Development of a Wet-Chemical Method for the Speciation of Iron in Atmospheric Aerosols

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The ability to quantify the chemical and physical forms of transition metals in atmospheric particulate matter (PM) is essential in determining potential human health and ecological effects. A method for the speciation of iron in atmospheric PM has been adapted which involves extraction in a well-defined solution followed by oxidation state specific detection. The method was applied to a suite of environmental aerosols. Ambient atmospheric aerosols in an urban area of St. Louis (the St. Louis environmental aerosol) were collected on Teflon substrates and were leached in one of four different solutions: (1) >18.0 MΩ water; (2) 140 µM NaCl solution; (3) pH = 7.4 NaHCO₃ solution; and (4) pH = 4.3 acetate buffering system. Fe(II) was determined directly using the Ferrozine method as adapted to liquid waveguide spectrophotometry using a 1 m path-length cell. Fe(III) was determined similarly after reduction to Fe(II). It was found that, at low ionic strength, pH exerted a major influence on Fe(II) solubility with the greatest Fe(II) concentration consistently found in the pH = 4.3 acetate buffer. Soluble Fe(III) (as defined by a 0.2 µm filter) varied little with extractant, which implies that most of the Fe(III) detected was colloidal. To characterize well-defined materials for future reference, NIST standard reference materials were also analyzed for soluble Fe(II) and Fe(III). For all SRMs tested, a maximum of 2.4% of the total iron (Urban Dust 1649a) was soluble in pH = 4.3 acetate buffer. For calibration curves covering the ranges of 0.5–20 µg/L Fe(II), excellent linearity was observed in all leaching solutions with R² values of >0.999. Co-located filters were used to test the effect of storage time on iron oxidation state in the ambient particles as a function of time. On two samples, an average Fe(II) decay rate of 0.89 and 0.57 ng Fe(II) g⁻¹ PM day⁻¹ was determined from the slope of the regression, however this decrease was determined not to be significant over 3 months (95% confidence). As an application of this method to mobile source emissions, size-resolved PM₁₀ samples were collected at the inlet and outlet of the Caldecott Motor Vehicle Tunnel in northern California. These samples indicate that the coarse fraction (PM₁₀—PM₂.₅) contains almost 50% of the total soluble Fe(II) in the aerosol.

Introduction

Iron is present in the environment either in the Fe(II) or the Fe(III) forms with transformations between these states readily occurring. Because Fe(II) is generally more soluble (and thus mobile) than Fe(III), the oxidation state in which iron is found in the environment can be the most significant predictor of solubility and environmental fate (1,2). Photo-reduction of Fe(III) to Fe(II) has been shown by researchers to be an important transformation pathway of iron in atmospheric environments with the hydroxyl radical generated in the process (3). Further, the efficiency of the reduction is, in part, determined by the organic electron donors present (4). In general, Fe(II) species are oxidized to Fe(III) by molecular oxygen resulting in the formation of the O₂⁻ free radical (5). Fe(III) (primarily as [Fe(III)(OH)(H₂O)₅]²⁺) also plays a large role in the red-ox chemistry in environmental systems by catalyzing the oxidation reaction with O₂ which converts S(IV) to S(VI) (6, 7).

There have been many studies measuring the total iron content in atmospheric particles. Using graphite furnace atomic absorption spectroscopy (GFAAS) and inductively coupled plasma—mass spectrometry (ICP—MS), researchers found ambient iron concentrations in an urban area (College Park, MD) to range from 1000 to 4000 ng Fe m⁻³ air while background levels were close to 150 ng m⁻³ (8, 9). The same study (8) shows that up to 90% of the iron mass is concentrated in the coarse fraction of particles (PM₁₀—PM₂.₅) with a much smaller mode under 1 µm. Atmospheric iron-containing particulate matter with an aerodynamic size under 1 µm (PM₁) generally originates from the combustion of fossil fuels and is therefore present in automobile exhaust. Coarse particles may have sources which include resuspended soils or automobile brake dust (10).

Numerous studies of ocean and rain water have focused on the photochemically mediated speciation of iron (11, 12). Similar studies have determined the lability of iron in atmospheric PM by extracting the iron and then analyzing the extract using atomic absorption spectrometry (13). This results in solubility information, and very little information on the oxidation state of the iron in solution in achieved. A thorough review of iron speciation measurements in seawater can be found in Turner and Hunter (14).

