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Inter-conversion of Chromium Species During Air Sampling: Effects of O₃, NO₂, SO₂, Particle Matrices, Temperature and Humidity

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Abstract

The inter-conversion between Cr(VI), a pulmonary carcinogen, and Cr(III), an essential human nutrient, poses challenges to the measurement of Cr(VI) in airborne particles. Chamber and field tests were conducted to identify the factors affecting Cr(VI)-Cr(III) inter-conversion in the basic filter medium under typical sampling conditions. In the chamber tests, isotopically enriched ⁵³Cr(VI) and ⁵⁰Cr(III) were spiked on diesel particulate matter (DPM) and secondary organic aerosol (SOA) that were pre-collected on a basic MCE filter. The filter samples were then exposed to clean air or the air containing SO₂ (50 and 160 ppb), 100 ppb O₃, or 150 ppb NO₂ for 24 hours at 16.7 LPM flow rate at designated temperature (20 and 31°C) and RH (40% and 70%) conditions. Exposure to 160 ppb SO₂ had the greatest effect on ⁵³Cr(VI) reduction, with ⁵³Cr(VI) recovery of 31.7 ± 15.8% (DPM) and 42.0 ± 7.9% (SOA). DPM and SOA matrix induced ⁵³Cr(VI) reduction when exposed to clean air while reactive oxygen species in SOA could promote ⁵⁰Cr(III) oxidation. Deliquescence when RH increased from 40% to 70% led to conversion of Cr(III) in SOA, whereas oxidized organics in DPM and SOA enhanced hygroscopicity and thus facilitated Cr(VI) reduction. Field tests showed seasonal variation of Cr(VI)-Cr(III) inter-conversion during sampling. Correction of the inter-conversion using USEPA method 6800 is recommended to improve accuracy of ambient Cr(VI) measurements.

Keywords

hexavalent chromium; trivalent chromium; inter-conversion; diesel exhaust particulate matter; secondary organic aerosol; ambient particulate matter

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1. Introduction

Hexavalent chromium (Cr(VI)) is a human pulmonary carcinogen [1-5], whereas trivalent chromium (Cr(III)) is an essential trace nutrient to human beings [1-5]. Based on the evidence from toxicological and occupational epidemiological studies, Cr(VI) has been listed as one of the 18 core hazardous air pollutants (HAPs) by the US EPA (USEPA, 2004). Therefore, accurate measurements of Cr(VI) in ambient air is needed to assess health effects associated with inhalation exposure to ambient Cr(VI).

Both Cr(VI) and Cr(III) are reactive species [6-8]. In aqueous environment, Cr(VI)-Cr(III) inter-conversion easily occurs in the presence of Fe(II), Fe(III), Mn(IV) and carboxylates [9-15]. The instability of Cr species between these two valence states will directly affect the accuracy of the measurement of Cr(VI) in ambient particulate matter (PM) [16-18]. As a result, efforts have been made to examine their inter-conversion during PM sampling and analysis. For instance, the conversion of Cr(III) and Cr(VI) was assessed by Sheehan et al. [19], Krystek et al. [20] and Li et al. [3]. In these studies, impingers filled with alkaline solutions were used for sampling. The Cr(VI) recoveries were reported to be 85 - 95% [3, 19, 20], while the conversions from Cr(III) to Cr(VI) were reported to be 2 - 13% [3, 19, 20]. Given the limitations of the cumbersome impinger technique, most air monitoring programs use filters to collect PM for the analysis of Cr species. Research Triangle Institute (RTI) [21] conducted a chamber study to characterize the stability of Cr(VI) and Cr(III) on blank filters when sampled with air containing a variety of gaseous pollutants. The Cr species were sprayed on blank polyvinyl chloride (PVC) filters. Noticeable reduction of Cr(VI) was only observed after exposure to SO₂, formaldehyde, m-xylene and propylene in the presence of H⁺ [21].

However, the RTI study was conducted on blank filters with neutral pH, and it did not include the effects of the PM matrix on Cr conversion. Possible PM matrix effects raise doubts about the observed Cr(VI)-Cr(III) inter-conversion, which may not fully represent the inter-conversion between Cr(VI) and Cr(III) in airborne PM where oxidants and reductants may be present. In addition, RTI [21], as well as Seigneur et al. [22], solely considered the effects of redox reagents that are common in aqueous chemistry on the inter-conversion between airborne Cr(VI) and Cr(III), which included but were not limited to Fe(II), Fe(III), SO₂, As, Mn(II), Mn(IV) and formic acid [21, 22]. Recent studies such as Werner et al. [23], Nico et al. [24] and Torkmahalleh et al. [25] reported the effects of atmospheric oxidants including HO₂, •OH and ozone (common reactive oxygen species (ROS) in the atmosphere) on Cr(VI)-Cr(III) speciation in fine PM during simulated atmospheric aging. Given such, it is important to investigate the association between ROS and Cr speciation during sampling, as ROS are prevalent redox reagents in atmosphere [26-28].

