-blaster 14-ore sampler 15-manual miner 16-roof control 33-maintenance 36-gunpowder mix	Excavator: 13-excavator 21-loader	Transportation: 21-loader 23-train driver 24-diesel operator 32-cement sprayer 33-maintenance
33 Copper	Driller: 11-driller 14-ore sampler 16-roof control 25-pipeline worker 33-maintenance	Loader: 16-roof control 21-loader 22-unloader	Transportation: 22-unloader 23-train driver
34 Copper	Driller: 11-driller 14-ore sampler 31-timber worker	Dragline: 12-blaster 21-loader 23-train driver	Transportation: 23-train driver
35 Copper	Driller: 11-driller 12-blaster 14-ore sampler 31-timber worker 33-maintenance	Driller: 11-driller 12-blaster 32-cement sprayer 33-maintenance	Transportation: 21-loader 24-diesel transport operator
36 Copper	Driller: 11-driller 12-blaster 13-excavator (diesel) 15-manual miner 16-roof control 33-maintenance	Loader: 21-loader 33-maintenance 42-engineer, manager 43-dust control worker 44-signal worker	Transportation: 21-loader 23-train driver 24-diesel transport operator

data were available and so that the locations would be representative of high, medium, and low dust exposures. Tongji Medical University (TMU) staff provided samplers customarily used to monitor dust exposures in Chinese mines and factories. The Chinese-supplied samplers and National Institute for Occupational Safety and Health (NIOSH)-supplied samplers were placed side by side at each station. Each was operated according to its own sampling routine to make the results comparable. The following discussion describes the operation of each type of sampler used at each of the sampling stations.

The Chinese airborne dust sampler was a battery-operated sampler that collected total airborne dust directly onto an exposed preweighed filter. Sampling with a flow rate of 25 L/min, the sampler was typically operated for 15 minutes while the observed task was in progress. After sampling, the filters were placed in glassine envelopes and returned

to the laboratory where they were postweighed to determine the total airborne dust concentration.<sup>6</sup>

At each sampling location, settled (bulk) dust samples were collected by brushing the dust into a small polyethylene bottle. A portion of the sample was returned to the TMU laboratories in Wuhan, and a portion of the bulk sample was sent to the NIOSH contract laboratory in Salt Lake City, Utah (DataChem Laboratories). The Chinese portions of the samples were analyzed for percentage of silica using a form of the Talvitie method, which is described as follows:<sup>6</sup> The samples were ground to fine particle size using a mortar and pestle. A 0.1-g sample was carefully weighed into a flask to which was added 15 ml of pyrophosphoric acid. The dust was stirred in the pyrophosphoric acid at a temperature of 245° to 250°C for 15 minutes. The remaining residue was neutralized and washed with distilled water through a residue-free filter. The filter was placed in a tared crucible, dried, then ashed at 850°C in a muffle furnace. The crucible was weighed, with the mass gain taken to be crystalline "free silica." This mass, divided by the original allocation, gave the fraction and percentage of silica in the sample. According to the Chinese standard, if the silica concentration in the dust exceeded 10%, then the total dust levels must be controlled below 2 mg/m<sup>3</sup>.

The bulk dust sample that was returned to the NIOSH laboratory was analyzed by X-ray diffraction (XRD).<sup>7</sup> Briefly, a 2-mg aliquot of each sample was weighed onto FWS-B filters prior to analysis. The filters were then dissolved in tetrahydrofuran, and the residue was redeposited on a silver membrane filter. These filters were then mounted in the diffractometer and scanned for primary, secondary, and tertiary peaks for quartz, cristobalite, and tridymite. Observed peak intensities were normalized to the net intensity of a reference spectrum and compared to the calibration graph to determine mass present for each silica polymorph.

Respirable dust was measured using NIOSH dust sampling procedures. A preweighed 37-mm FWS-B filter mounted in a plastic cassette was placed downstream from a 10-mm nylon cyclone preseparator operating at 1.7 L/min. Sampling mechanically generated dusts at this rate, the cyclone has penetration characteristics similar to the human respiratory system for alveolar deposition. After sampling, the cassette was removed from the sampling train and returned to the laboratory for gravimetric analysis, with the weight gain divided by the sample volume yielding the respirable dust concentration.<sup>8</sup> These filters were then dissolved in tetrahydrofuran and analyzed for respirable crystalline silica by the method described above for bulk dust by XRD.<sup>7</sup>

Each selected station was sampled for total dust and particle size distribution using cascade impactors. Modified cassette impactors previously described were constructed and used for this purpose.<sup>9</sup> The impactors collected full-shift samples at 20 L/min, giving particle size fractionation as described in Table II. Mean particle diameter,  $d_{p50}$ , was

TABLE II.

