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Airborne Respirable Silica near a Sand and Gravel Facility in Central California: XRD and Elemental Analysis To Distinguish Source and Background Quartz

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Despite the potential toxicity of respirable quartz to humans, little is known about the transport of airborne quartz from sources to receptors and how to distinguish anthropogenically generated quartz from natural background in a receptor sample. Airborne quartz emissions near a sand and gravel facility were determined using PM₁₀ and PM_{2.5} filter samples collected at four downwind sites (D1: 22 m, D2: 62 m, D3: 259 m, and D4: 745 m from the facility) as well as one upwind site (U1: 1495 m) during summer sampling. X-ray diffraction was used to determine quartz concentration and elemental composition was analyzed using PIXE, XRF, PESA, and HIPS techniques. Elemental composition of the PM samples was used to determine the X-ray mass absorption coefficients that are essential for accurate quartz quantification by XRD. Elemental composition was found to be a useful tool to distinguish source and background crystalline silica. Both PM₁₀ and PM_{2.5} samples collected at the D1, D2, and D3 sites contained more Si, Al, and Fe and less H, Na, and S, compared to those at the U1 site, whereas site D4 sample compositions were similar to those at the U1 site. A composite variable, SOIL/(H+Na+S), where SOIL = 2.20Al + 2.49Si + 1.63Ca + 1.94Ti + 2.42Fe, was used to distinguish source materials from background. Average dry season quartz concentrations in replicate PM₁₀ samples were 4.6 (± 0.9) μg m⁻³ at U1, 60.6 (± 5.4) μg m⁻³ at D1, 62.4 (± 3.6) at D2, 32.6 (± 2.1) μg m⁻³ at D3, and 9.4 (± 0.9) μg m⁻³ at D4. The mass fraction of quartz was the highest at the D1 site and decreased with increasing distance from the facility. The mass of PM_{2.5} samples was too low to determine quartz concentrations. These results identify the facility as the main source of quartz and other silicate minerals downwind of the plant and that the air quality of the most remote sampling site, located ~750 m downwind, was still impacted by the facility's activity.

Introduction

Two crystalline silica (CS) polymorphs, quartz and cristobalite, were classified as "carcinogens to humans" by the

International Agency for Research on Cancer (IARC) in 1997 (1). In California, stationary sources are required to submit estimates of crystalline silica emissions for emission inventory purposes. In 1999, California's stationary sources were estimated to emit over 10³ tons of crystalline silica, and 21 facilities emitted more than 9.1 ton/y with 4 estimates of more than 45 ton/y (2). These sources include cotton gins, rock quarries, construction sites, mines, sand and gravel operations, and fiberglass, asphalt, and paint manufacturers. These sources are located statewide, often in close proximity to sensitive receptors and yet little is known about the transport and fate of the fine particulate fraction of CS emitted from these sources. Crystalline silica is currently not listed as a toxic air contaminant in California due to the lack of field studies on airborne CS concentrations that will enable regulators to determine personal exposure levels. The present study provides initial data to begin these assessments.

The CS emissions from stationary sources are of human health concern if they comprise significant portions of the ambient PM_{2.5} and PM₁₀ concentrations. Currently, there is no quantitative data available on the size distribution and concentration of CS in inhalable particulate matter downwind of CS sources in California, despite the reported high CS mass emission rates and the documented adverse health effects of crystalline silica. One reason for the lack of information is the difficulty of collecting and analyzing CS in particulate matter (PM) samples because the required X-ray diffraction (XRD) analysis techniques are time-consuming and require significant sample mass for quantitative analysis.

Several previous field studies reported PM concentrations downwind of stone crushing quarries across the United States but concluded that there was no significant difference between upwind and downwind PM_{2.5} mass concentrations due to the stone crushing operations (3–6). However, the PM mass concentrations reported in these studies were based on averages of 24-hour samples collected over 30-day periods, regardless of wind direction; and, in one study, the PM_{2.5} samplers were located over 300 m from plant structures (6). In the one case where downwind concentrations exceeded upwind concentrations, the net downwind-upwind mass difference was attributed to diesel exhaust PM, not mineral particulate matter (4). In these studies, only one filter sample for PM₁₀ was submitted for XRD analysis of crystalline silica and the determined concentration was 2.8 μg m⁻³ (5). There was insufficient PM_{2.5} mass collected for XRD analysis in the stone quarry studies.