Since H⁺ can catalyze Cr(VI) reduction, basic, NaHCO₃-impregnated filters were recently used for ambient PM collection to preserve Cr(VI) [17, 18, 29]. For instance, Tirez et al. [16] used a NaHCO₃-impregnated, ashless, cellulose filter for PM collection and reported an average of 103% Cr(VI) recovery and <0.5% Cr(III) conversion in laboratory studies. Meng et al. [18] optimized the E.R.G. protocol [29] and utilized enriched isotope (⁵³Cr(VI) and ⁵⁰Cr(III)) spiked NaHCO₃-impregnated, mixed cellulose ester (MCE) filter for PM collection. The recovery of ⁵³Cr(VI) was on an average of 95% for blank filters and 89% for NIST 1648 particles coated on a filter [18]. The conversion from ⁵⁰Cr(III) to ⁵⁰Cr(VI) averaged 2.6% for blank filters and 5% for NIST 1648 particles coated on a filter [18]. When the basic filters were used for PM sampling in the field, both Cr(VI) recovery and Cr(III) oxidation showed large variation [16, 18]. These observations suggest that a variety of environmental factors promoted Cr(VI)-Cr(III) inter-conversion even using the basic

filter sampling medium, which can affect the measurement of Cr(VI) in ambient PM. However, inter-conversion between Cr(VI) and Cr(III) in airborne PM in the basic filter medium under typical sampling conditions is poorly understood. Identification of these factors would help improving sampling method to obtain accurate measurements of Cr(VI) in ambient PM.

The objective of this study was to examine the environmental factors affecting stability of Cr species in ambient PM in basic filter matrix under typical sampling conditions. Enriched isotope spikes ($^{53}\text{Cr(VI)}$ and $^{50}\text{Cr(III)}$) were used to monitor the Cr(VI)-Cr(III) inter-conversion. Controlled chamber and field experiments were conducted. The factors examined included major air pollutants, i.e. SO_2 , O_3 and NO_2 , as well as temperature, humidity, and PM type. For the PM type, diesel exhaust particulate matter (DPM) and secondary organic aerosol (SOA) were selected because they are two of the major types of ambient PM. SOA contains many ROS species such as hydroperoxides and organic peroxides [26, 30, 31], while DPM contains primarily reducing components. We attempted to understand the mechanisms underlying the observed transformation processes for chromium species. Suggestions for improvement of ambient Cr(VI) measurements are given at the end of this paper.

2. Experiment

2.1. Materials, reagents and instruments

Mixed cellulose ester filters (MCE, No support Pad, $0.8\ \mu\text{m}$, 47 mm, SKC Inc., Eighty Four, PA) were used for PM collection. The filter cleaning and treatment procedures are given by Meng et al. [18]. The Cr working standards were freshly prepared before sample analysis with deionized (DI) water ($18.2\ \text{M}\Omega$, Milli-Q system (Millipore, MA)), high purity natural abundance Cr(VI) standard (1000 ppm Cr(VI) in H_2O solution, 99.998%, High Purity Standards, Charleston, SC) and high purity natural abundance Cr(III) standard (1000 ppm Cr(III) in 2% HCl solution, 99.998%, High Purity Standards, Charleston, SC). Diluted enriched isotope spike solutions were prepared from stable isotope-enriched $^{50}\text{Cr(III)}$ and $^{53}\text{Cr(VI)}$ standard solutions ($10\ \mu\text{g/g}$, AIT Inc., Sunnyvale, CA). The gases used in the chamber tests included NO_2 (Certified Standard-Spec grade, Airgas Inc., Radnor, PA), SO_2 (Certified Standard-Spec grade, Airgas Inc., Radnor, PA) and O_3 (generated by OREC Ozone Generator, Ozone Research & Equipment Corporation). A Dionex ion exchange chromatography system with a GS50 gradient pump (Dionex, Bannockburn, IL) was used for Cr speciation. Cr species were analyzed using VG PlasmaQuad PQIII quadrupole ICPMS system (VG Instruments, Winsford, Cheshire, UK). The detailed analytical conditions of IC-ICPMS were given by Meng et al. [18].