Stage	Jet Diameter, mm	Aerodynamic Diameter, $d_{50}$ $\mu\text{m}$	Respirable Fraction of Stage*
1	4.76	9.8	0.0
2	3.94	7.4	0.032
3	3.14	5.2	0.16
4	1.46	1.65	0.97

\*Final filter collects all that passes Stage 4 and is considered to be 100% respirable.

calculated using empirical and theoretical models.<sup>10</sup> In addition to measuring the particle size distribution, the weight changes determined from each stage of the impactor and the final filter were summed to give a time-weighted average total dust concentration.

The measurements described thus far were all designed to define the relationship between historical Chinese dust and silica measurements and the types of measurements typically made during NIOSH field surveys. It was also important for the epidemiological analysis to characterize other potential exposures that could be associated with excess lung cancer mortality.

On alternate survey days, samples were collected to measure exposure to PNAs and the toxic trace metals arsenic, nickel, and cadmium. The PNA samples were collected using Teflon<sup>®</sup> (TFE) filters in an opaque cassette. Following the filter in the sampling train was a sorbent tube filled with XAD-2 resin to collect vapor phase PNAs. After sampling, the filters were removed from their cassettes and transferred to glass vials to which 100 mg of additional XAD-2 resin had been placed. This modification in the procedure was made to adsorb any PNA volatiles that might evolve from the stored filters and during shipment because refrigeration of the samples in the field was impossible. The sorbent tubes were capped, labeled, and shipped with their companion filters. These samples were analyzed by capillary column gas chromatography with a flame ionization detector.<sup>11</sup> The reported mass of each species measured was summed to report a value of total PNA.

On the second survey day, total dust samples were collected on a 0.8- $\mu\text{m}$  cellulose ester membrane filter at each sampling station. These samples were returned to the laboratory and analyzed for elemental composition by inductively coupled plasma (ICP) atomic emission spectroscopy.<sup>12</sup> Quantified results were obtained for arsenic, nickel, and cadmium. A portion of each bulk sample also was prepared and analyzed by the ICP method, giving bulk elemental composition data.

In a variety of locations at each site, samples were collected and analyzed for radon progeny. Radon progeny samples were collected with a 25-mm glass fiber filter, sampling for 5 minutes at 2 L/min. After the air sampling was complete, the filter was held for 50 minutes to allow the short-lived isotope Ra A ( $^{218}\text{Po}$ ) to decay so that only Ra C (or  $^{214}\text{Po}$ ) was counted. The alpha activity of the filter was counted with a calibrated field alpha counter. The radon

level was then calculated in working levels using the formula developed by Kusnetz.<sup>13</sup> Gamma radiation was also detected using a standard gamma counter. Radon and gamma radiation were measured at the three chosen sampling stations and other areas where radon and gamma radiation might be expected, such as near underground springs, along fault lines, and in dead-end entries.

Although regulations for collecting dust and silica have been in effect for Chinese mines for many years, there were no clear regulations for measuring the confounding agents discussed above. Some sporadic data were available from historical radon measurements, but these were typically from special surveys conducted by outside research institutions and were not part of a systematic sampling program.

The sampling protocol for all agents is summarized in Table III.

## Results

One of the primary survey objectives was to examine the relationship between historical total dust measurements recorded for the mines under study and the measurements made with NIOSH dust monitoring equipment. Table IV summarizes the findings for total and respirable dusts. The value reported in each cell was the average of two successive days' sampling. Measurements made with NIOSH sampling equipment were typically full-shift samples collected for a nominal 8-hour shift. In fact, some samples were collected for as little as 4 hours. Sampling times had to be adjusted to the length of the shift actually observed. Some mines had a policy that when an established production quota was met by the worker they were free to leave. Thus, an industrious worker could complete his work at the mine in a few hours and have time to work in a private garden for outside income. The Chinese sampling method was to sample for a short time (usually 30 minutes) at a workstation, and only when work was actually in progress. This schedule had a tendency to bias the daily exposure estimate upward because during nonwork times less dust was usually present.

The NIOSH and Chinese total dust measurements were correlated despite these differences in sampling strategy. Regression on the total dust measurements indicated that the NIOSH measurements were about 73% (NIOSH = 0.728\*CHINESE - 0.004) of the corresponding Chinese total dust measurements, with a linear model accounting for 77% ( $r^2 = 0.77$ ) of the variability. These data are plotted in Figure 2 along with the calculated regression line. For this analysis the observation for face workers at Mine 35 was not included because the value was so high it probably represented an overloaded sample and would not be valid ( $r^2 = 0.84$  if this point was included).

