

Use of Micro-XANES to Speciate Chromium in Airborne Fine Particles in the Sacramento Valley

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While particulate matter (PM) in the atmosphere can lead to a wide array of negative health effects, the cause of toxicity is largely unknown. One aspect of PM that likely affects health is the chemical composition, in particular the transition metals within the particles. Chromium is one transition metal of interest due to its two major oxidation states, with Cr(III) being much less toxic compared to Cr(VI). Using microfocused X-ray absorption near edge structure (micro-XANES), we analyzed the Cr speciation in fine particles (diameters $\leq 2.5 \mu\text{m}$) collected at three sites in the Sacramento Valley of northern California. The microfocused X-ray beam enables us to look at very small areas on the filter with a resolution of typically 5–7 micrometers. With XANES we are able to not only distinguish between Cr(VI) and Cr(III), but also to identify different types of Cr(III) and more reduced Cr species. At all of our sampling sites the main Cr species were Cr(III), with Cr(OH)₃ or a Cr-Fe, chromite-like, phase being the dominant species. Cr(VI)-containing particles were found only in the most urban site. All three sites contained some reduced Cr species, either Cr(0) or Cr₃C₂, although these were minor components. This work demonstrates that micro-XANES can be used as a minimally invasive analytical tool to investigate the composition of ambient PM.

Introduction

Understanding the concentrations, composition, and sources of atmospheric particulate matter (PM) is crucial since inhaling these particles can cause a wide array of negative health effects, including mortality and morbidity due to cardiovascular and pulmonary disease (1). There are many characteristics that can affect the toxicity of PM, including its physical and chemical properties (2). While PM contains an enormous variety of organic and inorganic chemical species (3), certain classes of these compounds are of particular interest because of their toxicity. For example, transition metals such as Fe, Ni, and Cr have been linked to adverse health effects through field and laboratory studies (4).

Our focus in this work is on Cr, which has two predominant oxidation states in the atmosphere: +3, which

is an essential nutrient in low doses, and +6, which is highly toxic and carcinogenic (5). Costa et al. have suggested that Cr(VI) is toxic because, unlike Cr(III), it can cross cell membranes, and then be reduced to Cr(III) within the cell, which reacts with hydrogen peroxide to make the highly damaging hydroxyl radical (6).

Particulate Cr has both natural and anthropogenic sources. Natural sources are primarily Cr(III) species formed from the erosion of rock and soil and released in volcanic emissions, though reported emission rates vary widely (7). Anthropogenic sources, such as metallurgical, refractory, and chemical industries, as well as combustion of fossil fuels, release both Cr(III) and Cr(VI) into the atmosphere (8). Major anthropogenic sources of atmospheric Cr include steel production, Cr chemical production, and combustion of coal and oil, with estimated emission rates of 2900, 450–900, 740, and 560 tons of Cr/year, respectively. In addition, Wang et al. report that diesel exhaust is also a source of Cr, with an emission rate of 4.7 mg Cr/km (9).

According to the U.S. EPA Toxic Release Inventory (10), industrial point sources and fugitive air sources emitted 30 000 kg of Cr into the atmosphere in the United States in 2003. Of this total, approximately 1800 kg of Cr was emitted in California, with a little over 2.5 kg being emitted in Sacramento County (10). Data from the California Air Resources Board indicate that identified point sources released approximately 0.6 kg of airborne Cr(VI) in Sacramento County in 2003 (11). Ambient concentrations of Cr in fine particles in urban and suburban regions of the U.S. are typically between 2–20 ng/m³, both in the eastern U.S. (12, 13) as well as in California (14).

