

Chemical Analysis of World Trade Center Fine Particulate Matter for Use in Toxicologic Assessment

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The catastrophic destruction of the World Trade Center (WTC) on 11 September 2001 caused the release of high levels of airborne pollutants into the local environment. To assess the toxicity of fine particulate matter [particulate matter with a mass median aerodynamic diameter < 2.5 μm ($\text{PM}_{2.5}$)], which may adversely affect the health of workers and residents in the area, we collected fallen dust samples on 12 and 13 September 2001 from sites within a half-mile of Ground Zero. Samples of WTC dust were sieved, aerosolized, and size-separated, and the $\text{PM}_{2.5}$ fraction was isolated on filters. Here we report the chemical and physical properties of $\text{PM}_{2.5}$ derived from these samples and compare them with $\text{PM}_{2.5}$ fractions of three reference materials that range in toxicity from relatively inert to acutely toxic (Mt. St. Helens PM; Washington, DC, ambient air PM; and residual oil fly ash). X-ray diffraction of very coarse sieved WTC PM (< 53 μm) identified calcium sulfate (gypsum) and calcium carbonate (calcite) as major components. Scanning electron microscopy confirmed that calcium-sulfur and calcium-carbon particles were also present in the WTC $\text{PM}_{2.5}$ fraction. Analysis of WTC $\text{PM}_{2.5}$ using X-ray fluorescence, neutron activation analysis, and inductively coupled plasma spectrometry showed high levels of calcium (range, 22–33%) and sulfur (37–43% as sulfate) and much lower levels of transition metals and other elements. Aqueous extracts of WTC $\text{PM}_{2.5}$ were basic (pH range, 8.9–10.0) and had no evidence of significant bacterial contamination. Levels of carbon were relatively low, suggesting that combustion-derived particles did not form a significant fraction of these samples recovered in the immediate aftermath of the destruction of the towers. Because gypsum and calcite are known to cause irritation of the mucus membranes of the eyes and respiratory tract, inhalation of high doses of WTC $\text{PM}_{2.5}$ could potentially cause toxic respiratory effects. **Key words:** carbon analysis, ICP-AES, ICP-MS, inhalation toxicology, neutron activation analysis, scanning electron microscopy, X-ray diffraction, X-ray fluorescence. *Environ Health Perspect* 111:972–980 (2003). doi:10.1289/ehp.5930 available via <http://dx.doi.org/> [Online 20 November 2002]

The attack on the World Trade Center (WTC) in New York City on 11 September 2001, in addition to causing the immediate and tragic loss of thousands of lives, resulted in the release of significant quantities of pollutants into the environment of the surrounding neighborhoods, including particulate matter (PM), asbestos, metals, and organic compounds [U.S. Environmental Protection Agency (U.S. EPA) 2002b]. Dust infiltrated indoors into homes and apartments, in many cases up to several inches in depth. Fires at the WTC site continued for several months before finally being extinguished, and recovery and reconstruction efforts contributed to emissions of fine [particulate matter with a mass median aerodynamic diameter (MMAD) < 2.5 μm ; $\text{PM}_{2.5}$], coarse (> 2.5 and < 10 μm ; $\text{PM}_{2.5-10}$), and larger (> 10 μm) PM fractions. As people have returned to their residences and businesses, potential exposure issues are associated with redispersal of residual dust.

Recent studies have assessed the chemical and physical properties of bulk samples of WTC PM. The dust particles from the WTC site appear to be quite alkaline in nature,

probably because of partial dissolution of concrete, gypsum, and glass fiber particles [U.S. Geological Survey (USGS) 2002]. Liou and co-workers (2002) found that bulk settled-dust samples of WTC PM were composed of particles of cement, carbon, cellulose, and several fiber types including mineral wool, fiberglass, cellulose, and asbestos. These authors also found significant concentrations of phthalate esters, polycyclic aromatic hydrocarbons (PAHs), and other hydrocarbons (Offenberg et al. 2003). However, a detailed analysis of the $\text{PM}_{2.5}$ fraction of WTC dust has not been previously reported.

Exposure to ambient air PM has been associated with both acute and chronic adverse health effects, especially in sensitive populations (Dockery et al. 1993). Both fine- and coarse particles are readily inhaled into the human respiratory tract. Reviews of current literature suggest that fine particles are more strongly implicated in cardiovascular effects than coarse particles, while both impact respiratory end points (U.S. EPA 2002c). Fine particles are typically formed from gases or from combustion processes, whereas coarse

particles are produced by mechanical breakdown of crustal material. However, the $\text{PM}_{2.5}$ size range may also include a significant fraction of coarse particles that are broken down into smaller particles by strong mechanical forces (U.S. EPA 2002d). The unique situation of the WTC disaster may have generated a significant amount of crustal (building) material-derived particles in the $\text{PM}_{2.5}$ size range. Although $\text{PM}_{2.5-10}$ may have adverse health effects, quantities of WTC PM samples in this size range were limited (see “Size fractionation of bulk samples” in “Materials and Methods”). In addition, $\text{PM}_{2.5}$ is very relevant toxicologically, as it is associated with epidemiologic findings of adverse health effects in humans (Dockery et al. 1993). Consequently, our objective in this article was to describe the collection, size fractionation, and chemical analysis of samples of WTC $\text{PM}_{2.5}$ for use in toxicologic studies. To determine whether respirable WTC $\text{PM}_{2.5}$ is more or less toxic than typical ambient air $\text{PM}_{2.5}$, we compared the toxicity of WTC $\text{PM}_{2.5}$ with well-characterized reference $\text{PM}_{2.5}$ samples in a companion article (Gavett et al. 2003).

In this study we collected samples of settled dust from several sites in the immediate vicinity (< 0.5 miles) of Ground Zero on 12 and 13 September 2001. Samples were separated into fine, coarse, and larger fractions that could be studied for toxicologic effects. We thoroughly characterized the WTC $\text{PM}_{2.5}$ samples using a number of chemical and physical techniques to compare

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the composition of these samples with other well-studied PM_{2.5} reference samples. Solid samples of WTC and reference PM_{2.5} were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence (XRF), carbon fraction analysis, and neutron activation analysis (NAA). Analyses were also carried out on water-extracted or 1 M hydrochloric acid–extracted suspensions of WTC and reference PM_{2.5}, including pH, endotoxin, and inductively coupled plasma–mass spectrometry (ICP-MS) and inductively coupled plasma–atomic emission spectrometry (ICP-AES). The analytical results will contribute to the understanding of the composition and possible mechanisms of toxicity of PM_{2.5} derived from the destruction of the WTC.

Detailed experimental findings of these studies are available in a U.S. EPA report (2002a).

Materials and Methods

Collection of World Trade Center PM samples. Using a paper scoop, we sampled several outdoor locations as well as one indoor location, all of which appeared undisturbed since the collapse of the towers, as judged by the presence of a smooth uniform layer of dust and the absence of indicators of recent human activity. All samples were collected within a half-mile of Ground Zero and labeled with

numbers (1–13) on 12 September 2001, and letters (A–F) on 13 September 2001. After examination of the available inventory of samples, we selected seven locations (8, 11, 13, B, C, E, and F) to assess toxicity of samples from different geographical locations as well as overall toxicity of a pooled sample from these locations (Figure 1). The locations were selected to represent a distribution surrounding Ground Zero, with more collection sites in the east reflecting the direction of the predominant winds during the collapse of the WTC towers and surrounding buildings.