The respirable fraction presented in Table IV was calculated based on the impactor-measured particle size distribution. A portion of the mass collected on each impactor's stage was allocated to the respirable fraction according to preestablished deposition criteria. The respirable fractions

**TABLE III. Summary of Sampling Protocol**

Analyst	Type of Sampler	Assay Items	Number of Locations	Frequency	Flow Rate or Amount Collected	Duration
NIOSH	Cyclone	Respirable dust	3	2 days	1.7 L/min	4-8hr/day
	Cyclone	Quartz in respirable dust	3	2 days	1.7 L/min	4-8hr/day
	Cyclone	Cristobalite in respirable dust	3	2 days	1.7 L/min	4-8hr/day
	Impactor	Total dust	3	2 days	2.0 L/min	4-8hr/day
	Impactor	Particle size	3	2 days	2.0 L/min	4-8hr/day
	Total, filter	30 elements	3	1 day	2.0 L/min	4-8hr/day
	Filter and tube	17 PNAs	3	1 day	2.0 L/min	4-8hr/day
	Bulk	30 elements	3	1 day	± 5 g	Hand pick
	Bulk	Quartz	3	2 days	± 5 g	Hand pick
	Bulk	Cristobalite	3	2 days	± 5 g	Hand pick
NIOSH Tongji	α counter w/filter	Radon	5-8 points	2 days	2.0 L/min	5 min Δ 50 min
	γ counter	γ radiation	5-8 points	2 days	—	Instant reading
Tongji	Chinese dust sampler	Total dust	3	2 days	25 L/min	15 min
	Chinese dust sampler	Particle size	3	2 days	25 L/min	15 min
	Bulk	Quartz	3	2 days	± 5 g	Hand pick
Local dust samplers	Chinese dust sampler	Total dust	3	2 days	25 L/min	15 min

**TABLE IV. Comparison of Dust Measurements Using NIOSH and Chinese Samplers<sup>a</sup>**

Mine	Station (no.)	Full-Shift TWA Respirable, mg/m <sup>3</sup> (NIOSH)	Full-Shift TWA Total, mg/m <sup>3</sup> (NIOSH)	30-min TWA Total, mg/m <sup>3</sup> (Chinese)	Respirable Fraction, % (NIOSH)
31	Face workers (2)	1.2	0.92	3.7	83.5
	Loading, hauling (1)	0.14	0.50	1.1	54.1
	Transportation (3)	0.25	0.36	1.9	37.0
32	Face workers (1)	0.94	N/A	6.2	N/A
	Loading, hauling (2)	1.9	N/A	5.2	N/A
	Transportation (3)	1.0	1.2	2.2	90.2
33	Face workers (1)	0.64	3.0	2.0	38.6
	Loading, hauling (2)	0.46	0.85	1.2	78.7
	Transportation (3)	1.0	1.9	0.8	86
34	Face workers (1)	5.1	6.6	8.6	87.4
	Loading, hauling (2)	0.19	0.73	1.3	56.8
	Transportation (3)	0.21	1.0	1.7	34.7
35	Face workers(1,2) <sup>b</sup>	5.8	9.2	21.6	69.1
	Transportation (3)	2.9	4.2	4.8	72.9
36	Face workers (1)	0.13	0.47	1.1	29.1
	Loading, hauling (2)	0.22	1.0	1.6	42.8
	Transportation (3)	0.17	0.75	0.5	66.1

<sup>a</sup>Except as noted below, values were average of two days' sampling.<sup>b</sup>Station values from two face areas were averaged.

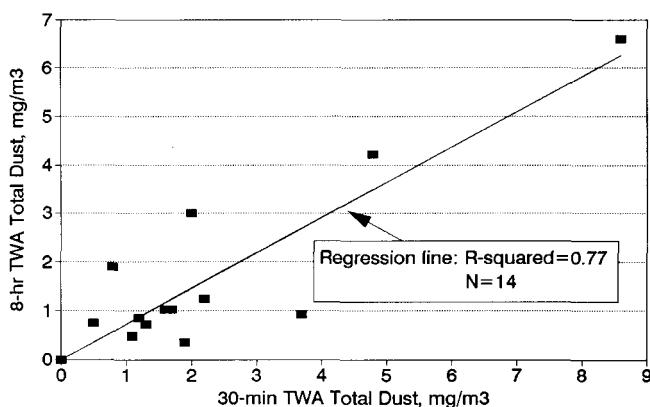


FIGURE 2. Total dust measured as an 8-hour time-weighted average (TWA) compared to the Chinese 30-minute TWA method.