Maximum airborne quartz concentrations measured in ambient monitoring locations ranged from nondetect to 1.9 μg m⁻³ for PM_{2.5} and 0.9 to 8.0 μg m⁻³ for PM₁₅ in 22 U.S. cities (7) and from 0.6 to 1.5 μg m⁻³ for PM₁₀ in Rome, Italy (8). Quartz content in airborne particulate samples collected in an industrial area of Utah ranged from 9.6 to 16.1 wt % for high-volume filter samples and 10.4 to 21.7 wt % for low-volume filter samples (9). Personal exposure to crystalline silica was measured for different types of California agricultural operations and the weight fraction of quartz in dust ranged 0–10.6% (average: 7.4%) for inhalable dust samples (<100 μm) and 4.8–23.0% (average: 18.6%) for respirable dust samples (PM₄) (10). Combined with data on dust mass concentration, the average quartz mass concentration was estimated to be 365 μg m⁻³ for inhalable dust and 97 μg m⁻³ for respirable dust (10).

The present study was conducted to satisfy two objectives: (1) to provide preliminary data for exposure assessment at sensitive receptors located near crystalline silica stationary sources in California and (2) to develop analytical techniques

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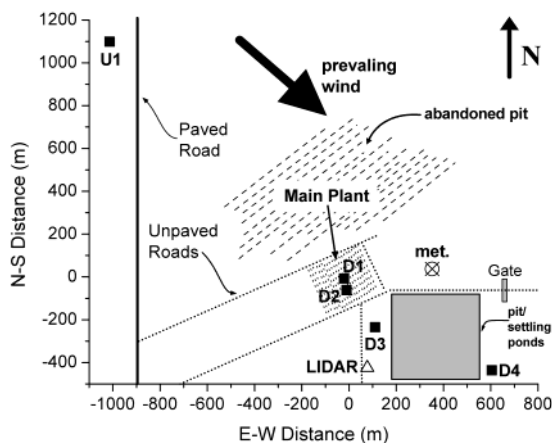


FIGURE 1. Relative locations of the sampling sites at the sand and gravel plant. Note that the X and Y axis scales are different. The origin of the coordinate system (0, 0) was the pile of road base product material near site D1 that was sampled for soil analysis and PM₁₀ resuspension. X–Y coordinates of each sampling site and the meteorological tower were U1 (–1013.4, 1099.2), D1 (–20.7, –7.5), D2 (–10.2, –61.5), D3 (110.5, –234.5), D4 (604.7, –436), and meteorological tower (351.8, 37.4). The shaded area around site D1 encompasses the Main Plant where conveyor/separating/crushing equipment and product piles were located.

to distinguish source and background crystalline silica contributions so exposure is not overestimated. Field sampling upwind and downwind of a sand and gravel plant in central California provides preliminary data on near-source crystalline silica concentrations. X-ray diffraction (XRD) was used to quantify quartz concentration in filter samples. Elemental composition of the PM samples was used to determine the X-ray mass absorption coefficients that are essential for accurate quartz quantification by XRD, and elemental composite signatures were examined as tools to distinguish source and background crystalline silica.

Experimental Methods

Sampling. Field PM measurements were made at one location upwind (U1) and four locations downwind (D1, D2, D3, and D4) of sand and gravel processing operations in Tracy, California (Figure 1). PM₁₀ and PM_{2.5} were collected on 25 mm stretched Teflon filters (3 μm Teflo, Gelman R2P1025) using Interagency Monitoring of Protected Visual Environments (IMPROVE) aerosol samplers (11, 12).

The PM samplers at the five locations were sampled in eight separate test periods between June 13 and June 21, 2000. The sampling height was 3 m from the ground at all locations. Meteorological data was collected (1 min averages) at the site using a 10-m tower (“met.”, Figure 1) located > 100 m away from any obstructions and outfitted with instruments for temperature and wind speed at four heights (1, 2, 4, and 7.5 m), wind direction (4 m), relative humidity (4 m), and solar radiation (4 m). Laboratory PM₁₀ samples were collected by resuspending sieved (<75 μm) bulk soil collected at the downwind D1 site using a dust resuspension chamber (13).

Elemental Analysis. Prior to elemental analysis, gravimetric mass of all Teflon filters was determined by pre- and post-weighing using a Cahn electrobalance with 1 μg sensitivity. After the post-weighing, elemental carbon (soot) concentration was determined using the light absorption hybrid integrating plate and sphere (HIPS) technique (14, 15). Then, the filters were analyzed for the elements heavier than iron by X-ray fluorescence (XRF). Finally, the filters were analyzed using Proton Induced X-ray Emission (PIXE) for elements with atomic numbers from sodium through iron

and simultaneously analyzed for hydrogen using Proton Elastic Scattering Analysis (PESA). PIXE and PESA analyses were performed using the 150 cm isochronous cyclotron at Crocker Nuclear Laboratory, University of California, Davis. The energy of the proton beam was 4.5 MeV, and the filters were irradiated with a 30 nA average beam current for 100 sec. The detection system was accurately calibrated with thin-film standards. Details of the PIXE and PESA analyses are described elsewhere (16, 17).