Size fractionation of bulk samples. Bulk samples of the seven dust samples described above were sieved with a 53- μ m diameter mesh screen (USA Standard Testing Sieves; Fisher Scientific, Pittsburgh, PA) on a shaker (Portable Sieve Shaker; Tyler Industrial Products, Mentor, OH). We processed the sieved material (PM₅₃) in an apparatus designed to isolate different PM fractions (Figure 2). The PM₅₃ fraction was aerosolized through a 10- μ m aerodynamic diameter cut Wedding inlet (Anderson Instrument Co., Fultonville, NY) to remove particles in the 10–53 μ m range and isolate the PM₁₀ fraction. The PM₁₀ fraction was then passed through a 2.5- μ m cut cyclone (BGI, Inc., Waltham, MA) to remove the coarse fraction. The PM_{2.5} fraction was collected on Teflon filters (Zefluor Supported PTFE, 2- μ m pore size, 47-mm

diameter; Pall Gelman Sciences, Port Washington, NY). Ten to 40 filters were used in the size fractionation of each WTC sample. Roughly half the sample was in the PM₅₃-sieved fraction. About 80–89% of the PM₅₃ fraction was in the 10- to 53- μ m size range, which is too large to use in respiratory toxicology studies, as deposition of particles > 5 μ m is minimal in small laboratory animals (Raabe et al. 1988). The amount of the 2.5- to 10- μ m fraction was very small (0.04–1.14% of the PM₅₃ fraction, except 3.23% in sample 13) and was therefore not feasible to study. The PM_{2.5} fraction, however, was present in sufficient amounts (2.29–4.06% of PM₅₃ fraction) to study for potential respiratory health effects. The sum of the size fraction percentages does not total 100% of the original PM₅₃ fraction because of sample loss during fractionation. After overnight desiccation, filter weights were determined using an electrobalance (Model C-30; Thermo Cahn, Madison, WI). A total quantity of about 50 mg from each site, collected on 1–3 filters per site, was used in the study (Table 1). Mechanical scraping did not efficiently remove the PM_{2.5} from the filters, so it was necessary to isolate the PM_{2.5} using an aqueous extraction procedure.

Extraction of PM_{2.5} from Teflon filters. Filters containing the PM_{2.5} fraction were extracted using a modification of a method by Biran and co-workers (1996). Filters from each of the seven individual collection sites were extracted into distilled water (Gibco Invitrogen, Carlsbad, CA) in the ratio of 0.5 mL/mg sample (24.96–27.14 mL water).

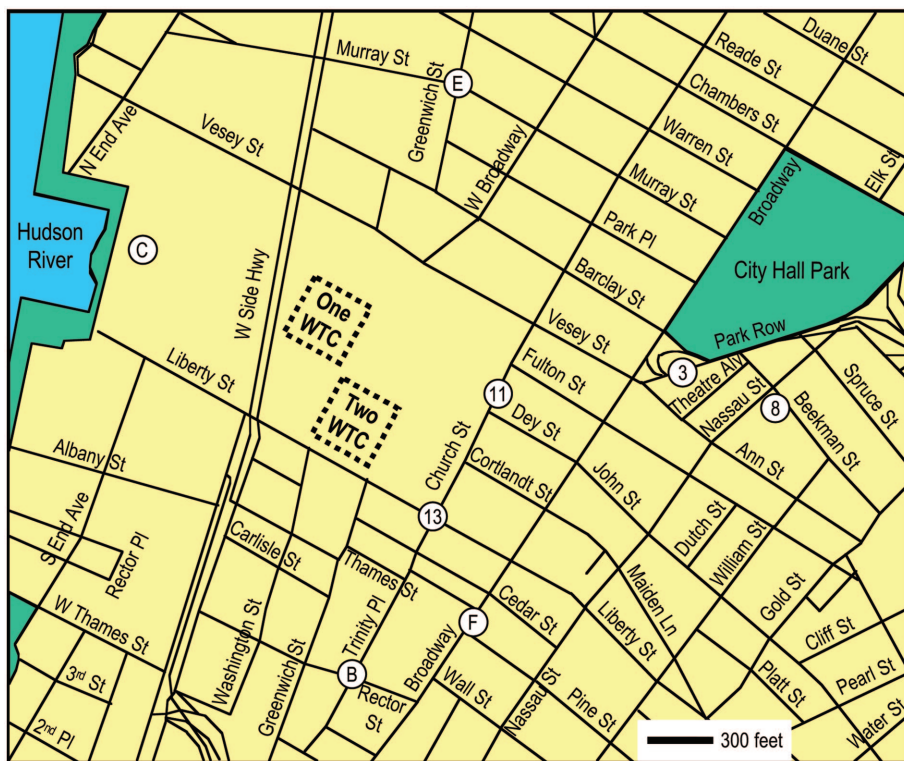


Figure 1. WTC dust samples were collected by New York University scientists from 13 sites on 12 September 2001 (numbers) and from 6 sites on 13 September 2001 (letters). Collection sites are shown only for samples reported in this article. Map reference: U.S. Census Bureau (2002).

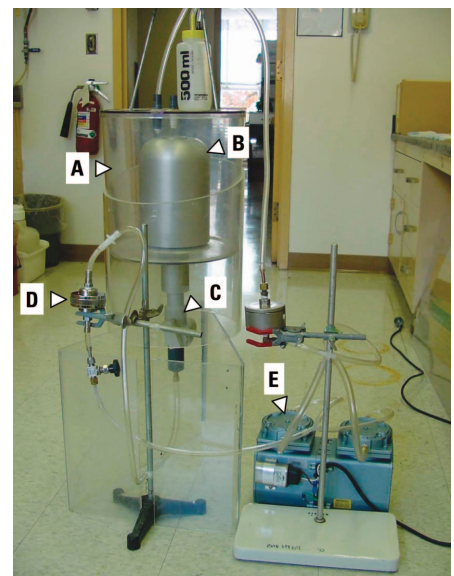


Figure 2. Apparatus used to separate bulk samples of WTC PM into different size fractions. Sieved WTC dust (PM₅₃) was aerosolized in the resuspension chamber (A), then passed through a 10- μ m cut inlet (B) and a 2.5- μ m cut cyclone (C). PM_{2.5} were collected on Teflon filters (D) and pulled through by a pump (E).

This volume of water was pipetted into a 100-mL sterile plastic cup containing a 3 mm-thick Teflon ring on the bottom designed to support the filter. Each filter was wetted with 200 μ L 70% ethanol on the particle side, placed on top of the ring with the particle side down, and a 6 mm-thick Teflon ring was placed on top of the filter. The cup with the filter was placed on ice and secured to an orbital shaker (Titer Plate Shaker; Lab-Line Instruments, Melrose Park, IL). Samples were shaken at a low speed and sonicated for 30 min at a power setting of 30 (Sonic 300 Dismembrator; Artek Systems Corp., Farmingdale, NY). Ten milliliters was pipetted from each of the seven samples into a single sterilized 150-mL Erlenmeyer flask on ice to make a pooled sample (WTCX). The pH of the pooled and individual site samples was determined immediately after extraction (Model 440; Corning Incorporated, Corning, NY). Sonicated filters were desiccated before reweighing to determine quantity extracted (i.e., removed) from the filters (Table 1). Pooled and individual site samples were frozen at -80°C and lyophilized for 2 days at -55°C and 140 mtorr (Virtis Company, Gardiner, NY). Lyophilized samples were stored at 4°C and subsequently brought to room temperature

for chemical or physical analysis, or for use in toxicologic studies in mice (Gavett et al. 2002).