apportioned from each stage are presented in Table III. The respirable dust estimates determined from the impactor samples were compared to the cyclone-measured respirable dust observations in Figure 3 along with the calculated regression line (IMPACTOR =  $1.07 \times$  CYCLONE + 0.128). The impactor-calculated respirable dust and the fraction that was observed by direct cyclone sampling of respirable dust fit the linear model, accounting for 98% ( $r^2 = 0.98$ ) of the variability. This result was consistent with previous studies.<sup>14</sup>

Table V presents the average total dust measurements made during the current study with station estimates from the preceding two periods. Historical job–task exposures were estimated by local industrial hygienists. They based these estimates on available historical area sampling data, records of process changes, and the documented history of the use of engineering controls such as forced ventilation. The station averages reported for the preceding periods in Table V were computed by averaging job estimates according to the station–job title matrix of Table I. In cases where multiple jobs had previously been assigned the same historical exposure estimate based on prior station–area sam-

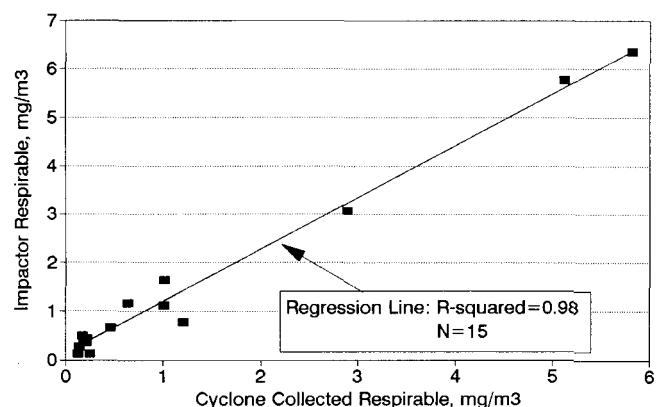


FIGURE 3. Respirable dust concentrations calculated from impactor sampling methods compared to respirable dust collected directly using a 10-mm nylon cyclone operated at 17 L/min.

TABLE V. Historical Estimates and Current<sup>a</sup> Average Total Dust (mg/m³)

Mine	Station (no.)	1984–1985	1986–1988	Current <sup>a</sup>
31	Face workers (2)	3.1	2.7	3.7
	Loading, hauling (1)	2.3	2.2	1.1
	Transportation (3)	2.3	2.0	1.9
32	Face workers (1)	4.2	5.8	6.2
	Loading, hauling (2)	7.5	10.7	5.2
	Transportation (3) <sup>b</sup>	1.0	0.9	2.2
33	Face workers (1)	1.2	1.5	2.0
	Loading, hauling (2)	1.6	2.0	1.2
	Transportation (3)	1.6	2.3	0.8
34	Face workers (1)	2.6	2.5	8.6
	Loading, hauling (2)	1.1	3.6	1.3
	Transportation (3)	0.4	N/A	1.7
35	Face workers (1,2) <sup>c</sup>	4.6	3.0	21.6
	Transportation (3)	2.8	2.8	4.8
36	Face workers (1)	1.8	1.9	1.2
	Loading, hauling (2)	1.7	1.7	1.6
	Transportation (3)	1.6	1.5	0.5

<sup>a</sup>Current survey refers to the industrial hygiene surveys conducted for this project; single samples except mines 32, 35, and 36 were 2-day averages.

<sup>b</sup>Did not include values for Job 32, cement sprayer, which were 56.3 and 59.8 mg/m³ for the two historical periods respectively.

<sup>c</sup>Did not include values for Job 32, cement sprayer, which were 77.8 and 67.9 mg/m³ for the two historical periods respectively.

pling, those jobs were not double-counted for purposes of station averaging. Across the study, average total dust levels were 2.3, 2.9, and 2.8 mg/m³ for the 1984–1985, 1986–1988, and current time periods, respectively. Geometric means (geometric standard deviations) for these periods were 1.9 (1.9), 2.4 (1.8), and 2.0 (2.2) mg/m³, respectively. These results do not include the observation from Mine 35–Station 1, which, as previously discussed, appeared abnormally high. There was no statistically significant ( $p = 0.05$ ) difference between the current survey measurements and the recent-past historical estimates compiled by the Chinese industrial hygienists.