Airborne Cr has been analyzed by many different techniques including UV–vis spectroscopy, inductively coupled plasma–mass spectrometry, atomic absorption spectroscopy, and X-ray analyses (14–17). All but the X-ray techniques have two limitations: most can only measure total Cr and those that can distinguish between Cr(VI) and Cr(III) require a wet extraction/separation step. For example, the standard methods of EPA, NIOSH, and OSHA for determination of Cr(VI) and Cr(III) in particles all require an extraction step (e.g. ref 18). There are two large advantages of X-ray absorption near edge structure (XANES) for analysis of Cr and other metals: (1) no sample preparation (e.g., extraction) is required, and (2) the technique can distinguish between different compounds of the same metal, including different oxidation states (e.g., Cr(VI), Cr(III), and Cr(0)) as well as different compounds with the same oxidation state (e.g., Cr₂O₃ vs Cr(OH)₃). Previously, XANES has been used to determine the contribution of Cr(VI) to total Cr in combustion particles (17), to speciate Mn in exhaust particles from automobiles burning gasoline containing methylcyclopentadienyl manganese tricarbonyl (19), and to distinguish between Fe(II) and Fe(III) in ambient particles (20). These studies used either bulk XANES, where the width of the X-ray beam is rather large ($\sim 2 \times 10 \text{ mm}$), or relatively coarse micro-XANES with a spot size of approximately 60 \times 40 microns.

The goal of this current study was to use microfocused XANES, with a beam size as small as 5 \times 5 μm , to examine Cr speciation in ambient particles from three locations in northern California: Sacramento, a large urban area; Davis, a small city; and Placerville, a rural area.

Experimental Section

Bulk ambient fine particles (aerodynamic diameters $\leq 2.5 \mu\text{m}$) were collected using an IMPROVE PM_{2.5} sampler at a flow rate of 23 liters per minute. Sacramento and Placerville

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samples were collected using a version 2 sampler, while the Davis samples were collected using a version 1 sampler. After collection, all samples were stored in the dark in a nitrogen-purged box until analysis.

Samples from both Placerville (38°43'29" N, 120°49'19" W; Golden Nugget Highway) and Sacramento (38°33'08" N, 121°20'20" W; Branch Center Road) were collected onto 25 mm Teflo filters (0.2 μm pore; Pall-Gelman). These samples were collected in two 24 h increments (12:00 am to 11:59 pm) on Friday, September 10 and Saturday, September 11, 2004. The Davis samples (38°32'06" N, 121°45'10" W) were collected on May 30 and June 2, 2003 (each starting at 12:00 AM) onto 47 mm Zeffluor filters (0.2 μm pore; Pall-Gelman) for a 72 and 36 h sampling period, respectively.

We analyzed the ambient particle samples for Cr using micro-XANES at two beamlines. The majority of our data was taken at beamline 10.3.2 at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory using a dual bounce Si(111) monochromator (21). Other data were collected at the GSECARS beamline 13-BM at the Advanced Photon Source (APS) of Argonne National Laboratory using a 16 element Ge detector and a Si (111) monochromator.

Whole filters were mounted with Kapton tape onto slide mounts then placed in the beam. Samples were run in fluorescence mode at a 45° angle to the incident beam; the fluorescent intensity was normalized to the incident X-ray intensity (I_0), which was measured using an ionization chamber. Micro-X-ray fluorescence was used to find or "map" various elements in the PM on the filter (21). These elements included Cr as well as S, V, Zn, Cu, Fe, Mn, Ca, Ni, and Ti. The incident X-ray energy was 10 000 eV for maps looking at multiple elements and between 6500 and 7000 eV for Cr-specific maps. The dimensions of the X-ray beam during mapping and XANES collection were changed depending on the area being mapped, but were generally between 5 × 5 and 7 × 7 microns. Elemental maps were used to identify areas of enhanced Cr concentration. These areas, termed Cr spots, were then investigated further using micro-XANES. The signal from each Cr spot was optimized by moving the sample stage to position the spot in the path of the beam and then "jogging" the stage in one micrometer or smaller steps to maximize the collected fluorescence intensity. Once the sample position was optimized, XANES spectra from ~5950 to 6150 eV were collected. We refer to these portions of the filter where XANES spectra were taken as "spots", while the entire filter we term a "sample".