Sample used for inhalation exposure toxicity testing. Because we needed to conduct a nose-only inhalation exposure study to assess upper airway responses of test animals (Gavett et al. 2003), a sufficient quantity of sample was necessary for the exposure system (> 2 g). As there was not enough $\text{PM}_{2.5}$ or $\text{PM}_{2.5-10}$ sample available to conduct this study, we decided to use a PM_{53} sample (sieved but not further fractionated) that was available in sufficient quantity to run through the inhalation exposure system. The inhalation exposure system uses a 2.5- μm cut cyclone to remove larger particles (Ledbetter et al. 1998), and therefore measurement of the PM concentration in the exposure zone of the chamber represents exposure to $\text{PM}_{2.5}$. A sample of PM_{53} from location no. 3 (Figure 1; WTC3 in Table 1), 0.3 miles east of Ground Zero (in the predominant wind direction), was available in sufficient quantities for the nose-only inhalation exposure study.

Control PM samples. To assess the relative toxicity of WTC $\text{PM}_{2.5}$, pooled and individual site samples were compared with three other well-characterized control $\text{PM}_{2.5}$ samples. We chose samples representing an urban ambient

PM with moderate toxicity, a crustal PM with low toxicity, and an emission source PM with high toxicity (Table 1). National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1649a is an urban ambient PM collected in the Washington, DC, area in 1976–1977 over a 12-month period and represents a time-integrated sample (NIST 2001). This material was selected for comparison of toxicity of WTC $\text{PM}_{2.5}$ with other typical urban air $\text{PM}_{2.5}$ (albeit from an earlier era when leaded gasoline was still in use). This material was collected as a total suspended particulate (TSP) sample with a large amount of coarse PM and larger nonrespirable PM. Consequently, SRM 1649a was size-fractionated and extracted using the procedures described above for comparison with the WTC $\text{PM}_{2.5}$ samples.

WTC $\text{PM}_{2.5}$ was also compared with a previously size-separated $\text{PM}_{2.5}$ fraction of ash from Mt. St. Helens (MSH) in Washington State (Graham et al. 1985). About half of MSH is crystalline in nature, primarily plagioclase, a series of compounds beginning with sodium aluminum silicate ($\text{NaAlSi}_3\text{O}_8$) and ending with calcium aluminum silicate ($\text{CaAl}_2\text{Si}_2\text{O}_8$) that show continuous solid solution from albite to anorthite, with CaAl replacing NaSi as the series progresses. The remaining portion is amorphous (glass) and contains minor amounts of cristobalite (3%) and quartz ($< 1\%$). The $\text{PM}_{2.5}$ fraction of MSH has low toxicity in rats and mice (Hatch et al. 1984).

Residual oil fly ash (ROFA) is a PM sample with a high content of bioavailable transition metals including vanadium (V), nickel (Ni), and iron (Fe). Numerous studies have demonstrated that these metals are associated with lung injury in both healthy animals and animal models of cardiopulmonary injury (Dreher et al. 1997; Gavett et al. 1999; Kodavanti et al. 1998). For this study, we chose a sample of ROFA (no. 3; Kodavanti et al. 1998) from a boiler system that is toxic, yet not as soluble in water as previous samples of ROFA, and is therefore more comparable to WTC PM samples, which are not extremely water soluble. ROFA sample no. 3 has an MMAD of 2.665 μm , slightly larger than other $\text{PM}_{2.5}$ samples used in this study but still acceptable for toxicity testing.

Overview of analytical methods. Analytical chemistry of WTC, SRM 1649a, MSH, and ROFA $\text{PM}_{2.5}$ samples entailed measurements of both solid samples and their liquid extracts. Solid (including lyophilized) samples were characterized by SEM/energy dispersive X-ray analysis (SEM/EDX), XRD, NAA, XRF, and carbon fraction analysis of the organic, elemental, and carbonate fractions (OC/EC/CC). Deionized water extracts were characterized by pH, endotoxin, and ion chromatography (IC) analysis. Elemental and sulfate (SO_4) content

Table 1. Description of samples used in study.

Sample code	Collection date	Location, description	Size fraction	Total weight on filters	Extracted weight (mg) % Extracted
WTC site samples					
WTC8	12 Sept. 2001	Beekman St.: filters #9, #14 0.4 miles E of Ground Zero	$\text{PM}_{2.5}$	53.316 mg	46.70 87.6
WTC11	12 Sept. 2001	55 Church St.: filters #13, #14, #15 In front of Millennium Hilton Hotel 0.1 miles E of Ground Zero	$\text{PM}_{2.5}$	50.097 mg	29.79 59.5
WTC13	12 Sept. 2001	Church and Liberty Sts.: filters #4, #5 0.1 miles SE of Ground Zero	$\text{PM}_{2.5}$	51.006 mg	46.29 90.8
WTCB	13 Sept. 2001	Trinity Pl. and Rector St.: filter #4 From a car hood and windshield 0.25 miles S of Ground Zero	$\text{PM}_{2.5}$	52.969 mg	42.31 79.9
WTCC	13 Sept. 2001	Winter Garden Park: filters #4, #7 From a park bench facing the Hudson River 0.2 miles WNW of Ground Zero	$\text{PM}_{2.5}$	54.285 mg	47.67 87.8
WTCE	13 Sept. 2001	Murray and Greenwich Sts.: filters #5, #6 From a window ledge 0.25 miles NNE of Ground Zero	$\text{PM}_{2.5}$	49.919 mg	45.13 90.4
WTCF	13 Sept. 2001	Inside 120 Broadway: filters #2, #12 From a marble staircase with no footprints 0.25 miles SE of Ground Zero	$\text{PM}_{2.5}$	53.600 mg	38.73 72.3
WTC3	12 Sept. 2001	23 Park Row: ground sample in front of J&R Electronics (across City Hall Park) 0.3 miles E of Ground Zero	$\text{PM}_{<53}$	21.521 g sieved material	Not extracted; size-separated during exposure
Control PM samples					
SRM 1649a	1976–1977	SRM 1649a (urban dust collected in Washington, DC)	$\text{PM}_{2.5}$	47.984 mg ^a	39.33 82.0
MSH	1980	Mt. St. Helens ash, Washington State, from Graham et al. (1985)	$\text{PM}_{2.5}$	> 10 g ^a	Previously size- separated
ROFA	1994	Residual oil fly ash, ROFA sample 3 from Kodavanti et al. (1998)	MMAD: 2.665 μm	> 2 g ^a	Milled; not extracted

Abbreviations: E, east; NNE, north-northeast; S, south; SE, southeast; WNW, west-northwest.

^aWeight available.

of deionized water and 1 M HCl extracts were measured using ICP-MS and ICP-AES. The two extraction liquids are used to estimate easily bioavailable and total bioavailable metal content, respectively. Although this speciation scheme is a rough approximation of bioavailability for PM_{2.5} samples of complex multielemental composition, it has proven useful in characterizing inhalation toxicology end points for various source and ambient particulates (Costa and Dreher 1997; Kodavanti et al. 1998).

Sufficient quantities of MSH, ROFA, and pooled WTCX samples were available to perform all analyses. Quantities of the individual site WTC samples and SRM 1649a were very limited (Table 1), and analyses were prioritized to yield the greatest information possible. SEM/EDX testing required < 1 mg and was selected for all samples. NAA was chosen as the next most applicable analysis to provide total elemental composition data to support SEM/EDX. We performed OC/EC/CC, ICP-MS, ICP-AES, and IC analyses on remaining samples where possible. XRD and XRF analyses were performed only on the WTC3 sample.