Oxidation-state resolved measurements of iron can give indications of the red-ox chemistry occurring in an environment. Resolution of Fe(II) and Fe(III) in atmospheric particulate matter (PM) has been successfully achieved using Mössbauer spectroscopy (15), however large amounts of PM are required. Other red-ox sensitive methods used for these measurements include voltammetric techniques, chemiluminescence, and the Ferrozine method (15–19). Spectrophotometric techniques (such as the Ferrozine method) are powerful and sensitive tools for characterization of Fe species in atmospheric PM when dissolved in solution (20, 21). However, few studies have been performed which link the release of soluble Fe(II) and Fe(III) to the nature of the extractant. Further, no studies have determined if storage
time will change the iron speciation in atmospheric PM. This paper will detail a wet-chemical method for Fe speciation in atmospheric PM and present new soluble Fe(II) and Fe(III) data. The data presented here will focus on the efficiency of the extractant, potential Fe(II) loss due to particle storage, and applications of the method to mobile source emissions.

Materials and Methods

Reagents and Standards. All bottles and vials used in this procedure were cleaned using a rigorous multi-acid-leach (3 days each in 2.5 N hydrochloric acid followed by 0.3 N hydrochloric acid) finished with a rinse in > 18.0 MΩ water. All acids used were Fisher Scientific trace-metal grade. SigmaUltra-grade ammonium iron sulfates were used for Fe(II) and Fe(III) standards. Working standards were prepared daily by dilution from a 1000 ppm Fe(II) standard (prepared gravimetrically) and ranged from 0.5 to 20 μg/L. De-oxygenated water was not used, but the standards were found to be stable for at least one week when stored in the dark at 4 °C. Ferrozine solution was prepared by adding 133 mg of solid [SigmaUltra-grade Ferrozine (3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-4,5′-disulfonic acid sodium salt)] to 50 mL of water containing 65 μL of concentrated HCl. The hydroxylamine hydrochloride (HA) solid (Sigma) was 99.9999% pure and the solution was prepared daily by dissolving 19.3 mg HA into 50 mL of water. Sodium bicarbonate (140 μM) and sodium chloride (140 μM) solutions were prepared from certified ACS-grade reagents (Fisher). Acetate buffer (500 μM acetate) was prepared from glacial acetic acid (Fisher Certified ACS Plus) and sodium acetate (SigmaUltra).

Air Sampling. Atmospheric PM was collected from the U.S. Environmental Protection Agency (EPA)-funded St. Louis Midwest Supersite in East St. Louis, IL. The site is in an urban residential/light commercial area about 3 km east of St. Louis, MO. With samplers built specifically for this study, two PM10 inlets (URG Corp.) were used to collect atmospheric PM at a total flow of 64 L per minute (Lpm). Downstream of each inlet, flow was separated into 5 air streams and passed through 5 aluminum filter holders (URG Corp.), thus allowing for 10 co-located filters each sampling day. The use of aluminum filter holders resulted in elevated aluminum levels in the field blanks, but did not have any significant effect on soluble Fe(II) levels. Analysis of field blanks yielded soluble Fe(II) content averaging around 0.050 μg/L (<0.020–0.105 μg/L), which is just above the method detection limit. The 10 co-located PM samples were collected at a flow rate of 6.5 Lpm for 24 h on 47 mm acid-cleaned Teflon filters (Teflo, 2.0 μm pore size, Pall Life Sciences Inc.). Sampling was carried out every other day for 7 days in East St. Louis from March 13 to March 31, 2005. Air flows were calibrated in the laboratory and checked in the field before and after sampling. The pre-cleaned filters were weighed on a microbalance (Mettler) in a constant humidity and temperature environment pre- and post-sampling. For all sampling and analysis, trace-metal clean techniques were used throughout. All pre- and post-sampling handling of the substrates were performed in a laminar flow HEPA hood or in a dedicated trace-metal clean room. Before use, all collection substrates were subjected to a rigorous acid-washing procedure which has been shown to minimize trace-metal contamination. For the Teflon filters, this procedure includes a 5 min soak in 30 mL of 2 N high-purity HCl. The acid is then pumped through the filter at a rate of 3 mL/min using an oilless vacuum pump. This step is then repeated with 30 mL of 2 N HNO3. Finally, 60 mL of > 18.0 MΩ water is pumped through the filter at 3 mL/min. The filter is then placed in an acid-cleaned polystyrene dish and dried under a laminar flow clean bench.