To identify what types of Cr were present in our samples, we also analyzed several key standards: K₂CrO₄, Cr₂O₃, Cr(OH)₃, Cr₃C₂, Cr(0), and chromite (FeCr₂O₄, a Cr-Fe spinel). The data for the standards were collected in transmission mode. In spite of this, the chromite and Cr₂O₃ standards appeared to be slightly over-absorbed when compared with spectra of experimental spots (21). Therefore, the iterative self-absorption (over-absorption) correction module of SixPack's least-squares fitting routine (22) was used to correct any self-absorption (over-absorption) artifacts present in these standards. The chromite sample was obtained from Ward's Natural Science as "Chromite Research Mineral" and is used to represent Cr in the form of a mixed phase Cr-Fe spinel. The rest of the standards were obtained from commercial Cr compounds (Sigma-Aldrich) with the exception of the Cr(OH)₃, which was prepared by Dr. Christopher Oze (Bryn Mawr College) and Dr. Matthew Newville (Advanced Photon Source at the Argonne National Laboratory). With the exception of the Cr(0) standard, which was measured as a thin film of Cr metal, the standards were prepared for analysis by grinding with a mortar and pestle and applying the resulting fine powder in a thin layer to cellophane tape.

Collected data were processed using the SixPack program (22) to determine the fraction that each Cr species contributed

to the total amount of Cr in each spot. Multiple scans were taken of some spots to increase data quality and to check for beam induced changes in Cr oxidation state. Such changes were not observed in the data collected at the ALS but were seen in the APS data. If beam-induced Cr reduction was observed, only the first data scan was used for analysis. All spectra were adjusted so that the Cr(VI) preedge peak was at 5994.5 eV and the postedges of all standard and sample spectra were normalized to unity. Using the least-squares fitting program of SixPack, the Cr spectra of the sample spots were initially fit using all six of the standards. After each fitting, any standards that accounted for less than 5% of the total Cr in the spot were removed from the fitting to eliminate both minor components and erroneous fittings. After this the spot spectrum was fit again with only the standards of the remaining Cr species. This process was repeated until the spot spectrum was described by one or more standards each accounting for 5% or more of the total Cr. To improve fit quality, in some cases a linear function was added to the fitting parameters to compensate for differences in normalization or background subtraction between the standards and a given sample.

We estimated the accuracy of our procedure by analyzing mixtures of Cr₂O₃/K₂CrO₄ with Cr molar ratios of 100/0, 80/20, 50/50, 20/80, and 0/100. The fitted data showed good accuracy for Cr(VI) and were fit with a linear trend line with a slope of 0.98, intercept of -1.7, and $r^2 = 0.994$. The average absolute error in the Cr(VI) fraction was 2.7%. The calculated Cr₂O₃ was also fit well with a linear trend line with slope of 0.94 and intercept of 1.6 and $r^2 = 0.990$. The average absolute error in the Cr₂O₃ fraction was 3.4%. The error in Cr₂O₃ was mostly due to some fraction of Cr(OH)₃ being returned in the fits. This could represent an actual small fraction of Cr(OH)₃ in our Cr₂O₃ sample or the result of imperfections in the standard or sample spectra. Based on all of the above results, we estimate that the Cr composition results from the fittings are accurate to a relative uncertainty of approximately 5–10%.

We examined our sample results in three ways. The first, termed "percent frequency", is the percent of all spots at a given site that contained a particular Cr species i :

$$\text{percent frequency of species } i = \left(\frac{n_i}{n_{\text{tot}}} \right) \times 100\% \quad (1)$$

where n_i is the number of spots at a given site that contained species i and n_{tot} is the total number of spots from the same site. The second calculated quantity, the "atomic abundance", represents the average composition of the Cr pool at a given site taking into account results from all spots from that site:

$$\text{atomic abundance} = \frac{\sum_k f_{ki}}{n_{\text{tot}}} \quad (2)$$

where f_{ki} is the fraction of the signal from spot k coming from species i (determined from the SixPack data analysis), normalized so that $\sum_k f_{ki} = 1$. The final quantity that we calculated is the "weighted atomic abundance", which semiquantitatively accounts for the different amounts of Cr in each spot:

$$\text{weighted atomic abundance} = \frac{\sum_k f_{ki} \beta_k}{\beta_{\text{tot}}} \quad (3)$$

The value β_k is the brightness of spot k , which is a semiquantitative, relative measure of the total amount of Cr in each spot determined as the edge-step height, which is

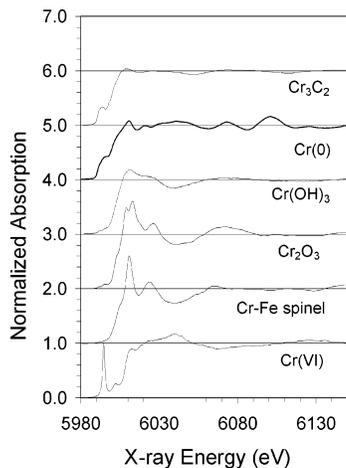


FIGURE 1. Chromium standards used to fit the spot spectra.