SEM/EDX analysis. SEM/EDX provided physical and chemical characterization of particles and fibers found in the control samples and lyophilized WTC PM_{2.5} samples, and on PM_{2.5} on polycarbonate filters taken during the inhalation exposure study using the WTC3 sample. SEM/EDX was carried out using a Personal SEM (PSEM) (formerly R.J. Lee Instruments, Ltd., now Aspex Instruments, Trafford, PA) as previously described (U.S. EPA 2002e). For lyophilized WTC or control samples, a small amount was applied to an adhesive carbon tab affixed to an aluminum SEM stub. For filter samples, small pieces (< 1 cm²) were affixed to aluminum SEM stubs using a carbonaceous suspension. Because only 15–30 images were examined from each sample, the results should not be interpreted as quantitative or comprehensive (Mamane et al. 2001). Rather, these qualitative results were used primarily to determine consistency with other analytical techniques described below.

X-Ray diffraction analysis. XRD was used to qualitatively determine the presence of any crystalline compounds in the WTC3 sample used in the inhalation exposure study. The PM₅₃ sample was side-drifted into an aluminum holder and mounted into the Siemens D-500 diffractometer (Bruker Analytical X-Ray Systems, Madison, WI). The generator, set at 45 kilovolts and 40 milliamperes (mA), generated X-rays from a copper-target X-ray tube. The filament current was 3.46 mA. Intensities were collected by a lithium-drifted silicon detector fitted with a monochromator riding on a goniometer in the coupled $\theta/2\theta$ mode, where θ = diffraction angle. Peaks were collected in the range $2\theta = 5$ to 85

degrees. Collection software used was Datascan (version 3.2; Materials Data, Inc., Livermore, CA). Evaluation software was MDI Jade 5 using the pattern library Powder Diffraction File (PDF), release 2000 (International Centre for Diffraction Data, Newtown Square, PA).

Neutron activation analysis. NAA was used to determine the total elemental content of lyophilized WTC and control PM_{2.5} samples (NCSU 2002). Samples of these materials (3–7 mg) were packaged in precleaned polyethylene vials in a clean hood, and irradiated as follows. For aluminum (Al), chlorine (Cl), copper (Cu), magnesium (Mg), manganese (Mn), sodium (Na), titanium (Ti), and V content, samples were irradiated for 30 sec at ≤ 900 kW_{th}, decayed for 10–30 min, and counted for 5 min. For all other elements, samples were irradiated for 6 hr at ≤ 900 kW_{th}. For arsenic (As), potassium (K), molybdenum (Mo), and antimony (Sb) content, samples were decayed for 1 week and counted for 15 min each. For Fe, Ni, barium (Ba), calcium (Ca), chromium (Cr), strontium (Sr), and zinc (Zn) content, samples were decayed for 2 weeks and counted for 30 min each. γ -Ray spectra were counted and compared against calibration and quality control standards, and quantitative analyses were performed.

X-Ray fluorescence analysis. Five polycarbonate filters (Isopore 0.8 μ m, 47-mm diameter, Millipore Corporation, Bedford, MA) loaded with the WTC3 PM_{2.5} sample, with five lot-matched blank filters, were mounted in liquid-type polyethylene sample cups, placed in a stainless steel sample holder, and analyzed. X-ray intensities were collected with the Philips PW2404 XRF (Philips Analytical, Natick, MA) using the Philips proprietary software SuperQ. Net intensities (peak–background) were analyzed using the standardless software UniQuant 4 (Omega Data Systems, Veldhoven, the Netherlands) after subtraction of the intensities due to the blank filter system. The constituents of the dust were evaluated as oxides.

Carbon fraction analysis. Carbon speciation into OC/EC/CC fractions was performed on control and lyophilized WTC PM_{2.5} samples and on quartz filters taken during the inhalation exposure to WTC3 PM_{2.5}. The thermo-optical method, based upon sequential pyrolytic vaporization and detection of the three carbon fractions, was performed (Sunset Laboratory, Forest Grove, OR) as previously described (Birch and Cary 1996; Sunset 2002).

Endotoxin analysis. One-milliliter aliquots of filter extracts from each individual site sample were analyzed for endotoxin content using the limulus amoebocyte lysate gel-clot method (Associates of Cape Cod, Inc., Falmouth, MA). Samples were titered using a 2-fold dilution scheme against control standard endotoxin [CSE; lot no. 85, *Escherichia coli* O113,

5 endotoxin units (EU)/ng]. Preliminary inhibition tests (positive product controls) were performed on the undiluted samples spiked with CSE equivalent to twice the sensitivity (λ ; 0.03 EU/mL). The error of the gel-clot method is \pm one 2-fold dilution.

ICP-MS and ICP-AES. Control PM_{2.5} samples, lyophilized WTC PM_{2.5} samples, and polycarbonate filters taken during the inhalation exposure to WTC3 PM_{2.5} were extracted with deionized water or 1 M HCl and analyzed for their elemental content. Samples (4–6 mg) were extracted with 1.6 mL of either liquid. Polycarbonate filters containing 2–3 mg WTC3 PM_{2.5} were extracted with 13 mL of either liquid. High-speed centrifugation was used to separate the liquid and solids (17,000 $\times g$ for 1.6-mL samples; 51,000 $\times g$ for 13-mL samples). After dilution, extraction solutions were analyzed quantitatively using ICP-MS (ELAN 6000; PerkinElmer Instruments, Shelton, CT) and ICP-AES (Model P40; PerkinElmer Instruments) as previously described (U.S. EPA 2002f, 2002g, respectively). Filter blanks levels for all elements were negligible compared with the levels in the PM samples.

Ion chromatography of deionized water extracts. Deionized water extracts from the ICP sample prep as described above were analyzed quantitatively for anion and cation content using IC (ManTech Environmental, Research Triangle Park, NC). A DX-500 ion chromatograph (Dionex, Sunnyvale, CA) was used with an AS14 column (Dionex) for anion analysis in Suppressor-ASRS Ultra-AutoSuppressor Recycle mode, with 3.5 mM Na₂CO₃/1.0 mM NaHCO₃ eluent. A CS12 column (Dionex) was used for cation analysis in Suppressor-CSRS II Ultra-AutoSuppressor Recycle mode, with 20 mM methanesulfonic acid eluent.

Results

Analytical chemistry of solid samples.

SEM/EDX analysis. Water-extracted and lyophilized WTC PM_{2.5} samples were dominated by large snowflake-like crystals composed of Ca, sulfur (S), and oxygen (O) (Figure 3A). Aggregates of fine particles composed of various combinations of Ca, Mg, Al, S, O, and silicon (Si) were also prominent (Figure 3B). Fibers approximately 1 μ m in diameter were found in most of the samples and had a composition similar to the fine particle aggregates (Figure 3C). Metallic particles [mostly Ti and Fe, although Zn, lead (Pb), Ba, and Cu were also found] were found typically as inclusions in the large aggregates of fine particles (Figure 3D).