The average mass fraction of all detectable major and minor elements (H, C, Na, Al, Si, S, Cl, K, Ca, Ti, Mn, and Fe) of both the PM₁₀ and PM_{2.5} samples, X_i (X_i = mass of i th element/raw gravimetric mass of PM on filter), was calculated using the PIXE, PESA, HIPS, and gravimetric results. The mass fraction of oxygen was calculated as the difference between the theoretical total mass fraction (unity) and the sum of mass fractions of all elements measured (i.e., from H to Fe).

X-ray Diffraction. The PM₁₀ samples of three sampling periods (6/16/00, 6/20/00 am, and 6/20/00 pm) were chosen for XRD analysis of quartz concentration. In addition to the field samples, resuspended PM₁₀ in soil collected near site D1 was analyzed by XRD. XRD analyses of two PM_{2.5} samples indicated that sample mass was too low for reliable quantitative analyses.

After elemental analysis was complete, the PM samples were transferred from the Teflon filters onto silver membrane filters (Osmonics, 0.45 μm, #1145341). Each Teflon filter was sonicated for 10 min in 2–3 mL of 2-propanol in a small beaker. After removing the Teflon filter from the beaker, an aliquot of the suspension was placed onto a preweighed silver membrane filter using a micropipet. The suspension was carefully dropped within an area of 10 mm × 10 mm on the silver filter; this area corresponds to the size of the X-ray beam at $2\theta = 26.6^\circ$ (2θ position for quartz primary peak). After drying overnight, the silver membrane was weighed to determine the loaded sample mass. Due to missing data, the mass of PM₁₀ transferred to the silver membrane for the U1 site collected on 6/16/00 had to be estimated. The minimum mass transferred from the Teflon to the silver membrane filter for the 14 other samples (i.e., 36% of total PM₁₀) was assumed. Because of this assumed sample mass, the quartz concentration of this sample is reported as a maximum value.

The respirable quartz standard (alpha-quartz, NIOSH standard Q-1) was prepared from an aqueous suspension. After suspension preparation, an aliquot of the suspension was dropped onto double-sided adhesive copper-tape (Cu-tape) and dried with gentle heating. The standard was also deposited onto silver membrane filters to examine the substrate effect on the intensity of the quartz primary peak. Specimens using Cu-tape substrates were initially prepared for the quantification of impactor samples; results not reported in this paper. However, no significant difference in intensity of the quartz primary peak was observed for standard specimens prepared on the two substrates.

The mass fraction of quartz, X_{qtz} , was determined based on the following relation (18)

$$I_{qtz} = \left(\frac{1}{\mu_t^*} \right) \left(\frac{K_{qtz}}{\rho_{qtz}} \right) (X_{qtz} M_s) \quad (1)$$

where I_{qtz} is the total intensity of X-rays diffracted by a quartz plane [counts], μ_t^* is the total mass absorption coefficient of the sample mixture [$\text{cm}^2 \text{g}^{-1}$], K_{qtz} is a constant [$\text{counts cm}^{-1} \text{g}^{-1}$] that depends on the crystallographic nature of a diffraction plane and the geometry of the diffraction apparatus, ρ_{qtz} is the density of quartz [g cm^{-3}], and M_s is the mass of the sample [g]. First, using resuspended PM₁₀, it was confirmed that a linear relationship between I_{qtz} and M_s existed up to $M_s = 479 \mu\text{g}$ (5 mass concentrations, $r^2 = 0.996$).