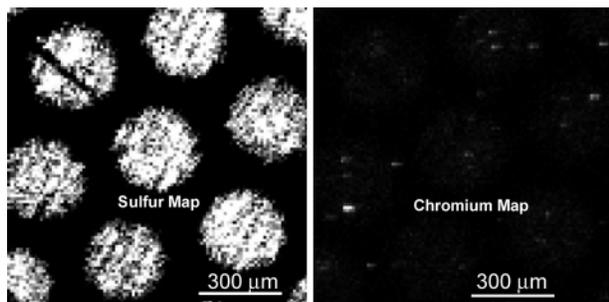


FIGURE 2. Maps of sulfur (left) and Cr (right) in $PM_{2.5}$ from Sacramento. Images were generated simultaneously, on the same portion of the filter, using a $7 \times 7 \mu m$ X-ray beam at an energy of 10 000 eV. The image on the left is the response from sulfur, while the image on the right is for Cr. Lighter spots represent pixels with higher amounts of the element of interest.

calculated during normalizing the spectra. β_{tot} here is the sum of the brightnesses of all spots at a given site.

Results and Discussion

Standards. Figure 1 shows spectra of the six Cr standard compounds used to fit our sample spectra. There are three general components of each Cr XANES spectrum: the “preedge” (including the preedge peak used to identify Cr(VI)), which refers to the region at energies lower than the position of the major absorption edge; the “near-edge” region, which refers to the ~ 30 eV wide region immediately surrounding the major absorption edge, and the “postedge” region, which refers to the area > 30 eV beyond the absorption edge. From these standards we can see that, in general, each Cr compound here has distinct spectral features, such as the large preedge peak for Cr(VI) and the large postedge oscillation that occurs in the Cr-Fe spinel. In addition, Cr(OH)₃ has broader peaks in its near-edge oscillations compared to the sharp double peak in the near-edge of Cr₂O₃.

Mapping. An example of an XRF map taken at 10 keV with a 7×7 micron beam is shown in Figure 2. Although our main interest here is characterizing the speciation of Cr, we also collected data for several other elements, including sulfur as illustrated in the left side of Figure 2. As shown in this figure, sulfur is quite abundant on our filters and is a common constituent in all of our PM samples. The bright circles in this figure show where PM was collected on the filter and are a result of the hole pattern on the grid that the IMPROVE sampler uses beneath the filter.

The map on the right side of Figure 2 is the exact same portion of the filter as that shown on the left but now showing the response from Cr. As this map demonstrates, while there