SEM/EDX analysis of the aerosolized PM_{2.5} fraction of WTC3 (not water extracted) showed the same overall chemistry as the extracted and lyophilized WTC PM samples;

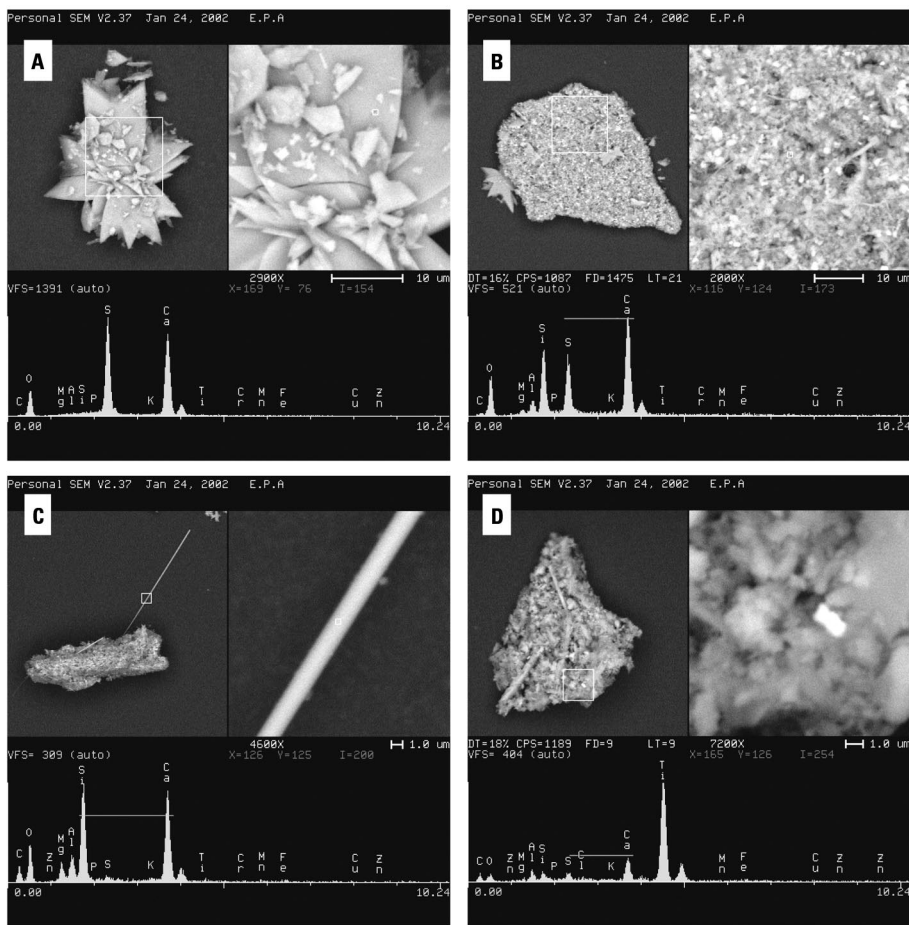


Figure 3. SEM/EDX results from water-extracted lyophilized WTCX PM sample. The upper-left quadrant of each photomicrograph shows a field of view with the particle of interest within the smaller square in that field. The upper-right quadrant shows a zoomed-in view of the feature (the area from within the square in the upper-left quadrant), and the lower half shows the elemental spectrum acquired with the electron beam centered on the small (barely visible) square in the zoomed-in view. (A) Example of crystal with Ca, S, and O, which dominated the samples. (B) Example of fine particle aggregate that was prominent in the samples. (C) Example of fiber found in the samples. (D) Example of metallic particle (Ti) within fine particle aggregate.

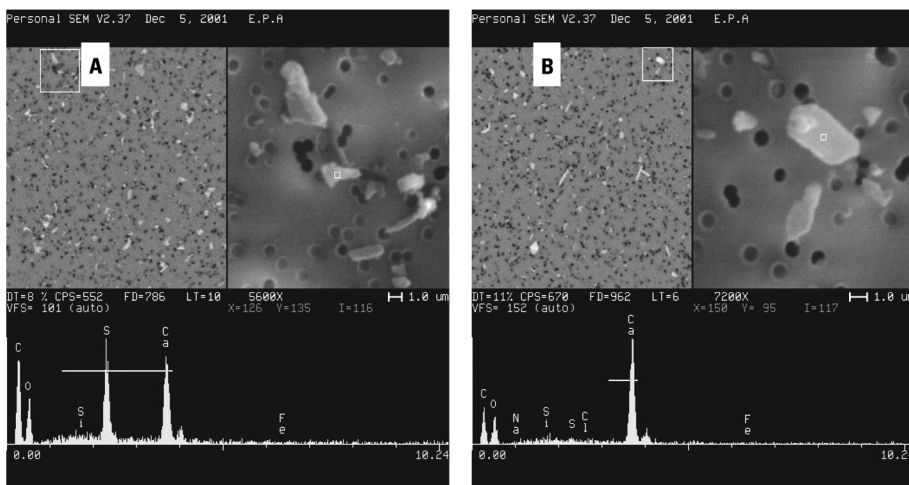


Figure 4. SEM/EDX results showing predominant particle types found in aerodynamically size-separated WTC3 PM_{2.5} sample used in nose-only inhalation exposure study (Gavett et al. 2003). (A) Example of particle containing Ca, S, O, and carbon. (B) Example of particle containing Ca, O, and carbon without significant levels of S.

the majority of particles were composed of Ca, carbon, and O with S (Figure 4A) [or without significant levels of S (Figure 4B)] and some also contained Si. In contrast to the crystals and aggregates of the lyophilized samples described above and shown in Figure 3, the WTC3 particles were small, typically about 1 μm , with rough, irregular features. The different physical form of the Ca-based particles in WTC3 reflects the dry size segregation of the inhalation exposure system. These results suggest that the large crystals and aggregates observed in the lyophilized samples were not originally present in the PM_{2.5} Teflon filters but were formed during the aqueous extraction and lyophilization process.

Particles with other compositions were found with far less frequency. These included particles composed of Fe, carbon, and Sb–Zn (one example found). One or more possible asbestos fibers (Mg–Si composition) were also found; however, polarized light microscopy rather than SEM/EDX is the preferred method for identifying asbestos in bulk materials. SEM/EDX analysis performed on MSH, SRM 1649a PM_{2.5}, and ROFA showed results typically found in previous analyses of these materials (data not shown).

X-Ray diffraction analysis. XRD analysis of WTC3 PM₅₃ (before size segregation by the inhalation exposure system) showed a complex pattern containing 25 peaks, indicating the presence of several crystalline materials. The peak area above the background curve was 50.6%. The 49.4% below the curve indicated that WTC3 PM₅₃ consisted of about half amorphous materials. Four patterns were identified as being consistent with peaks identified in the dust. Figure 5 shows the XRD spectra of WTC3 PM₅₃ and those of the matched compounds. Two compounds were identified as major constituents [calcium sulfate dihydrate (gypsum) and calcium carbonate (calcite)], and two were identified as minor constituents [basanite (calcium sulfate hemihydrate) and quartz (silicon dioxide); Table 2]. The predominance of Ca-based compounds by XRD supports the major findings of the SEM/EDX analysis of WTC PM_{2.5}—the WTC PM materials are composed predominantly of Ca compounds, some of which are water soluble. The sample of MSH was also analyzed by XRD, and the results were consistent with those previously reported (Graham et al. 1985; data not shown).

Total elemental analysis by neutron activation analysis and X-ray fluorescence analysis. Both NAA and XRF analyses showed that there were large amounts (range 22–33%) of Ca in the WTC PM_{2.5} samples (Table 3). XRF analysis showed 37.5% S as SO₄ in the WTC3 PM_{2.5} sample. Together, Ca and SO₄ account for 64% of the WTC3 PM_{2.5} sample, in good agreement with the SEM/EDX and XRD analyses. For all other elements, NAA and XRF

results for the various WTC PM_{2.5} samples show good agreement. This consistency in composition is remarkable, considering the wide area over which the original WTC dust samples were collected (Figure 1). Besides Ca and SO₄, only Si, Al, Mg, and Fe are present in levels approaching or greater than 1% of total mass. The relative weight–percent ratios of Al, Mg, and Fe are in the range of those found in portland cement, a major component of concrete (McKetta 1978). Of the transition and heavy metals and other toxic elements such as Sb and As, only Zn and Ti are present in levels approaching 0.5% of total mass, whereas all others are present at maximum levels of hundreds of micrograms per gram (parts per million). Within the group of seven WTC PM_{2.5} samples analyzed using NAA, WTCE has the highest content of total metals and toxic elements (e.g., Sb and As); combined levels of these elements were about twice those of the other WTC samples. Comparison of the total metal and toxic elemental content of the WTC PM_{2.5} samples with the control dusts shows the overall metal levels as MSH < WTC < SRM 1649a < ROFA.