All standard and sample measurements were performed within this range. Then, for the pure quartz standard, the $K_{\text{qtz}}/\rho_{\text{qtz}}$ ratio was determined to be $22.8 (\pm 0.3) \times 10^6$ (counts $\text{cm}^{-1} \text{g}^{-2}$) from the I_{qtz} vs M_s plot (4 mass concentrations, $r^2 = 0.998$) and assuming a value of $34.4 (\text{cm}^2 \text{g}^{-1})$ for μ_t^* (18) (Note that $X_{\text{qtz}} = 1$ for pure quartz). The mass fraction of quartz in the filter samples was determined using eq 1 with the values for $K_{\text{qtz}}/\rho_{\text{qtz}}$ and μ_t^* calculated from the sample's elemental composition. The value of μ_t^* for each filter sample was calculated using the equation

$$\mu_t^* = \sum \mu_i X_i \quad (2)$$

where μ_i and X_i are the mass absorption coefficient and the mass fraction of constituent elements, respectively. The elements included in the calculation were H, C, O, Na, Al, Si, S, Cl, K, Ca, Ti, Mn, and Fe. Values of mass absorption coefficients adopted for each element were 0.435 for H, 4.60 for C, 11.5 for O, 30.1 for Na, 48.6 for Al, 60.6 for Si, 89.1 for S, 106 for Cl, 143 for K, 162 for Ca, 208 for Ti, 285 for Mn, and 308 for Fe (18). The mass fraction of quartz in the site D1 resuspended PM_{10} sample was determined by the internal reference method (18–21) using TiO_2 as the internal reference material.

A Rigaku Miniflex diffractometer with an X-ray beam area of $10 \text{ mm} \times 10 \text{ mm}$ at $2\theta = 26.6^\circ$ was used for quantitative measurement of the PM_{10} filter samples. In all quantitative measurements, the quartz primary diffraction peak was measured using a 0.01° step scan (30 s/step) from $2\theta = 26.0^\circ$ to 27.5° at 30 kV and 10 mA. Under these measurement conditions, each reported Cu-tape measurement was an average of scans collected at four different sample orientations that were perpendicular to each other. For the analysis of the samples on silver membrane filters, two sample orientations were averaged because some samples showed much less sensitivity to sample orientation. The peak intensity was determined as the area above a baseline drawn by the JADE software (JADE Inc., Livermore, CA) (baseline was trimmed manually when necessary). A DIANO model XRD8000 was used for the internal reference measurement of the resuspended PM_{10} and for wide range scans of filter samples. DIANO operating conditions were 40 kV and 20 mA. For all XRD measurements, Cu $K\alpha$ radiation was the X-ray source.

Results and Discussion

PM Mass Concentrations. The daily wind direction, wind speed, relative humidity, and temperature during the eight separate test periods between June 13 and June 21, 2000 were relatively uniform, with the exception of about 80% higher mean relative humidity on the morning of June 20 compared to the other seven sampling periods. The range of mean meteorological values over the sampling test periods were as follows: wind direction, N–NW; wind speed, 2.6 – 4.2 m s^{-1} ; relative humidity, 20.4–40.5%; temperature 27.0 – 33.2°C . Average meteorological data for each sampling period can be found in the Supporting Information.

Statistics of PM_{10} and $\text{PM}_{2.5}$ sample mass concentrations (Table 1) show that PM_{10} concentrations ranged from ~ 26 to $1026 \mu\text{g m}^{-3}$ over all sample test periods, and $\text{PM}_{2.5}$ was not detected gravimetrically for 22 of the 39 samples after subtracting field blanks. The average ratio of $\text{PM}_{2.5}$ to PM_{10} was about 8% ($\pm 18\%$) for all of the samples collected. The mean upwind mass concentrations were $35.2 (\pm 7.6)$ and $1.6 (\pm 4.5) \mu\text{g m}^{-3}$ for PM_{10} and $\text{PM}_{2.5}$, respectively. Downwind average concentrations were $191 (\pm 181)$ and $16.9 (\pm 20.6) \mu\text{g m}^{-3}$ for PM_{10} and $\text{PM}_{2.5}$, respectively. The highest measured concentrations occurred at the second downwind location, D2, 62 m downwind of the source.

TABLE 1. Mass Concentration Statistics for Teflon Filter Samples by Sampling Location^a