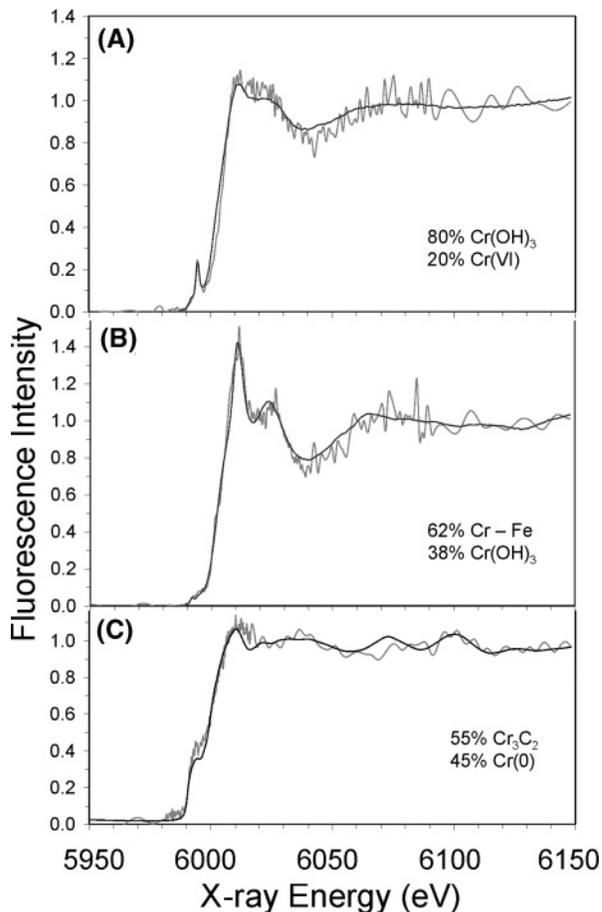


FIGURE 3. Representative spot spectra from the Sacramento $PM_{2.5}$ samples. The percentages represent the fraction of total Cr in that spot that is contributed by the given Cr species. The gray line (noisy) is the acquired data, while the black line (smooth) is the least-squares regression fit to the data.

are a number of bright (hot) spots, Cr is far less abundant and less evenly distributed than sulfur in our PM samples. Our qualitative Cr and S results here are consistent with previous sampling in the Central Valley of California, which show that Cr in fine particles is present at approximately 10^{-3} the concentration of sulfur (14, 23). After collecting fine maps for each sample (such as that shown in Figure 2), we pinpointed the Cr spots, acquired a XANES spectrum for each spot, and determined the Cr speciation in the spot based on fitting our standards to the sample spectrum.

Cr Speciation in Sacramento $PM_{2.5}$. Sacramento is a large, sprawling metropolitan area with a population of ~ 500 000 located approximately 144 km east-northeast of San Francisco. There are several major stationary sources of Cr within 24 km of our sampling site, including chrome-plating plants, power plants, and incinerators (11). The site where we sampled, which is ~ 8 km from the city center, is classified by the California Air Resources Board as suburban with ~ 50 000 vehicles per day passing within 300 meters. On our Friday sampling day the winds were 0–8 mph from the west in the morning and from the south in the evening. On Saturday winds ranged from 0 to 8 mph and were from the south in the morning and evening and from the northwest in the afternoon (24). A total of 28 spots were analyzed from the two Sacramento filter samples: 22 spots from Friday and 6 spots from Saturday.

Figure 3 shows three examples of spot spectra from the Sacramento site along with their fits. Chromium in the spot shown in Figure 3a is from the Friday sample and is composed of $\sim 80\%$ Cr(OH)₃ and $\sim 20\%$ Cr(VI). (Note that all percentages

given in this paper are expressed on a Cr atom basis.) Four other spots in the Friday sample contained Cr(VI) but this species was not present in the spots analyzed from the Saturday sample. While this difference could be due to the fact that fewer spots were analyzed on the Saturday sample, it is also possible that it reflects differences in emissions between weekdays and weekends. For example, two possible local sources of Cr(VI), a chrome-plating plant approximately 6 km southwest of the sampling site and a facility which makes and recycles building material within 1.5 km south of the sampling site, were both in operation on Friday but not on Saturday. These sources released, respectively, 0.14 and 0.1 kg of Cr(VI) to the atmosphere during 2003 (11). The building material facility also emitted approximately 0.8 kg of other Cr species in 2003, while total Cr emissions from the chrome-plating plant are not available (11).

As illustrated in Figure 3b, the combination of a Cr-Fe spinel phase (as approximated by the chromite standard) and Cr(OH)₃ in a single spot was common in particles from Sacramento, as it was in Davis and Placerville. Particles containing the Cr-Fe spinel frequently contained other forms of Cr(III), primarily Cr(OH)₃. From our previous study of flame-generated Cr ultrafine particles, we found that the Cr-Fe spinel is formed during combustion of fuel containing both Cr and Fe (17). In addition, similar Cr-Fe spinel phases have been found in soil particulates (25, 26). Thus we cannot unambiguously identify the source of Cr-Fe spinel in our ambient PM_{2.5} since soil particles, although generally coarse, can also be smaller than 2.5 μm in diameter (3). The possible sources of the other Cr species are even less clear since, as far as we can determine, there have been no studies of the speciation of particulate Cr from different emission sources except for the general distinction between Cr(VI) and Cr(III).