Carbon fraction analysis. The WTC PM_{2.5} samples had low total carbon content, in the range of 1.5–8.5% (Table 4), in contrast with control samples such as SRM 1649a (26%) and ROFA (16%). MSH had almost no carbon, as expected from this crustal PM sample. The WTC3 PM_{2.5} sample used in the inhalation study had about 4 times as much carbon as the

other two WTC PM_{2.5} samples. This result may be due to differences in the method by which the samples were isolated (physical separation vs. aqueous extraction and lyophilization) or may simply be due to variability in carbon content of samples from different locations. Despite the variation in total carbon content of WTC PM samples, the ratios of the carbon fractions were similar. Carbonate carbon is most likely associated with Ca (as calcite, Table 2) and other alkaline earth metals (e.g., Mg). The level of carbonate carbon is relatively small compared with the overall alkaline earth content, yet levels are high enough to make Ca and/or other alkali earth carbonates the likely source(s) of the high pH values measured (see below). Elemental carbon levels (an indicator of carbon black produced by incomplete combustion during the fires prior to collapse) were low, indicating that the fine fraction of WTC PM_{2.5} was dominated by the presence of pulverized building materials rather than the products of incomplete combustion. Organic carbon levels are relatively high and can be attributed to many sources in the WTC building and to jet fuel (Lioy et al. 2002).

Analytical chemistry of aqueous extracts of samples. pH and endotoxin levels. pH levels of water-extracted WTC PM_{2.5} and control samples are shown in Table 5. The pH of water-extracted WTC PM_{2.5} samples before lyophilization ranged from 8.88 in WTCE to 10.00 in WTC8. The alkaline pH results from the building materials comprising much of the

dust, most likely the alkaline earth (Ca, Mg) compounds. Calcium carbonate, identified by XRD, is a major component of cement (McKetta 1978) and other building materials. It is almost insoluble in water (14 µg/mL), yet a saturated solution produces a pH of 9.4 (Weast 1985). For a 2 mg PM/mL ratio, this requires < 7 µg soluble calcium carbonate/mg PM. Such a level is easily attainable in the WTC samples, given the percent ranges of Ca and carbonate carbon measured by elemental and OC/EC/CC analysis. The pH of lyophilized WTC PM_{2.5} reconstituted in unbuffered saline was very close to neutral (pH 7.36), whereas MSH was only slightly acidic (pH 6.61) and ROFA was moderately acidic (pH 3.74). It is not known why the pH of WTC PM_{2.5} should be close to neutral after reconstitution in saline.

Endotoxin levels in WTC PM_{2.5} samples were minimal compared with other urban PM samples such as SRM 1649a, which was also low (Table 5). Several thousand times this level of endotoxin caused an acute neutrophilic response in the lungs of CD-1 mice (Dhingra et al. 2001). The level of endotoxin in the samples used in this study would not be anticipated to contribute directly to any inflammatory response in the lungs.

Extractable elemental/ion analysis by ICP-MS, ICP-AES, and IC. Elemental and ion compositions were consistent within each sample group tested (Table 6). The ICP-AES data for S were treated as SO₄, as both XRD and XRF showed S was present in this oxidized form. The SO₄ content of the WTC PM_{2.5} samples ranged from 38 to 44% of total weight, and the WTC3 ICP-AES and XRF results (Table 3) were nearly identical. The ICP-AES data showed that water-soluble Ca accounted for 18–19% of WTC PM_{2.5} samples, which was about 8–15% lower than results from XRF and NAA analyses (Table 3). This may reflect an incomplete extraction in the 1-hr time frame, the relatively mild solutions and conditions used in the extraction method, or the presence of other insoluble

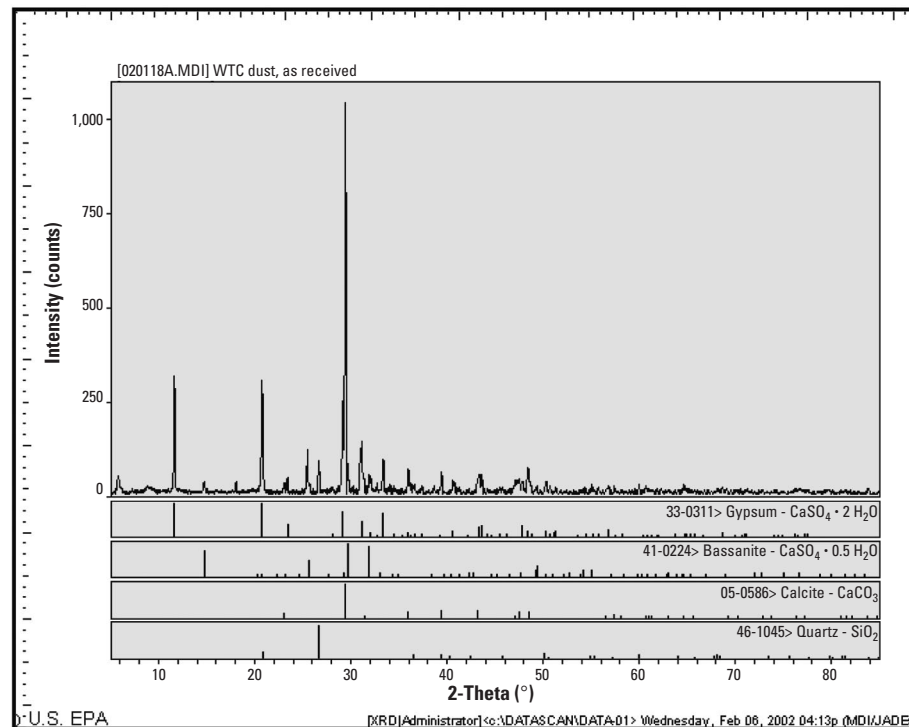


Figure 5. X-Ray diffraction analysis of sieved WTC3 sample (PM₅₃ before aerodynamic size separation). Peaks were collected in the range of 2θ = 5–85°. Collection software used was Datascan (version 3.2; Materials Data, Inc.).

Table 2. XRD analysis of compounds present in WTC3 sample.^a

ICDD no.	Formula	Mineral	Relative amount
05-0586	CaCO ₃	Calcite	Major
33-0311	CaSO ₄ ·2H ₂ O	Gypsum	Major
41-0224	CaSO ₄ ·0.5H ₂ O	Bassanite	Minor
46-1045	SiO ₂	Quartz	Minor

ICDD, International Centre for Diffraction Data.

^aSample was sieved (PM₅₃) but not further size-separated. Analysis showed about half crystalline materials (50.6% above background), and the remainder was amorphous. After smoothing and subtracting background, evaluation software (Jade 5; Materials Data, Inc.) was used to match patterns with library available from the Data Diffraction File (release 2000; International Centre for Diffraction Data). Relative amounts: major is > 20 weight %; minor is > weight % but < 20 weight %.

forms of Ca in the WTC PM_{2.5} samples. ICP data for the 1 M HCl-soluble extracts of WTC PM_{2.5} showed an additional 1–2 weight percent Ca content relative to the water-soluble extracts. The increase may be attributed to calcite or other water-insoluble Ca salts that are soluble in 1 M HCl.