site		duration (h)	$\text{PM}_{2.5}$ mass ($\mu\text{g m}^{-3}$)	PM_{10} mass ($\mu\text{g m}^{-3}$)	$\text{PM}_{2.5}/\text{PM}_{10}$ ratio (%)
U1 ($n = 8$)	min	2.7	<D.L.	26.5	0.0
	max	11.5	12.8	45.2	30.4
	avg	7.2	1.6	35.2	3.8
	SD	2.8	4.5	7.6	10.7
	med	7.2	0.0	33.2	0.0
D1 ($n = 7$)	min	2.7	<D.L.	170.7	0.0
	max	9.2	53.9	324.7	22.4
	avg	5.7	24.0	230.0	9.8
	SD	2.4	21.6	51.2	8.2
	med	4.5	23.4	240.9	9.7
D2 ($n = 8$)	min	2.8	<D.L.	140.5	0.0
	max	8.8	61.1	1026.3	17.0
	avg	5.8	31.4	340.1	10.8
	SD	2.2	18.8	294.3	5.7
	med	5.4	32.9	206.1	12.6
D3 ($n = 8$)	min	2.7	<D.L.	75.8	0.0
	max	9.6	18.0	226.7	10.6
	avg	6.0	3.8	132.2	2.3
	SD	2.4	7.3	45.6	4.3
	med	5.7	0.0	121.0	0.0
D4 ($n = 8$)	min	2.7	<D.L.	33.0	0.0
	max	9.2	61.7	104.6	109.2
	avg	5.8	9.3	66.4	15.5
	SD	2.2	21.6	25.3	38.2
	med	5.4	0.0	60.6	0.0

^a n , number of samples; D.L., detection limit ($\text{PM}_{2.5}$ mass detection limit ranged from 7.6 to $32.1 \mu\text{g m}^{-3}$ depending on sampling site and duration). For calculation of average, standard deviation (SD), and median (med), values below detection limit were counted as 0. Raw PM data and detection limits can be found in the Supporting Information.

Elemental and Mineral Composition. Table 2 lists the average elemental compositions (in wt %) of the PM_{10} and $\text{PM}_{2.5}$ samples. The concentrations of Mg and P were below detection and C was below 0.01 wt % for all samples. The PM_{10} samples at the three nearest downwind sites (D1, D2, and D3) had similar average elemental compositions and these average compositions were significantly different from samples collected at sites U1 and D4. Samples D1–D3 had higher Si, Al, and Fe contents and smaller S, Na, and H contents than the U1 and D4 samples (Table 2). For $\text{PM}_{2.5}$, similar elemental signatures to that of PM_{10} were observed. However, at each sampling site, the average mass fraction of Si and Al in $\text{PM}_{2.5}$ was smaller than that in PM_{10} , and the average mass fraction of S, H, and O in $\text{PM}_{2.5}$ was larger than that in PM_{10} .

The wide-range XRD scans ($2\theta = 2$ to 35°) of upwind and downwind PM_{10} samples collected at the U1 and D1 sites on 6/16/00 (Figure 2) show that both samples contained quartz, feldspar (plagioclase), kaolinite, mica (probably biotite), a 15-angstrom 2:1 clay mineral (smectite or vermiculite), and gibbsite. However, the relative intensities of the quartz (101), feldspar (101), and kaolinite (001) peaks to that of the 15-angstrom 2:1 clay mineral (001) were significantly larger in the site D1 sample than in the site U1 sample. Note that peak ratios were compared because different sample masses prevent comparison of the U1 and D1 samples directly. The mineral ratios suggest that the site D1 sample contained more quartz [SiO_2], feldspar [$(\text{Na},\text{K})\text{AlSi}_3\text{O}_8$ – $\text{CaAl}_2\text{Si}_2\text{O}_8$], and kaolinite [$\text{AlSi}_2\text{O}_5(\text{OH})_4$] than the site U1 sample. The U1 sample, on the other hand, was relatively enriched in the 15-angstrom 2:1 clay mineral [smectite and vermiculite compositions are $(\text{Na},\text{Ca}_{0.5})_{0.7}(\text{Al},\text{Mg},\text{Fe})_4(\text{Si},\text{Al})_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ and $(\text{Mg},\text{Ca})_{0.7}(\text{Al},\text{Mg},\text{Fe})_6(\text{Si},\text{Al})_8\text{O}_{20}(\text{OH})_4 \cdot 8\text{H}_2\text{O}$, respectively (22)]. Thus, the differences in mineralogy measured by X-ray diffraction agree qualitatively with the average elemental compositional differences reported for site D1 and

TABLE 2. Average Elemental Composition (in wt %, 95% Confidence Limits) of Teflon Filter Samples for Eight Sampling Periods^a