As shown in Figure 3c, other spots from Sacramento contained forms of Cr that are more reduced than Cr(III), namely Cr(0) and Cr₃C₂. In the case of the Figure 3c spot, the Cr atoms were present in nearly equal amounts of Cr(0) and Cr₃C₂. It is unclear what sources emitted the particulate Cr(0) and Cr₃C₂ found in our samples. One possible precursor, however, is stainless steel, which commonly contains variable amounts of Cr carbide for strengthening (27). Although the similarity in the spectra of Cr(0) and Cr₃C₂ make it hard to unambiguously assign the two species, taken together they represent Cr in aerosol particles that is more reduced than Cr(III).

Most of the Cr spots from the Sacramento samples contained a mixture of Cr types: 18% of the spots had only one Cr component, 57% of the spots contained two Cr species, 21% had three Cr components, and 4% (one spot) contained four Cr species. Of the five spots that contained only one Cr component, three were Cr-Fe spinel, one was Cr(OH)₃, and one was Cr₂O₃. Sacramento had the most diverse speciation of all of the sampling sites, which might be expected since there are multiple Cr sources in the area (11).

Cr Speciation in Davis PM_{2.5}. Davis is a small city, primarily residential, located ~24 km west of Sacramento with a population of ~60 000. Based on 2003 data from CARB (11), there are no known point sources of atmospheric Cr within Davis, and no Cr(VI) sources within 16 km of the sampler, but there are six point sources within 16–32 km that emit a total of approximately 1.4 kg of Cr(VI) annually. In addition, the sampling site is ~1 km north of a major interstate highway and there was a construction project ~20 feet south of our site during sampling. The wind near our sampling site was 0–12 mph on the sampling days coming from the south in the morning and evening, and from the north during the day (24). There were a total of 18 spots analyzed in Davis: 33% contained one Cr species, 44% contained two, and 22% contained three Cr species.

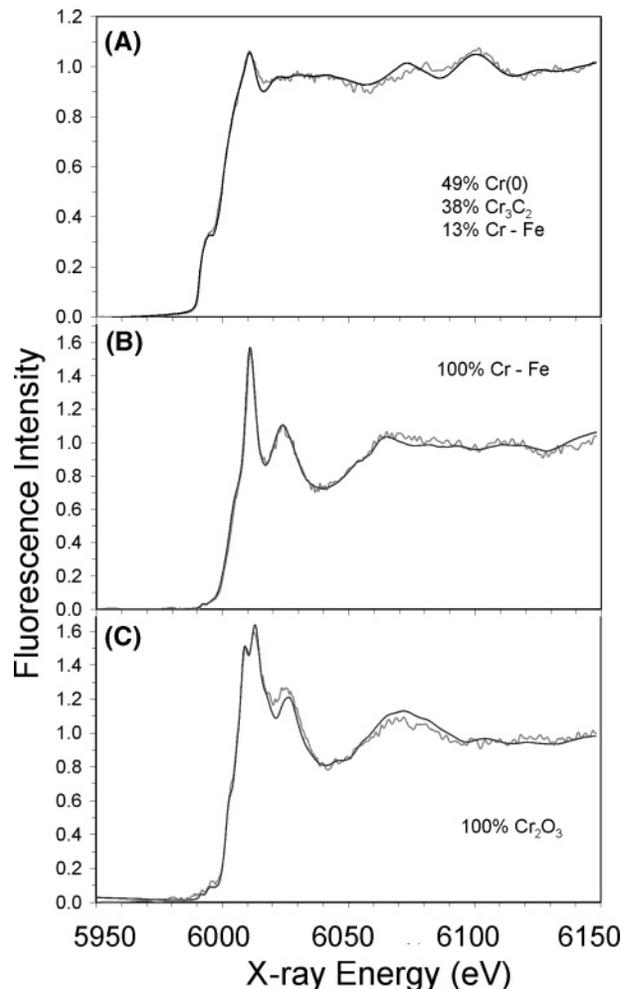


FIGURE 4. Representative spot spectra from the Davis PM_{2.5} samples. The percentages represent the fraction of total Cr in that spot that is contributed by the given Cr species. The gray line (noisy) is the acquired data, while the black line (smooth) is the least-squares regression fit to the data.