The range of silica concentrations measured in bulk dust samples is presented in Table VI. In four mines, the upper range of quartz concentrations from the TMU-analyzed dusts was higher than that observed in the NIOSH analysis. To examine this potential discrepancy, the residues from

TABLE VI. Comparison of Silica Content Measured by NIOSH and TMU

Mine	Silica Content (%) <sup>*</sup>	
	NIOSH Method 7500 (bulk)	Chinese Phosphoric Acid Method
31 Iron	<1.5–2.6	2.8–5.1
32 Iron	<1.5–6.8	1.5–21.5
33 Copper	<1.5	3.6–4.6
34 Copper	3.5–8.9	18.1–30
35 Copper	4.2–14	9.9–25.4
36 Copper	<1.5–4.2	1.8–19.9

<sup>\*</sup>Three samples per mine.

the pyrophosphoric acid digestion step from several samples were examined microscopically and with X-ray diffraction and fluorescence. Residues from Mine 32 samples appeared microscopically as angular white crystals, characteristic of quartz. Elemental analysis revealed the presence of silicon, calcium, iron, aluminum, potassium, titanium, sulfur, and zinc. Residues from Mine 36 samples appeared beige to brownish-mauve with both white and brown particles. Elemental analysis revealed the presence of silicon, iron, calcium, phosphorus, potassium, titanium, and zinc. These results indicate that the digestion step in the Chinese procedure did not dissolve all interfering minerals. The final analysis was gravimetric, with the assumption that the residue was 100% crystalline silica, resulting in a positive bias. Interference by other silicates and materials resistant to dissolution has been previously described.<sup>6,15,16</sup> Factors that may affect the dissolution include the duration of heating with pyrophosphoric acid and the original particle size of the material being tested. The current TMU measurements are compared to historical silica measurements in Table VII. The range of silica concentrations reported historically overlapped those measured during the current survey using the Chinese methods, except for Mines 33 and 34. The historical data from Mine 33 exceeded the current survey's measurements but Mine 34 was lower than the current Chinese measurements. The range of NIOSH bulk silica analyses was consistently lower than both current and historical Chinese measurements.

The final objective for the survey was to catalog worker exposures to other carcinogenic agents that might be

present. Table VIII summarizes the findings for the metals — arsenic, nickel, and cadmium — as well as for radon and gamma radiation. Based on the observed total dust level and assuming uniform distribution of metals in the airborne mine dust, no excessive exposures would be expected for arsenic, nickel, and cadmium. Taking the average dust level as 2 mg/m<sup>3</sup> and the highest observed nickel content at 240 µg/g, an airborne concentration of 0.48 µg/m<sup>3</sup> nickel would be predicted. This was below the 15 µg/m<sup>3</sup> recommended exposure limit proposed by NIOSH.<sup>17</sup> The same type of calculation indicates that arsenic would be below its NIOSH recommended exposure limit of 2 µg/m<sup>3</sup>. Cadmium was not detected in any of the samples from these mines. Since these metals are carcinogens, NIOSH recommends that arsenic, nickel, and cadmium exposures be controlled to their lowest feasible limit.<sup>17</sup>

Radon progeny were measured at a number of points in each mine studied. The sampling protocol did not allow for long-term follow-up of each site, and no attempt was made to project personal exposures from our measurements. Historical data on radon exposures was virtually nonexistent in the Chinese mines. Therefore, considering the mobility of miners over a career and the changing physical configuration of a mine, detection of high radon progeny levels at any point in the mine demonstrates potential historical exposure for that mine. Relatively high radon levels were observed throughout Mine 36. The lowest observed level at this mine, 0.3 WL, was at the U.S. permissible exposure limit and was above the NIOSH recommended exposure limit of 0.083 WL.<sup>18</sup> For Mine 33, the observed levels were generally low, but one observation at 47.6 WL in a dead-end entry demonstrates a significant potential exposure risk. The other mines exhibit exposure levels that vary below 0.1 WL.

There are no exposure standards to use as a guide for assessing potential risk from exposure to PNAs. The observed PNA exposures are described in Table IX. Although the method reports analytical results for each compound, the data presented here display the sum of the mass concentrations for each PNA species measured as well as a listing of the majority species. The PNA species that were measured are listed in Table X along with their respective limit of detection (LOD) and limit of quantitation (LOQ). Since

TABLE VII. Comparison of Historical Data to Current Average Silica Concentration in Percentages