	U1	D1	D2	D3	D4
	(n = 8)	(n = 6)	PM ₁₀ (n = 7)	(n = 8)	(n = 8)
H	2.3 ± 0.2	1.1 ± 0.2	1.1 ± 0.1	1.4 ± 0.2	1.9 ± 0.4
Na	1.2 ± 1.1	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.39 ± 0.92
Al	5.1 ± 0.7	8.2 ± 2.1	10.1 ± 2.1	9.1 ± 1.6	7.6 ± 1.5
Si	14.4 ± 1.8	23.5 ± 5.7	27.3 ± 4.9	24.5 ± 3.4	17.2 ± 3.9
S	1.1 ± 0.4	0.15 ± 0.08	0.13 ± 0.05	0.28 ± 0.12	0.78 ± 0.30
Cl	0.08 ± 0.09	0.09 ± 0.06	0.12 ± 0.06	0.12 ± 0.04	0.11 ± 0.06
K	1.3 ± 0.2	1.5 ± 0.3	1.8 ± 0.2	1.7 ± 0.2	1.4 ± 0.3
Ca	2.7 ± 0.7	1.9 ± 0.4	2.4 ± 0.4	2.8 ± 0.5	2.4 ± 0.5
Ti	0.30 ± 0.03	0.29 ± 0.06	0.37 ± 0.05	0.35 ± 0.02	0.30 ± 0.02
Mn	0.07 ± 0.02	0.09 ± 0.02	0.11 ± 0.03	0.11 ± 0.01	0.08 ± 0.02
Fe	3.5 ± 0.3	4.1 ± 0.8	4.8 ± 0.7	4.7 ± 0.4	3.7 ± 0.6
O (calc)	68.2 ± 2.7	59.0 ± 9.2	51.8 ± 8.2	54.9 ± 5.7	64.1 ± 6.4
total	100.0	100.0	100.0	100.0	100.0
SOIL	60.5 ± 4.9	90.2 ± 14.9	106.3 ± 13.1	97.6 ± 9.3	73.1 ± 10.4
OMH	22.0 ± 2.3	12.2 ± 1.8	12.0 ± 1.0	14.2 ± 1.8	18.7 ± 4.1
	(n = 8)	(n = 7)	PM _{2.5} (n = 8)	(n = 8)	(n = 8)
H	3.3 ± 0.5	2.1 ± 0.6	1.9 ± 0.4	2.7 ± 0.5	3.0 ± 0.8
Na	1.6 ± 1.1	0.00 ± 0.00	0.00 ± 0.00	0.82 ± 1.07	1.5 ± 1.0
Al	1.3 ± 0.6	4.9 ± 0.7	5.6 ± 1.0	4.0 ± 1.1	3.0 ± 1.2
Si	4.4 ± 1.1	16.7 ± 3.7	15.1 ± 2.5	11.4 ± 2.8	7.8 ± 3.0
S	3.3 ± 0.9	1.1 ± 0.5	1.0 ± 0.4	1.8 ± 0.5	2.7 ± 0.9
Cl	0.00 ± 0.00	0.01 ± 0.02	0.00 ± 0.01	0.00 ± 0.00	0.00 ± 0.00
K	1.0 ± 0.2	1.7 ± 0.4	1.7 ± 0.3	1.5 ± 0.3	1.2 ± 0.4
Ca	1.2 ± 0.4	1.6 ± 0.2	2.0 ± 0.3	2.1 ± 0.7	1.5 ± 0.5
Ti	0.13 ± 0.02	0.24 ± 0.04	0.26 ± 0.05	0.24 ± 0.05	0.17 ± 0.06
Mn	0.05 ± 0.02	0.11 ± 0.03	0.10 ± 0.03	0.11 ± 0.02	0.08 ± 0.04
Fe	1.5 ± 0.3	4.0 ± 0.6	4.3 ± 0.6	3.5 ± 0.7	2.6 ± 0.9
O (calc)	82.2 ± 2.0	67.5 ± 6.0	68.1 ± 4.9	71.7 ± 4.3	76.5 ± 6.8
total	100.0	100.0	100.0	100.0	100.0
SOIL	19.8 ± 3.2	65.2 ± 9.5	64.1 ± 6.8	49.5 ± 7.6	35.0 ± 12.3
OMH	27.1 ± 6.1	20.0 ± 7.0	18.3 ± 4.5	25.2 ± 5.1	25.6 ± 14.2

^a SOIL and OMH are composite variables (see text).

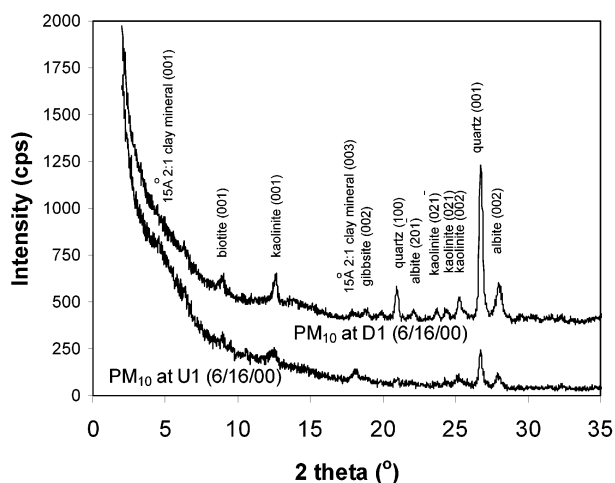


FIGURE 2. X-ray diffraction patterns of PM₁₀ samples collected at sites U1 and D1 on June 16, 2000.