The same ordering of water-soluble element < 1 M HCl-soluble element < total element content held for all other analytes. Total content measured by NAA/XRF and acid-soluble content measured by ICP agreed within 25% for elements such as Mg and Zn, which exist in compounds more amenable to acid dissolution (Budavari 1996; Weast 1985). Elements such as Al, Fe, and Ti, which are in the form of complex oxides usually in combination with Si, are much less soluble under the acid extraction conditions used in this study and do not agree as well (Budavari 1996; Weast 1985). Water-extractive contents were < 10% of the total content values for nearly all transition and heavy metals. Acid-extractive contents were almost all < 50% of the total content values.

Comparison of the water-soluble transition and heavy metal levels of the WTC samples with the control dusts used in this study shows the overall metal content trend as MSH < WTC < SRM 1649a < ROFA. ROFA has high levels of water-soluble transition metals, including V, Ni, and Fe, which are important in its toxicity (Kodavanti et al. 1998). The 1 M HCl-soluble metal content trend is MSH < WTC < ROFA (not enough

SRM 1649a PM_{2.5} sample was available to run this test). Extractable elemental content of the WTC samples more closely resembled the crustal MSH sample than the urban ambient SRM 1649a PM_{2.5} sample.

Discussion

We collected samples of fallen dust at various locations in the immediate vicinity of the WTC site 1 and 2 days after the WTC disaster and analyzed the PM_{2.5} fraction, using several physical and chemical techniques. The XRD analysis showed that the sieved WTC PM_{5.3} sample consists primarily of Ca-based compounds, specifically calcium sulfate (gypsum) and calcium carbonate (calcite; the main component of limestone). The NAA, XRF, and ICP analyses strongly suggest that these compounds are present in the PM_{2.5} fraction as well. Ca and SO₄ compose about two-thirds of WTC PM_{2.5} on a weight percent basis. Taken together, the total elemental analysis data account for 79% of the weight of the WTC3 PM_{2.5} sample and indicate that the main components are construction materials such as cement, concrete aggregate, ceiling tiles, and

wallboard. The remaining mass fraction is most likely due to moisture content and to O, hydrogen, and nitrogen associated with both the organic and inorganic constituents.

The content of transition and heavy metals and other toxic trace elements in WTC PM_{2.5} samples is low compared with that of combustion-derived ROFA, as expected from crustal-derived building materials. Levels of elements that could be attributed to metal wiring (Cu), plumbing (Fe, Cu, Pb), structural steel (Fe, Mn), and communication and computer equipment (Cu, Fe, Zn, others) are also low. This may be attributed to the relatively small proportion of metal-containing building contents compared with the building itself, or perhaps these materials resisted crumbling and pulverization into the PM_{2.5} fraction. Elemental analysis of water and acid extracts of WTC PM_{2.5} provides speciation information on chemical constituents that are potentially bioavailable after inhalation, or which can be easily released into the environment from rain and washing of streets and buildings. The extractable amounts of metals and toxic elements are low compared with

Table 4. Carbon fraction analysis of PM_{2.5} samples.^a

Carbon fraction	Sample					
	WTC3	WTCX (pooled)	WTCB	MSH	ROFA	SRM 1649a
OC	6.88	0.93	2.11	0.06	1.31	10.82
EC	0.31	0.00	0.01	0.07	13.63	15.10
CC	1.39	0.60	0.35	0.00	1.32	0.00
Total	8.58	1.53	2.47	0.13	16.26	25.92

^aCarbon fractions were analyzed as described in text. Results are expressed as percent of total mass of sample.

Table 3. Analysis of WTC and control PM_{2.5} samples by XRF or NAA (micrograms analyte per gram solid sample).^a

Sample: Method:	WTC8 NAA	WTC11 NAA	WTCB NAA	WTCC NAA	WTCE NAA	WTCF NAA	WTCXb NAA	WTC3c XRF	SRM 1649a NAA	MSH NAA	ROFA NAA
Analyte											
SO ₄ ²⁻								375,300			
Ca	242,000	226,000	333,000	257,000	205,000	243,000	287,000	265,600		29,800	
Si								30,000			
Al	15,400	13,500	7,560	10,600	23,900	16,000	5,810	9,930	37,600	97,200	27,700
Mg	7,040	5,340	2,870	4,540	9,070	5,150	2,900	6,550		6,900	
Fe	8,360	7,360	3,630	4,480	15,100	6,930	2,730	6,290	30,500	29,200	30,900
Cl	1,940	3,580	1,460	1,570	1,710	2,100	3,310	3,330	2,790	1,680	1,030
K					4,660		2,890	2,690	15,300	8,880	
Zn	2,310	1,960	1,380	1,280	5,860	2,020	813	1,760	1,330	56	9,760
Ti	2,630	5,730	1,230	1,820	4,920	2,640	1,130	1,450	3,550	3,060	
PO ₄ ³⁻								779			
Na	2,030	1,700	760	1,250	1,520	2,070	1,250	725	4,420	38,500	32,400
Mn	358	295	136	257	302	340	107		268	770	1,000
Cu		428			560	484			306		
Ba					84.7	344.0	97.0		958	371.0	762
Sb	102	63.0	64.2	59.3	308	81.8	49.3		73.1		681
Mo	48.7	35.7	29.3	19.9	125	36.5	23.8				355
Ni									252		20,500
Cr	178	196	62.3	78.9	225	131	56.4		302	17.9	582
As	3.5	3.6	2.2	2.9	6.1	4.0	2.2		102		82.7
V	65.7	280	29.5	72.0	158	103	38.3		583	75.3	45,400
Sr		826			1,100	506	557		422	646	
Total µg/g	282,466	267,297	352,213	283,030	274,609	281,940	308,764	704,404	98,756	217,157	171,153
% Total mass	28.3	26.7	35.2	28.3	27.5	28.2	30.9	70.4	9.9	21.7	17.1

^aWTC PM_{2.5} samples were extracted and lyophilized. Analytes are arranged in order of decreasing content in WTC3 sample (including liquid extract samples; Table 6) by whatever analysis provided highest content. S and P measured by XRF were oxidized and assumed to be SO₄²⁻ and PO₄³⁻, respectively. Sample WTC13 was not analyzed because of insufficient sample quantity. Missing values were either not determined or below detection limit. ^bWTCX = pooled sample of WTC8, WTC11, WTC13, WTCB, WTCC, WTCE, and WTCF. ^cWTC3 was size-separated to PM_{2.5} using nose-only inhalation exposure system; average values are shown (n = 5).

those of the ROFA and ambient air SRM 1649a samples, partly because of the small total amounts present in the original material, and partly because of the limited solubility of most of these elements at the alkaline pH

Table 5. pH and endotoxin levels of PM_{2.5} samples.

Sample code	pH in water ^a	Endotoxin ^b		pH in saline ^c
		EU/mL	Inhibition	
Extraction water	5.28			
WTC8	10.00	0.50	None	
WTC11	9.16	0.25	None	
WTC13	9.47	0.50	None	
WTCC	9.54	0.25	None	
WTCC	9.32	0.50	None	
WTCE	8.88	0.25	None	
WTCF	9.55	0.50	None	
SRM 1649a	4.20	25	None	
Sterile saline				6.67
WTCX	9.35			7.36
MSH				6.61
ROFA				3.74

^apH and endotoxin levels of SRM 1649a and all WTC samples after water extraction from filters in the ratio of 0.5 mL/mg PM_{2.5}. ^bEndotoxin levels measured as EU/mL water extract. Samples were tested for inhibition of the endotoxin assay (none was detected). ^cpH of samples after resuspension in sterile saline (2 mg/mL; pooled WTCX extract was lyophilized and resuspended); average of three to four measurements.

levels (8.9–10.0) of the water extracts (Hoffland 2002; Neubauer et al. 2000).