Particulate collection at the Caldecott motor vehicle tunnel in northern California was achieved by using the Sioutas personal cascade impactor sampler (PCIS, SKC Inc., Eighty Four, PA) (22). The PCIS is a size-resolved PM10 personal sampler which operates at 9 Lpm and collects particulate size fractions of 10–2.5, 2.5–1, 1–0.5, 0.5–0.25, and <0.25 μm (23). A series of 6 h samples was obtained at the inlets and outlets of Bore 1 (approximately 4% Diesel, 96% gasoline vehicles) and Bore 2 (gasoline only). Each bore was sampled on 4 separate days during afternoon rush hour. Impactor substrates on the first 4 stages of the PCIS were acid-cleaned 2.0 μm 25 mm Teflon (Pall Life Sciences) filters, while pre-cleaned 37 mm 2.0 μm Teflo substrate (Pall Life Sciences) filters were used in the smallest size-cut (<0.25 μm, after-filter). For all sampling, substrates were massed and then placed in a –20°C freezer until analysis.

Wet Chemical Analysis. Total Metal Analysis. Total iron measurements were achieved using a low-volume microwave-assisted digestion method shown to minimize trace-metal contamination followed by analysis by inductively coupled plasma—mass spectrometry (ICP—MS). The polynpentene support ring from the Teflo filter was removed and the filter membrane placed in a Teflon digestion bomb with a mixture of high purity acids (1.5 mL of 16 N HNO3, 0.5 mL of 12 N HCl, 0.2 mL of 28 N HF). Solubilization of the PM was achieved by subjecting the sealed Teflon bombs to a programmed microwave digestion (Ethos, Milestone) (9 min temperature ramp to 180 °C followed by a 10 min hold at 180 °C) and diluted to 30 mL with > 18.0 MΩ water. A typical analytical batch consisted of 22 unknowns, 6 standard reference materials (SRMs), 4 matrix blanks, 2 method blanks, and 2 matrix spikes. These included the following NIST SRMs: recycled auto catalyst (RAC; 2556), urban dust (1649a), and San Joaquin soil (2709). More details of the method can be found elsewhere (24).

Fe(II) Determination. Extractions were performed in acid-cleaned polypropylene vials by immersing a sampled Teflon substrate in 10 mL of one of four extractants: (1) > 18.0 MΩ water; (2) sodium bicarbonate solution; (3) sodium chloride solution; or (4) acetate buffer. Compositions of these leachates are detailed in Table 1. Experiments carried out to determine the kinetics of Fe(II) release from ambient PM showed that no additional soluble Fe(II) is detected in any of the leach solutions employed here after a leach period of 100 minutes. Therefore, the filters were leached under laboratory conditions (20–22 °C and diffuse light) while slowly rocked back and forth using a rotisserie shaker for 2 h and the leachate was immediately filtered through a 0.2 μm pore-size, acid-cleaned (1.2 N trace-metal grade HCl) polypropylene filter (Whatman). Ferrozine solution (100 μL/10 mL filtrate) was then added to each filtrate and the resulting solution was analyzed immediately or stored in the dark at 4 °C and analyzed within 24 h. A delay in analysis of the solution up to 24 h after Ferrozine addition was demonstrated not to have an effect on the iron signal when stored in the dark at 4 °C. For Fe(II) analysis, the solution (Ferrozine included) was pumped using a peristaltic pump (Cole Parmer) into a 1 m path-length liquid waveguide fiber optic cell spectrophotometer (World Precision Instruments Inc.) where the absorbance spectrum from 400 to 700 nm was obtained. Prior to analysis, the cell was rinsed with a surfactant (triethanolamine).
amine), methanol, and 2 N HCl. Between each sample, the spectrum of a Ferrozine blank in the same matrix as the extractant was obtained. If the Fe(II)–Ferrozine complex was less than 0.100 μg Fe(II)/L, then the next sample was analyzed. If an Fe(II)–Ferrozine signal was present in the blank, then the cell would be subjected to the above cleaning procedure until a clean blank was obtained. All spectrophotometric experiments were carried out with a Tidas I photodiode array detector using a D2H tungsten light source (World Precision Instruments, Inc.). The absorption of the Fe(II)–Ferrozine complex, and therefore soluble Fe(II) ([Fe(II)_{sol}]), was monitored at 562 nm and compared to a matrix-matched calibration curve. This combination allows for detection limits below 0.100 μg/L solution (or 1.7 nM) Fe(II). Under the sampling conditions employed at the St. Louis Supersite, this corresponds to a detection limit of under 0.11 ng Fe(II) m^{-3} air.