U1 samples (Table 2). Based on the average elemental composition, the site D4 PM₁₀ X-ray diffraction pattern should more closely resemble the U1 pattern than the D1 pattern. Similarly, the site D2 and D3 PM₁₀ mineralogy are expected to be similar to that measured for site D1.

The elemental composition data (Table 2) suggested that some elemental composite-variable ratios could be useful to distinguish background PM composition (i.e., measured at U1) from the source-derived PM detected in the near-downwind sites (D1 to D3). Several composite variables (23, 24) were examined. The ratios showing the largest difference

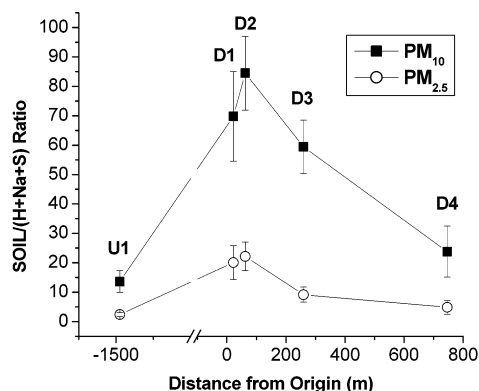
between these two sample subsets were SOIL/OMH, (Si+Al)/OMH, SOIL/(H+Na+S), and (Si+Al)/(H+Na+S). The composite variable SOIL was evaluated as $\text{SOIL} = 2.20\text{Al} + 2.49\text{Si} + 1.63\text{Ca} + 1.94\text{Ti} + 2.42\text{Fe}$, representing the major crustal elements measured in western U.S. ambient aerosol (23). OMH (organic matter by hydrogen) was calculated as the difference between total hydrogen and ammonium sulfate and was given by $\text{OMH} = 11 \times (\text{H} - 0.25\text{S})$ (24). Values of SOIL and OMH are listed in Table 2. Among these ratios, the average SOIL/(H+Na+S) ratio measured over all test periods at each sampling site showed the greatest difference between the near-downwind (D1 to D3) and the "background" site (U1) (Figure 3). The ratio for the D4 site was much smaller than that for the D1-D3 sites; however, it was significantly larger than that for the U1 site. This trend was observed for the other three ratios as well. Therefore, by this measure, particulate matter at site D4 was still affected by the activity of the sand and gravel facility.

Quartz Content in PM₁₀. For all three sampling periods analyzed by XRD, quartz content (mass fraction of quartz) at the D1 site was higher than that at the U1 site (Table 3). Downwind quartz content decreased gradually as a function of distance from the facility for all three sampling periods. This trend was the most distinct for the samples collected on 6/20/00 am. The quartz content in resuspended PM₁₀ from the site D1 soil was 0.163 (± 0.021), which was significantly smaller than that for PM₁₀ collected at the D1 site (Table 3). The higher quartz mass fraction measured in site D1-D3 samples compared to the U1 and D4 samples is consistent with the elemental composition results (Table 2).

The higher quartz mass fraction measured in site D1-D3 samples compared to U1, D4, and resuspended PM₁₀ samples

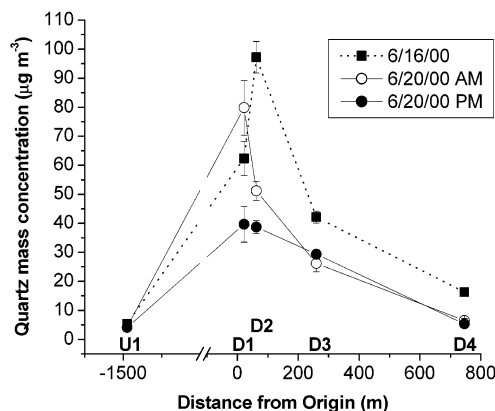
TABLE 3. Mass Fraction of Quartz, X_{qtz} , in PM₁₀ Samples^a

	resuspended PM ₁₀	6/16/00	6/20/00 am	6/20/00 pm
U1		0.161 (± 0.020)	0.100 (± 0.007)	0.151 (± 0.017)
D1	0.163 (± 0.023)	0.257 (± 0.023)	0.330 (± 0.037)	0.232 (± 0.035)
D2		0.210 (± 0.010)	0.244 (± 0.012)	0.201 (± 0.008)
D3		0.186 (± 0.006)	0.167 (± 0.017)	0.201 (± 0.005)
D4		0.171 (± 0.006)	0.100 (± 0.009)	0.162 (± 0.016)