Mine	Station (no.)	≤ 1985 <sup>A</sup>	1986–1988	Current
31 Iron	Face workers (2)	8	9	5.1
	Loading, hauling (1)	8	9	4.7
	Transportation (3)	8	9	2.8
32 Iron	Face workers (1)	8.5	3	5.8
	Loading, hauling (2)	8.5	3	1.5
	Transportation (3)	10	15	21.5
33 Copper	Face workers (1)	11.5	N/A	3.6
	Loading, hauling (2)	11.5	N/A	3.9
	Transportation (3)	11.5	N/A	4.6
34 Copper	Face workers (1)	9	10	18.1
	Loading, hauling (2)	9	10	24.3
	Transportation (3)	9	10	30.1
35 Copper	Face workers (1,2)	15	5	17.7 <sup>B</sup>
	Transportation (3)	15	5	9.9
36 Copper	Face workers (1)	12.5	19	19.9
	Loading, hauling (2)	11.5	12	12.5
	Transportation (3)	2	2	1.8

<sup>A</sup>Mine 31: reported in 1983

Mine 32: 9% in 1971, 8% in 1974, and 9% in 1983

Mine 33: 7% in 1971; 16% in 1974

Mine 34: reported in 1965

Mine 35: reported in 1980

Mine 36: reported in 1965

<sup>B</sup>Station 1 and 2 values averaged; others were single-sample values.

TABLE VIII. Environmental Concentrations for Various Agents<sup>A</sup>

Mine	As, µg/g	Ni, µg/g	Cd, µg/g	Radon W.L.	Gamma Radiation, mR/hr
31 Iron	<2–30	38–120	<1	0.01	0.02–0.03
32 Iron	<20	14–240	<1	0.07	N/A
33 Copper	<2	13–26	<1	0.02–47.6 <sup>B</sup>	0.02–2.0
34 Copper	3–8	3–14	<1	0.02	0.02–0.4
35 Copper	<2–13	5–10	<1	0.04	0.03–0.04
36 Copper	<20	5–79	<1	0.3–2.2	0.02–0.1

<sup>A</sup>Three samples per mine each for As, Ni, Cd. Six to ten spot samples per mine for radon and gamma radiation.

<sup>B</sup>Collected in an unventilated dead-end entry. Next highest value in this mine was 0.16 W.L.

**TABLE IX. Exposures to Polynuclear Aromatic Hydrocarbons (PNAs)\***

Mine	PNA, $\mu\text{g}/\text{m}^3$	Majority Species
31 Iron	3–12	Naphthalene
32 Iron	10–40	Naphthalene, Acenaphthene
33 Copper	7–29	Naphthalene
34 Copper	4–195	Benzo(a)pyrene, Benzo(e)pyrene, Benzo(b)fluoranthene
35 Copper	113–532	Naphthalene, Dibenz(a,h)Anthracene, Benzo(a)pyrene, Benzo(e)pyrene
36 Copper	10–12	Benz(a)anthracene

\*Three samples per mine for PNAs.

the samples were collected over a 6- to 8-hour period with a sampling rate of 2.0 L/min, total sample volumes were approximately 800 liters (0.8  $\text{m}^3$ ). Therefore, a LOD of 0.5  $\mu\text{g}/\text{sample}$  translates to a sampling limit of detection of 0.6  $\mu\text{g}/\text{m}^3$ . The reported results from these analyses were totaled for each sample, reporting a single value for total PNAs in  $\mu\text{g}/\text{m}^3$ .

Each of the bulk samples returned to the NIOSH laboratory was examined with polarized light microscopy for the presence of asbestos.<sup>49</sup> None of the samples contained material with a fibrous morphology. During the field surveys, work areas were examined for the installation of asbestos materials, but no such installations were reported.

## Discussion

The evaluation of historical occupational exposures and the determination of known and suspected carcinogens was crucial in assessing the lung cancer risk in epidemiology studies of this cohort.<sup>20,21</sup> Even though lung cancer and silicosis may be the result of exposures in the distant past, current exposure measurements were important to corroborate historical data and to calibrate those data which were collected from different mines, employing different mining methods and using different measurement techniques. Thus the historical data became more generalizable and their reliability was improved.