As in Sacramento, we saw spots in Davis that also had reduced Cr (Figure 4a) as well as 100% Cr-Fe spinel (Figure 4b). As stated above, two potential sources of these Cr-Fe spinel particles are combustion and suspension of soil dust. We also saw two other types of Cr spots in Davis that contained only one Cr species: 100% Cr(OH)₃ (present in 2 of the 18 spots) and 100% Cr₂O₃ (one spot; shown in Figure 4c).

Cr Speciation in Placerville PM_{2.5}. The Placerville sampling site, which is categorized as remote by the CARB (11), is approximately 48 km east of Sacramento, 500 meters south of Highway 50, and sees ~15 000 vehicles per day. During the day of sampling winds ranged from 0–8 mph and were easterly during the morning and night and southerly during the day (24). The amount of particulate matter collected during the sampling event was quite low (based on visual observation of the filter), resulting in noisy XANES spectra and, consequently, relatively poor fittings of the spot spectra. Of the nine spots analyzed from Placerville, 11% (one spot) contained one Cr component, 55% (five spots) contained two Cr components, 22% (two spots) contained three Cr components, and 11% (one spot) contained four Cr components. This site is most likely to see particles from Sacramento and the highway to the north and does not have a Cr(VI) source within 16 km (11).

Frequency of Cr Species in Sacramento, Davis, and Placerville PM_{2.5}. The frequency of appearance (eq 1) of each Cr species at each of the sampling sites is shown in Figure

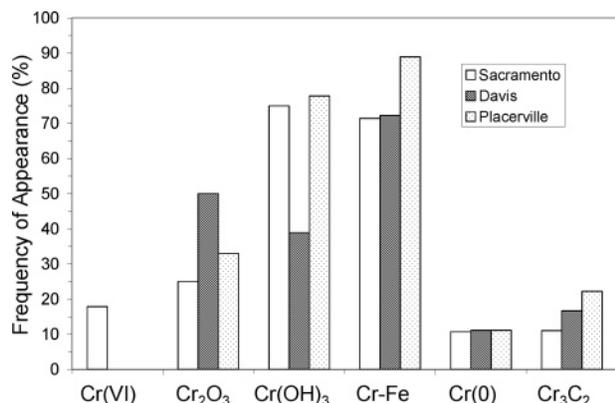


FIGURE 5. The frequency of appearance for each Cr species at each site, i.e., the percentage of spots at a given site that contained the listed Cr species (eq 1).

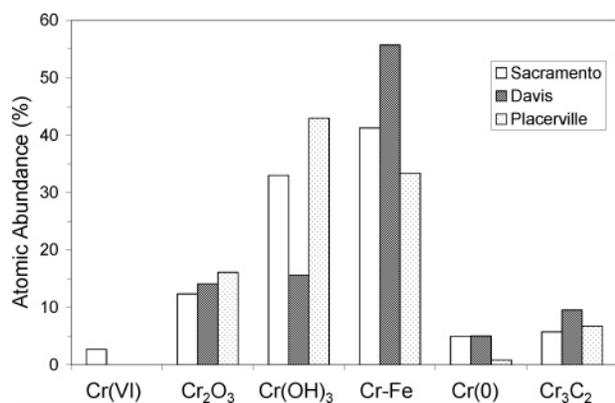


FIGURE 6. The atomic abundance of the Cr species at each site, i.e., the contribution of each Cr species to the total number of Cr atoms, averaged over all spots from that site (eq 2).

5. Particles from all sites most frequently contained Cr(III) species, with Cr(OH)₃ and the Cr-Fe spinel dominating. In Sacramento, Cr(OH)₃ was present in 75% of the spots while Cr-Fe appeared 71% of the time. Chromium(VI) occurred in 18% of the Sacramento spots analyzed, but only in the Friday sample as described earlier. The two reduced species (Cr(0) and Cr₃C₂) each appeared in 11% of the Sacramento spots analyzed. These more reduced Cr species were also present in a portion of the spots from Davis and Placerville, with Cr(0) and Cr₃C₂ appearing in 11 and 17% of the Davis spots (and 11 and 22% of the Placerville spots), respectively. In Placerville, Cr-Fe and Cr(OH)₃ were found most frequently, in 89 and 78% of the spots, respectively, which is similar to the Sacramento data. In Davis, Cr-Fe was found in 72% of the spots analyzed, with Cr₂O₃ and Cr(OH)₃ occurring in 50 and 39% of spots, respectively.