^a Numbers in parentheses denote one standard deviation.FIGURE 3. Average SOIL/(H+Na+S) ratio for PM₁₀ and PM_{2.5} from all sampling locations. Composite variable SOIL was defined by $SOIL = 2.20Al + 2.49Si + 1.63Ca + 1.94Ti + 2.42Fe$. Error bars (propagated errors from measurements in each elemental composition) denote one standard deviation. Note the break in X-axis scale.

strongly suggests that activities at the facility preferentially released mineral particulate, including quartz, into the atmosphere by breaking down larger fragments (i.e., during crushing operations), soil aggregates, and coatings on coarse mineral grains. The laboratory resuspension operation apparently did not result in a similar release of inhalable quartz. In addition, site D1 samples showed the strongest X-ray diffraction dependence on sample orientation, indicating that the D1 sample grains were larger than those found in other samples (25). This observation is consistent with the hypothesis that, for a source that generates particles of a wide range of aerodynamic diameters, larger particles will settle close to the source and smaller particles will be transported farther away. Previous studies using size-fractionated impactor samplers have shown that quartz is consistently detected in the larger size fractions (26–28), but no previous studies have reported downwind transects of size-fractionated quartz.

Airborne quartz PM₁₀ mass concentrations at each sampling site were obtained by multiplying the measured PM₁₀ mass concentration ($\mu\text{g m}^{-3}$) by the quartz mass fraction, X_{qtz} (Figure 4). For the three sampling periods analyzed, the quartz concentrations of the three downwind site samples (D1: 39.7–79.8 $\mu\text{g m}^{-3}$; D2: 38.7–97.2 $\mu\text{g m}^{-3}$; D3: 26.2–42.2 $\mu\text{g m}^{-3}$) were significantly higher than those of the upwind and D4 site samples (U1: 4.1 – <5.4 $\mu\text{g m}^{-3}$, 5.4 was a possible maximum for 6/16/00 (see Methods); D4: 5.4–16.3 $\mu\text{g m}^{-3}$). Quartz concentrations at the D1–D3 sites were also much higher than previously measured at a stone-crushing quarry in North Carolina (5) and in urban locations in the United States and Italy (7, 8). However, these airborne quartz concentrations were of the same order of magnitude as those measured in respirable dust during California agricultural operations (10). It should be noted, however, that the concentrations measured in this study are likely the maximum seasonal values, because sampling was undertaken only during the dry season. Quartz concentrations during

FIGURE 4. Quartz mass concentration in PM₁₀ at each sampling site on 6/16/00, 6/20/00 am, and 6/20/00 pm. Error bars (propagated errors from measurements in quartz mass fraction by XRD and PM₁₀ mass) denote one standard deviation. Note the break in X-axis scale.

the wet season are expected to be lower than those reported here, both due to reduced facility activity and reduced emissions when facility soil piles have higher moisture contents.

It is important to distinguish source CS from background because of the abundance of quartz in the natural environment. For the stationary source sampled during this study, the following factors further support the conclusion that the sand and gravel plant was the major source of the quartz measured in the downwind samples. First, the wind direction was very steady during all sampling tests, and the upwind sampler was therefore a reliable measure of background PM composition. Second, the downwind quartz and PM concentrations were very reproducible at a given sampling location from day-to-day and were significantly higher than the upwind concentrations (Tables 1 and 3). Third, simultaneous lidar aerosol backscatter measurements detected intense plumes that originated at the main plant and dispersed with distance away from the plant (25). The lidar scans routinely detected dust plumes above sampling site D4 (>700 m downwind of main plant) that extended vertically for a distance over 100 m. In addition to quartz concentration, the elemental signature of samples at all the downwind sites (even at the most remote site, D4) was different from that of the background (U1) site. Thus, the effect of the sand and gravel facility on downwind air quality was significant and detectable (at the ground elevation) out to ~750 m from the main facility operations.

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Supporting Information Available

Additional information is provided on the test period meteorological data and individual sample PM and quartz mass concentrations. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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