The results of this study differ in some respects from those of the USGS (2002) and Lioy and co-workers (2002), who performed chemical and physical analyses of whole (not size-separated) WTC PM samples collected within a 3-km radius of the WTC site. The USGS (2002) collected several dust samples on 17 and 18 September that had only limited protection from the rain that fell on 14 September and possibly changed sample composition. The USGS study found Ca in the whole dust approximately in the same proportion (average 18%) that we found in the PM_{2.5} fraction, but S averaged 3% (or 9% as SO₄), a level about 4-fold lower than reported here, suggesting that SO₄ may have been washed away by rain more easily than other species. The USGS also found a notably higher level of Si (average 15% vs. 3% here), probably reflective of a large amount of glass fiber present in very coarse fractions (Lioy et al. 2002; USGS 2002), which do not fragment into PM_{2.5} as easily as gypsum and other building materials. Lioy and co-workers (2002) collected three samples on 16 and 17 September

from sheltered locations and found that Ca and SO₄ in the settled dust were present in the same ratio as in our study. However, the combined levels comprised about 6% of the whole dust, a level about 10-fold lower than that found in the PM_{2.5} fraction in our study.

We conclude that water-soluble Ca-containing compounds were enriched in the WTC PM_{2.5} fraction compared with those in the whole settled dust. Additionally, the WTC PM_{2.5} samples were remarkably homogeneous in their overall elemental content, considering the wide geographic range of sample collection. These results were unexpected, given the complexity of the building material composition and scale of the disaster. However, they are reasonable, considering the prevalent use of gypsum in building materials such as ceiling tiles, wallboard, and cement, and the ease with which these materials can be crumbled into a fine powder, mix, and homogenize.

The likely major acute inhalation hazards of WTC PM_{2.5} based on the results from this study are due to the presence of gypsum, calcite, and cement or concrete dust components. Both gypsum and calcite irritate the mucus membranes of the eyes, nose, throat,

Table 6. Elemental and ion analysis of extracts of WTC and control PM_{2.5} samples.^a

Sample:	WTCB	WTCX (pooled)		WTC3		SRM ^b	MSH		ROFA	
	DI H ₂ O	DI H ₂ O	1 M HCl	DI H ₂ O	1 M HCl	DI H ₂ O	DI H ₂ O	1 M HCl	DI H ₂ O	1 M HCl
No. analyses:	1	2	1	4	4	1	2	1	2	1
Analyte										
SO ₄ ²⁻	432,600	439,100	379,400	376,500	344,400	86,720	955	973	275,000	242,300
Ca	183,800	187,500	196,700	184,900	218,000	12,650	352	1,971	18,590	19,660
Mg	354	651	2,258	1,113	5,414	1,141	37.3	1,250	24,900	24,660
Al	537*	555*	1,477	1,346	4,072	1,049	48.4*	1,260	6,740	8,604
Cl ⁻		2,699		2,851		1,164	1,103		302	
Fe	6.0*	6.7*	1,098	150*	2,450	407	0.1*	1,833	763	19,510
Zn	4.1	13.4	410	22.7	1,413	504	0.0*	3.7	6,556	5,932
Na ⁺		1,139		1,290		2,153	721		44,179	
NO ₃ ⁻		6,496		938		7,390	0.0		0.0	
F ⁻		799		406		466	0.0		352	
Ti	4.0	5.2	41.6	12.1	181	1.8	1.3	17.6	2.6	138
Pb	0.4	0.7	33.4	2.2	141	1,379	0.0*	0.5	17.9	790
Mn	0.7	1.8	24.0	4.5	108	77.2	3.8	38.4	365	459
Cu	4.7	6.4	21.8	5.5	76.0	83.6	0.6	6.8	573	628
Ba	7.2	8.7	31.0	25.6	75.6	11.2	0.1*	5.0	3.0	57.5
Sb	7.0	9.4	17.4	17.7	43.8	3.5	0.0*	0.0*	1.5	146
NO ₂ ⁻		0.0		38.0		0.0	0.0		0.0	
Mo	4.9	1.8	3.2	1.0	33.7	1.8	0.1	0.1	0.0*	339
Ni	1.8	4.1	3.1	2.6	19.7	32.2	0.0	0.9	17,030	16,990
Sn	0.1*	1.3	3.1	0.8	12.1	0.1*	0.0*	0.0*	0.0*	51.0
Cr	1.2*	1.4*		10.0		6.1	0.1*		6.1	
Cd	0.3	0.7	1.9	0.3	7.2	19.9	0.0	0.0	8.9	11.9
Be	-0.1*	0.3*	0.2*	0.0*	2.7*	0.1*	0.0*	0.0*	1.4*	1.7*
Co	0.1*	0.8	0.9	0.2*	1.6	2.1	0.0*	0.4*	495	510
NH ₄ ⁺		0.0		0.0		25,355	0.0		0.0	
PO ₄ ³⁻		0.0		0.0		3,317	0.0		0.0	
As	0.3	1.1	-0.4*	1.3	-10.4*	13.5	0.1	0.2	1.7	106
Tl	0.1*	0.5	-1.2*	0.1*	-25.5*	0.3	0.0*	-0.1*	0.0*	-0.2*
V									1,749	35,690
Total µg/g	617,300	639,000	581,600	569,600	576,500	143,900	3,223	7,362	397,600	376,700
% Total mass	61.7	63.9	58.2	57.0	57.6	14.4	0.3	0.7	39.8	37.7

Abbreviations: Be, beryllium; Cd, cadmium; Co, cobalt; F, fluoride; NH₄⁺, ammonium; NO₂⁻, nitrite; NO₃⁻, nitrate; Sn, tin; Tl, thallium. ^aResults shown are average values for number of analyses indicated, expressed as micrograms soluble analyte per gram solid sample extracted, for deionized (DI) water and 1 M HCl extractions. Analytes are arranged in order of decreasing content in WTC3 sample by whatever analysis provided highest content. Analyte concentrations were determined by ICP-MS, except values shaded in light blue, which were determined by ICP-AES, and values shaded in dark blue, which were determined by IC. ^bSRM 1649a size-classified to PM_{2.5} (see "Materials and Methods"). *Indicates value below detection limit.

and upper airways (Stellman 1998). Calcium carbonate dust causes coughing, sneezing, and nasal irritation (NLM 2002). These symptoms of inhalation exposure are similar to those reported by rescue and cleanup workers in the immediate aftermath of the WTC attack (Kelley 2001). The high content of gypsum and calcite in the WTC PM_{2.5} fraction suggests that potentially toxic effects may also extend into the smaller airways and lung parenchyma.

The physical and chemical characterization of the samples described here contributes to the understanding of biologic responses in the companion article (Gavett et al. 2003), which describes short-term acute respiratory tract toxicology of the WTC PM_{2.5} and control PM_{2.5} samples. Further detailed analyses and toxicity testing of the WTC PM_{2.5} fraction may be necessary to evaluate other components found in the bulk WTC fallout dust, which may be enriched in the smaller inhalable particle sizes, and which have known long-term health consequences. Identified WTC bulk PM components that are known inhalation hazards are asbestos, crystalline silica, and toxic organics such as PAHs, polychlorinated biphenyls, and dioxins (Liroy et al. 2002; Offenberg et al. 2003; USGS 2002). Calcite and gypsum are often contaminated with small amounts of silica, which is the main concern for long-term occupational health hazards (Stellman 1998). Minor amounts of silica were detected in the WTC PM samples (Table 2). The results of this study are also of special interest because of resuspension of the dust during cleanup operations of both the Ground Zero site and building interior surfaces throughout lower Manhattan (Johnson 2002). WTC PM that infiltrated into buildings is most likely of smaller particle sizes and more of an inhalation hazard than that found outdoors.

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