Atomic Abundance of Cr Species in PM_{2.5}. While knowing the frequency with which a Cr species occurs is useful, it is also interesting to examine the approximate relative abundances of the various Cr species at each site. Figure 6 shows the percent of all identified Cr atoms at a given site that were present in a particular Cr phase (eq 2). In Sacramento, the most abundant species were Cr(OH)₃ and Cr-Fe spinel, which accounted for 33 and 41%, respectively, of the total amount of Cr identified. The other Cr(III) species, Cr₂O₃, accounted for 12% of the total Cr atoms, while reduced Cr species (i.e., Cr₃C₂ and Cr(0)) accounted for a relatively small percentage of the Cr found in Sacramento (6 and 5%, respectively). Chromium(VI) accounted for 3% of the total Cr identified in spots from particles sampled in Sacramento. Though this species accounts for only a small percentage of the total amount of Cr atoms, the fact that Cr(VI) is present

in nearly one-fourth of the spots analyzed in the Friday sample suggests that there might be significant weekday exposures to this toxicant. This combination of a moderate frequency of appearance for Cr(VI), but low overall abundance, is consistent with previous work, which shows that combustion does not form pure Cr(VI) particles, even under extreme combustion temperatures, and that atmospheric aging reduces Cr(VI) to Cr(III) (17, 28).

In Davis, the Cr speciation is fairly simple, with 86% of the Cr species being Cr(III). Of the three Cr(III) species, Cr(OH)₃ accounted for 16% of total Cr, Cr₂O₃ contributed 14%, and the Cr-Fe spinel was the most abundant, accounting for 56% of Cr atoms in Davis spots (Figure 6).

As in Sacramento and Davis, the main species in the Placerville spots are Cr(III), which account for 92% of the total Cr found in the Placerville spots. Cr(OH)₃ was the most abundant Cr(III) species, accounting for 43% of total Cr, while the Cr-Fe spinel accounted for 33% and Cr₂O₃ accounted for 16% (Figure 6). We also found particles that contained Cr₃C₂ and Cr(0) at Placerville, together accounting for 8% of the total Cr.

Interestingly, the results of the weighted atomic abundance calculation (eq 3) (data not shown) are very similar to the atomic abundance (eq 2) results detailed in Figure 6. This shows that, in general, the Cr speciation in the spots that contained the most Cr is very similar to the speciation averaged over all of the spots, and indicates that there are no large changes in Cr speciation with the amount of Cr in a particle. The one exception was in the Sacramento sample that contained a single extremely bright spot of Cr(0). This anomaly could be due to one large Cr(0) particle making it through the sampler size cut point.

Uses of Micro-XANES and Environmental Implications.

As this study shows, micro-XANES can sensitively and quantitatively speciate Cr in atmospheric particles. Given that the technique can also speciate a variety of other elements, micro-XANES is a powerful tool for characterizing the composition of particulate matter. In addition, the detailed speciation available through micro-focused XANES could be used to complement existing techniques, such as studies of elemental composition as a function of PM size (29–31), to determine the sources of ambient particulate matter.

While other analytical techniques can distinguish between Cr(VI) and total Cr, this study demonstrates that aerosols contain a suite of different Cr(III) species, as well as more reduced Cr species, that have so far received very little attention. This is largely due to the fact that other techniques cannot readily provide chemical speciation information. This newly revealed complexity suggests that much more work needs to be done to understand both the reactivity and toxicity of the phases we have identified to more fully understand the significance of particulate Cr. For example, the fact that the Cr-Fe spinel phase was a major component at each of our three sites suggests that the chemistry and toxicity of this phase will likely play a key role in the Cr-associated health effects of ambient PM. The fact that this phase could be derived from either natural geological materials or from high-energy combustion processes presents an interesting challenge in distinguishing sources of Cr (32). However, in spite of this complexity, the different distributions of the Cr phases at the three sampling sites indicate that the sources of Cr vary with sampling location.

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