Our findings showed that past estimates of total dust concentrations were not significantly different from current measurements. There was no statistically significant difference between the two immediate-past sampling periods and the current sampling effort. The discrepancy observed between NIOSH and TMU quartz analysis from the current survey was not evident between current Chinese measurements and the historical measurements. Analysis of the acid-digestion residues from the current TMU quartz analysis revealed the presence of nonsilica materials, explaining the positive bias observed in the measurement. In this set of mines, past exposure to silica estimates based on historical silica concentration data will have a positive bias. Since the bias was introduced by the

**TABLE X. Analytes Quantified for Polynuclear Aromatic Hydrocarbons**

Analyte	LOD <sup>A</sup> ( $\mu\text{g}/\text{sample}$ )	LOQ <sup>B</sup> ( $\mu\text{g}/\text{sample}$ )
Naphthalene	0.5	1.5
Acenaphthylene	0.5	1.5
Acenaphthene	0.5	1.5
Fluorene	0.5	1.5
Phenanthrene	0.5	1.5
Anthracene	0.5	1.5
Fluoranthene	0.5	1.5
Pyrene	0.5	1.5
Benzo(a)anthracene	0.5	1.5
Chrysene	0.5	1.5
Benzo(b)fluoranthene	0.9	2.6
Benzo(k)fluoranthene	0.5	—
Benzo(e)pyrene	0.5	—
Benzo(a)pyrene	0.8	2.2
Indeno(1,2,3-cd)pyrene	0.5	—
Dibenz(a,h)anthracene	0.5	—
Benzo(ghi)perylene	0.5	—

<sup>A</sup>LOD: limit of detection

<sup>B</sup>LOQ: limit of quantitation

presence of interfering minerals during analysis, and because their presence cannot be predicted, it was not possible to quantify the extent of this effect.

Particle size measurements made with a small personal cassette impactor were used to predict the respirable mass from total dust measurements. The respirable mass predicted with this technique was correlated with the respirable dust levels measured directly with cyclone and filter samplers. By using the respirable fractions measured with the cassette impactors and applying them to historical dust measurements, estimates of past respirable dust exposures were used to develop an exposure matrix for the epidemiological analyses.

The short-term total dust measurements made according to the Chinese sampling system were about 38% higher than their corresponding NIOSH full-shift time-weighted average sample. Some of this difference was undoubtedly due to differences in the sampling characteristics of the equipment. However, the major difference probably was that the Chinese sampler was preferentially run during active working periods. The industrial hygienist started the sampling period while work was actively in progress. Over the duration of a shift, however, there were numerous times when no dust-generating activity was in progress. This systematically reduced the measured average exposures of a full-shift sampler.

Measured and predicted exposures to the trace metals arsenic, nickel, and cadmium were below U.S. permissible exposure limits, and most were below detectable levels. Asbestos was not found on any of the site surveys. Only exposure to radon presented a significant confounding exposure problem. In two of the copper mines the range of observed radon concentrations exceeded current U.S. permissible exposure limits by as much as a factor of 150. No detailed historical record was available for radon exposures in these mines. Based on current observations of elevated radon exposure levels, we conclude that there was a

potential for significant past exposures to radon at these sites. Further epidemiological assessment of workers at these mines must consider the radon exposures to be a potential confounder for lung cancer.

## Conclusion

The environmental study of several Chinese iron and copper mines was undertaken to examine the consistency of available historical records, to compare Chinese sampling methods and strategies to those employed by NIOSH, and to document exposures to potential carcinogens in the workplace. Although a systematic 38% positive bias was observed in dust exposures measured using the Chinese methods, overall the linear model relating those measurements accounted for 77% of the variability in the relationship. In several of the mines studied, a potential positive bias was observed in the estimates of silica concentration, because of nonsilica minerals that interfered with the Chinese analytical method. Since the magnitude of the interference cannot be inferred from the available data, the current X-ray diffraction measurements should be preferred as the basis for estimating silica exposures in this cohort. Based on the availability of total dust measurements made at these sites since the mid-1950s using a consistent sampling procedure, the workers at these mines can be included in studies of chronic dust-related diseases. The only serious confounding issue that must be considered for cancer mortality studies using this cohort relates to the potential for excess radon exposure where there was a paucity of historical data.

## Acknowledgments

The authors extend their thanks to Mr. Jerry Clere, who coordinated the preparation and shipment of samplers to the People's Republic of China; to Donald Dollberg, Barry Belinky, and DataChem Laboratories Inc. for coordination of sample analysis on the U.S. side; to Rochelle Althouse for statistical guidance; to Dr. Gu Naigu for translation of the Chinese dust sampling regulations; to Dr. Yuan and Director Lü in Huangshi; to Dr. Chen Rongan, who worked tirelessly at Tongji Medical University; and to the leaders and miners in the Wuhan Iron and Steel company who participated in our surveys. This study was funded by the National Cancer Institute in cooperation with the National Institute for Occupational Safety and Health and the Tongji Medical University.