Fe (III) Determination. In the remaining filtrate, Fe(III) was reduced to Fe(II) by adding HA solution (100 μL per 10 mL extract). After about 5 min, total soluble (as defined by the 0.2 μm filter) iron ([Fe(II)_{sol,tot}]) was measured in the solution by the Ferrozine method as outlined above. Thus, by subtraction, we can determine the soluble Fe(III) content, or [Fe(III)_{sol}], as per eq 1.

\[
[\text{Fe(III)}_{\text{sol}}] = [\text{Fe(II)}_{\text{sol,tot}}] - [\text{Fe(II)}_{\text{sol}}]
\]  

Results
Precision and Calibration Curves. Seven co-located filters from the St. Louis sampling site were extracted in an identical fashion using the pH 4.3 acetate solution. Fe(II) in each leachate was measured spectrophotometrically at least twice using the Ferrozine method. An average of 19.6 ± 1.4 ng soluble Fe(II) m^{-3} air was found, where the uncertainty is one standard deviation of all trials. This corresponds to a 7.1% relative standard deviation and reflects the overall precision for this technique (this includes sampling, extraction, and analysis errors).

Calibration curves from 0.5 to 20 μg/L Fe(II) in selected leachates are shown in Figure 1. For all curves R^2 values of >0.999 were achieved with slopes ranging from 19.4 (acetate + HA) to 22.3 (bicarbonate). For the calibration range shown here, the analytical uncertainty of this measurement (as ±1 standard deviation from the mean, n = 3) is less than 0.40%. Comparison of the acetate and the acetate + HA calibration curves indicates that the addition of HA has very little effect on the calibration slope or intercept.

Figure 2. Measurements of how storage in the dark at −20 °C affects the leachable Fe(II) content in these samples of atmospheric PM. All samples were leached in pH = 4.3 acetate buffer. The fraction of the total iron extracted is about 5%.

Oxidation State Stability in Storage. Both photoreduction of Fe(III) and oxidation of Fe(II) may alter the red-ox speciation of iron in atmospheric aerosols, however the magnitude and relative importance of these processes are unclear. Real-time or very rapid analysis may be required, but considering that in most field sampling campaigns it is not always practical or feasible to analyze the particles in this manner, experiments were carried out to test how soluble Fe(II) in the particles changes while stored in a dark freezer at −20 °C. Co-located St. Louis samples from two different sampling days were tested for soluble Fe(II) over the course of 6 months. At intervals of 1 week, 2 weeks, 3 weeks, 6 weeks, 3 months, and 6 months from the sampling date, separate filters were processed for Fe(II) measurement using the pH = 4.3 acetate extractant. The results are shown in Figure 2. For the March 29 sampling date after 1 week, an Fe(II) concentration of 538 μg Fe(II)/g PM was measured. This
corresponds to 4.6% of the total iron in the particles (as measured by ICP-MS). On March 29 and March 31, the average decrease of soluble Fe(II) was found to be 0.89 and 0.57 ng Fe(II) day$^{-1}$, respectively. These values represent the slope of the regression line. Using a 95% confidence level, it was found that there is no statistically significant decrease in Fe(II) over 6 months for the March 31 sampling date. Further, the March 29 sampling day did not show a significant decrease over 3 months, however, the change over 6 months was significant ($p = 0.007$). The March 31 data point at 21 days after sampling was left out due to analytical errors during analysis.

**Fe(II) Dependence on Extraction Solution Composition.**
As aerosols are emitted into the atmosphere, they may encounter a range of potential fluids in their life history. The labile iron will be determined by the mode of release into the solution and, thus, will primarily be dependent on the properties of these fluids. Four solutions with contrasting, but relevant properties were chosen for study: (1) pH = 7.4 sodium bicarbonate extractant was chosen because carbonate systems at this pH are physiologically relevant (25); (2) sodium chloride solution was chosen to match the ionic strength of the sodium bicarbonate buffer, but with a minimal buffering capacity; (3) pH = 4.3 acetate buffer was used because it is a lower pH buffer with environmental applications in that it is a good approximation of fog and rainwater, and similar extractants have been used to define labile metal pools in other studies (26); (4) Milli Q water was utilized as a clean, simple, standard solution to be compared to all other leaches.