## References

1. National Institute for Occupational Safety and Health: Criteria for a Recommended Standard—Occupational Exposure to Crystalline Silica. DHEW (NIOSH) Pub. No. 75-120, NIOSH, Cincinnati, OH (1974).
2. McDonald, J.C.: Editorial: Silica, Silicosis, and Lung Cancer. *Br. J. Ind. Med.* 46:289–291 (1989).
3. Goldsmith, D.F.; Guidotti, T.L.; Johnston, D.R.: Does Occupational Exposure to Silica Cause Lung Cancer? *Am. J. Ind. Med.* 3:423–440 (1982).
4. International Agency for Research on Cancer: IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol. 42, Silica and Some Silicates. IARC, Lyon, France (1987).
5. Ministry of Public Health: The National Standard of the People's Republic of China—Methods for Airborne Dust Measurement in the Workplace. Ministry of Public Health Standard GB 5748-85, Beijing, People's Republic of China (May 1, 1986).
6. Talvitie, N.A.: Determination of Free Silica: Gravimetric and Spectrophotometric Procedures Applicable to Air-borne and Settled Dust. *Am. Ind. Hyg. Assoc. J.* 25:169–178 (1964).
7. National Institute for Occupational Safety and Health: Method 7500, Silica, Crystalline. In: NIOSH Manual of Analytical Methods, 3rd ed. P. Eller, Ed. DHHS (NIOSH) Pub. No. 84-100. NIOSH, Cincinnati, OH (1984).
8. National Institute for Occupational Safety and Health: Method 0600, Nuisance Dust, Respirable. In: NIOSH Manual of Analytical Methods, 3rd ed. P. Eller, Ed. DHHS (NIOSH) Pub. No. 84-100. NIOSH, Cincinnati, OH (1984).
9. Jones, W.G.; Jankovic, J.; Baron, P.: Design, Construction and Evaluation of a Multi-Stage "Cassette" Impactor. *Am. Ind. Hyg. Assoc. J.* 44(6):409–418 (1983).
10. Marple, V.A.: Impactor Calculator. Sierra Instruments, Inc. P.O. Box 909, Carmel Valley, CA 93924 (1978).
11. National Institute for Occupational Safety and Health: Method 5515, Polynuclear Aromatic Hydrocarbons. In: NIOSH Manual of Analytical Methods, 3rd ed. P. Eller, Ed. DHHS (NIOSH) Pub. No. 84-100. NIOSH, Cincinnati, OH (1985).
12. National Institute for Occupational Safety and Health: Method 7300, Elements (ICP). In: NIOSH Manual of Analytical Methods, 3rd ed. P. Eller, Ed. DHHS (NIOSH) Pub. No. 84-100. NIOSH, Cincinnati, OH (1984).
13. Kusnetz, H.L.: Radon Daughters in Mine Atmospheres—A Field Method for Determining Concentrations. *Am. Ind. Hyg. Assoc. Q.* 17:85–88 (1956).
14. Cocalis, J.; Sandy, E.J.: The Relationship Between Particle Size Distribution, Free Silica Exposure, and Tasks Common to a Longwall Mining Operation. Coal Mine Dust Conference Proceedings. S.S. Peng, Ed. College of Mineral and Energy Resources, West Virginia University, Morgantown, WV (October 8–10, 1984).
15. Talvitie, N.A.: Determination of Quartz in Presence of Silicates Using Phosphoric Acid. *Anal. Chem.* 23(4):623–626 (1951).
16. Talvitie, N.A.; Hyslop, F.: Colorimetric Determination of Siliceous Atmospheric Contaminants. *Am. Ind. Hyg. Assoc. J.* 19:54–58 (1958).
17. National Institute for Occupational Safety and Health: Pocket Guide to Chemical Hazards. DHHS (NIOSH) Pub. No. 90-117. NIOSH, Cincinnati, OH (1990).
18. National Institute for Occupational Safety and Health: Radon Progeny in Underground Mines. DHHS (NIOSH) Pub. No. 88-101. NIOSH, Cincinnati, OH (1987).
19. National Institute for Occupational Safety and Health: Method 9002, Asbestos (bulk). In: NIOSH Manual of Analytical Methods, 3rd ed. P. Eller, Ed. DHHS (NIOSH) Pub. No. 84-100. NIOSH, Cincinnati, OH (1984).
20. Chen, J.Q.; McLaughlin, J.K.; Zhang, J.Y.; et al.: Mortality among Dust-Exposed Chinese Mine and Pottery Workers. *J. Occup. Med.* 34(3):311–316 (1992).
21. McLaughlin, J.K.; Chen, J.Q.; Dosemeci, M.; et al.: A Nested Case-Control Study of Lung Cancer among Silica Exposed Workers in China. *Br. J. Ind. Med.* 49:167–171 (1992).