As each leachate will provide estimates for various environmental and biotic fluid matrices which atmospheric particles may encounter, tests for Fe(II) content in each leachate were carried out. Four co-located filters from St. Louis, where the overall particulate mass agreed to within 10%, were each subjected to one of the four leaches listed in Table 1 and analyzed for soluble Fe(II) and Fe(III) content. Results of these experiments are summarized in Figure 3. In terms of Fe(II) solubility (white fraction of bars in Figure 3), the MQ and NaCl leaches are statistically indistinguishable (two tailed $t$-test, 95% confidence), while the pH = 4.3 acetate leach consistently recovers the greatest amount of Fe(II).

Aside from March 27 (the only weekend day shown here), the Fe(II) leached from bicarbonate was similar to that of the MQ and NaCl leach ($t$-test, 95% confidence). This implies that the iron release mechanisms for the St. Louis samples are similar in each of the three extractants (bicarbonate, NaCl, and MQ) for each day except March 27. Further, only very small deviations in $\frac{[\text{Fe(III)}]_{\text{sol}}}{[\text{Fe(II)}]_{\text{sol}}}$ were observed across the different extractants for a given sampling day. The data show that the very labile Fe(II) component is changing to a greater extent than the less labile Fe(III) pool across extractant. The relative differences observed in the MQ, NaCl, and bicarbonate extracts shows that varying emission sources and different atmospheric processing associated with day-to-day meteorology will have an effect on how the iron is bound in the particles.

**Tests to determine the relative iron pools addressable by the various extractions were also performed on NIST standard reference materials (SRMs). These included the following NIST SRMs: Recycled Auto Catalyst (RAC) (no. 2556), urban dust (no. 1649a), and San Joaquin soil (no. 2709). The results of these tests are presented in Figure 4. Overall, the SRMs showed similar dependence of soluble Fe(II) on extractant composition as seen in the ambient St. Louis samples. It can be seen from Figure 4 that the labile iron fraction in the urban dust SRM is significantly greater than the RAC and the San Joaquin soil SRMs. In the acetate extract, the relative leachable iron was 0.51%, 1.4%, and 0.01% for RAC, urban dust, and San Joaquin soil, respectively. Further, when combining the results for all leachates for urban dust and San Joaquin soil, it was found that, of the total leachable iron, about half of the iron was in the form of Fe(II) (53% and 41%, respectively). In contrast, about 98% of all leachable iron in the RAC was in the form of Fe(II).

**Caldecott Motor Vehicle Tunnel Test.** Determination of soluble Fe(II) emissions (ng m$^{-2}$) was achieved by subtraction of the Fe(II) concentration at the outlet from the inlet of each bore. Table 2 shows the soluble Fe(II) fraction compared with total iron emitted (PM2.5). Total iron analysis by X-ray fluorescence on co-located substrates showed that less than 2% (0.2–1.6%) of the total iron collected was detected as leachable Fe(II). Table 2 suggests that labile Fe(II) may be dependent on both the source and the extractant. PM2.5/
species at lower pH. Using a two-tailed t-test (95% confidence), we have found the bicarbonate solution consistently leached statistically similar or less Fe(II) than the NaCl and MQ leaches. This implies that pH may be a strong factor in the release of labile iron. In all samples (except the RAC SRM), the NaCl solution showed (t-test, 95% confidence) leachable Fe(II) similar to the Milli-Q leach. Therefore, iron leachability does not appear to be influenced by ion-exchange or chloride complexation, though more thorough investigations at varying ionic strengths would need to be conducted.

The nature of the Fe(III) in the extracts could either be of a thermodynamically truly dissolved species (Fe(III)aq) or as a colloid <0.2 μm in diameter (Fe(III)col). The limited solubility of Fe(III)aq in aqueous solutions could indicate that most of the dissolved Fe(III)aq (if present) in clean systems is present as a result of the oxidation of Fe(II) during the aqueous extraction process. Figures 3 and 4 show that soluble Fe(III) is a large and relatively consistent fraction (40–50%) of the total soluble iron, with the exception of the RAC, where Fe(III) makes up only about 2% of the total soluble Fe. If oxidation were the dominant mechanism producing Fe(III), then we would expect the RAC extracts to contain 40–50% Fe(III), as observed in most other samples. However, since only 2% of the soluble Fe in the RAC extract is Fe(III), the likely cause of the Fe(III) in all of our extracts is small colloidal Fe(III) particles which are subsequently reduced by the HA. Ambient aerosols (and NIST SRMs) have a very broad and heterogeneous size distribution and composition, both of which contribute to the presence of colloidal Fe(III) upon aqueous extraction.

Co-located filters from St. Louis were used to determine how rapid the soluble Fe(II) content of aerosols changes upon storage in a dark freezer. We found that, in storage, there is only a marginal decline in the Fe(II) content over 6 months. One sampling day (see Figure 2) showed no significant Fe(II) decline over six months and the other showed no significant loss over 3 months with only minor but significant (p = 0.007, α = 0.05) changes over 6 months. These data imply that Fe(II) loss in PM due to processes such as oxidation were the dominant mechanism producing Fe(III), then we would expect the RAC extracts to contain 40–50% Fe(III), as observed in most other samples. However, since only 2% of the soluble Fe in the RAC extract is Fe(III), the likely cause of the Fe(III) in all of our extracts is small colloidal Fe(III) particles which are subsequently reduced by the HA. Ambient aerosols (and NIST SRMs) have a very broad and heterogeneous size distribution and composition, both of which contribute to the presence of colloidal Fe(III) upon aqueous extraction.

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Table 3. Contributions of the Coarse Fraction to Fe(II) in Particles Collected in the Outlet of the Caldecott Tunnel Relative to Overall PM Concentration

<table>
<thead>
<tr>
<th>date (2004)</th>
<th>bore</th>
<th>extractant</th>
<th>Fe(II) emission (ng m⁻³)</th>
<th>Fe(II) concentration (ng m⁻³)</th>
<th>10% leachable Fe (as Fe(II))</th>
<th>PM2.5/PM10</th>
<th>PM10</th>
<th>PM2.5</th>
<th>PM10</th>
<th>PM2.5/PM10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aug 25</td>
<td>2</td>
<td>acetate</td>
<td>12.2 ± 0.7</td>
<td>760 ± 390</td>
<td>1.6 ± 0.9</td>
<td>0.57</td>
<td>36.7</td>
<td>43.7</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>Aug 26</td>
<td>2</td>
<td>bicarbonate</td>
<td>1.9 ± 0.4</td>
<td>1200 ± 500</td>
<td>0.2 ± 0.1</td>
<td>0.65</td>
<td>70</td>
<td>85.4</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>Aug 30</td>
<td>1</td>
<td>acetate</td>
<td>10.5 ± 1.8</td>
<td>890 ± 460</td>
<td>1.2 ± 0.8</td>
<td>0.55</td>
<td>80</td>
<td>94.3</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>Aug 31</td>
<td>1</td>
<td>acetate</td>
<td>6.4 ± 2.0</td>
<td>1200 ± 500</td>
<td>0.6 ± 0.4</td>
<td></td>
<td></td>
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</tbody>
</table>

a All filters were extracted in acetate buffer.

PM10 ratios for soluble Fe(II) and overall PM mass at the outlet of the Tunnel are compared in Table 3. These data show that a relatively small addition of coarse PM will result in a disproportionately large increase of soluble Fe(II).

**Discussion**

In this study, aspects of the aerosol chemistry of iron were probed using a range of chemical extractants and a modified version of the Fe(II)-sensitive Ferrozine method. The acetate buffer was the most efficient extractant of labile iron species, which is consistent with the greater solubility of many Fe-
(diesel versus gasoline) may affect the availability of iron in a given fluid.

Until now, application of the Ferrozine method to atmospheric PM has only been applied to aerosols in remote locations (26) and tests have not been performed where elevated iron levels are seen such as in urban areas and along major highways. Since the solubility and speciation of a metal likely have a major impact on its environmental fate, we feel that these measurements are necessary to better understand the atmospheric processing of aerosols and the role of iron red-ox chemistry on the transformations of other atmospheric contaminants. These experiments showed a wide range of Fe(II) solubility in pH 4.3 acetate buffer (0.01–13% of total iron) with the ambient samples from East St. Louis always showing the greatest fraction of labile Fe(II) (5–13% of total iron). This suggests that the PM collected from East St. Louis is in a more reduced state than the other samples analyzed in this study. The cause of the increased available iron could either be due to the varying sources in the area or reducing conditions present in the atmosphere. This results in a higher fraction of the iron becoming bioavailable and can have implications on human health (27).

Acknowledgments

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Supporting Information Available

Coal fly ash analysis results. This material is available free of charge via the Internet at http://pubs.acs.org.

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