2.2. Chamber study

2.2.1. Preparation of the test filter samples—Two types of PM, i.e. DPM and SOA, were used in the chamber study. A controlled environmental facility (CEF) was used for the lab tests. The description of the CEF as well as particle generation procedures have been previously reported [32, 33]. Briefly, DPM was generated by a 5500 Watt generator (Yanmar, Model YDG 5500EE), and SOA was generated by the reactions of *d*-limonene with O_3 . Generated DPM or SOA was diluted with clean air and driven into the $25\ \text{m}^3$ stainless steel environmental chamber [32, 33]. The clean air was filtrated through charcoal and HEPA filters, which removed PM, organics, NO_x , O_3 and SO_2 . The chamber background concentration was $< 3\ \text{ppb}$ for O_3 , and $< 20\ \text{ppb}$ for NO_x [32]. A 4-channel Partisol Speciation Samplers (Model 2300, Thermo Fisher Scientific) equipped with four PM_{10} cyclone cartridges was placed in the chamber. One MCE filter was loaded in each of the four channels to collect PM_{10} . After $\sim 300\ \mu\text{g/m}^3$ DPM or SOA was generated in the

chamber, sampling at 16.7 LPM was performed for 1.5 hours to collect ~0.4 mg DPM or SOA on each filter. The collected particle mass of 0.4 mg was similar to the mass of ambient PM samples. Isotopic Cr species (100 ng each of $^{50}\text{Cr(III)}$ and $^{53}\text{Cr(VI)}$) were spiked on the PM using an automatic pipette (50 μL each of 2 ng/ μL $^{53}\text{Cr(VI)}$ and $^{50}\text{Cr(III)}$ solutions). Isotope spikes were made to enable Speciated Isotopically Dilution Mass Spectrometry (SIDMS, US EPA 6800) to assess the inter-conversion between Cr(VI) and Cr(III) during sampling and extraction. Details of the assessment procedure are described in *Sample and data analysis*. The spiked filters were stored in a freezer (-10°C) for 4 days before chamber tests.

2.2.2. Laboratory tests—The prepared filters described above were used for test in the chamber under different experimental conditions (see Table 1). The air in the chamber contained 100 ppb O_3 , 160 ppb SO_2 , and 150 ppb NO_2 , which are the upper-bound ambient concentrations found in New Jersey [34]. Temperature, humidity, and air exchange rate (AER) were controlled during experiments (see Table 1) [32]. Another test was conducted at a lower SO_2 concentration (50 ppb) to confirm the observed reduction of $^{53}\text{Cr(VI)}$ spiked on SOA after the 24-hour exposure to 160 ppb SO_2 . Fifty ppb is the health standard for ambient SO_2 recommended by the American Lung Association [35]. The effects of high temperature (31°C) and RH (70%, the highest RH that could be achieved when the tests were conducted) were also examined.

Prior to the test, the DPM and SOA filter samples (spiked with isotope species) were loaded in two 4-channel PM samplers (Partisol 2300) placed inside the chamber. During the test, constant concentrations of the test gases (i.e. SO_2 , NO_2 and O_3) were maintained by continuously injecting the gases into the inlet stream. The concentrations of NO_2 , SO_2 , and O_3 were monitored by a $\text{NO-NO}_2\text{-NO}_x$ analyzer (Model 42C, Thermo Scientific), Pulse Fluorescence SO_2 analyzer (Model 43A, Thermo Scientific), and O_3 analyzer (Model 49i, Thermo Scientific), respectively. After achieving the test conditions, sampling was conducted at a flow rate of 16.7 LPM for 24 hours, a typical sampling period for ambient PM monitoring. The chamber was kept dark during experiments. The control samples (CA) were prepared in the same manner as the exposed samples but were not used for sampling. Filter controls (CAF) were prepared by directly spiking isotope species on blank filters. Both control and exposed samples were stored frozen and analyzed within 4 days. Previous lab evaluations showed that both Cr(VI) and Cr(III) are stable for up to 120 days when stored frozen [18].

2.2.3. Field study—The field test was conducted in 7 days between August 20 and September 22, 2008 and 7 days between February 9 and March 2, 2009 in Rahway, NJ (see Table 2). Rahway is an urban area typical of the northeast corridor of New Jersey. There are both mobile and stationary industrial sources of Cr in the surrounding area.

Two 4-channel Partisol Speciation Samplers (Model 2300, Thermo Fisher Scientific) with PTFE-coated inlets were deployed in the sampling site to collect ambient PM_{10} . NaHCO_3 -pretreated MCE filter was used for PM collection. The sampling flow rate was 16.7 LPM, with variations $< 5\%$ during 24-hour sampling period from midnight to midnight. Enriched isotope spikes ($^{53}\text{Cr(VI)}$ and $^{50}\text{Cr(III)}$) were added to four types of samples to assess Cr(VI)-Cr(III) inter-conversion. Two duplicate filter samples were spiked with 100 ng each of $^{53}\text{Cr(VI)}$ and $^{50}\text{Cr(III)}$ just before field sampling (BS) to evaluate the potential Cr inter-conversion during the entire sampling and analytical process. The same spike procedures as the chamber tests were used. Two duplicate filter samples were spiked with isotopic Cr species immediately after sampling (AS) to evaluate Cr inter-conversion during extraction and analysis. The differences in recovery and conversion of Cr species between BS and AS indicate the influence of sampling and exposure to outdoor environment on Cr stability.

Meanwhile, two types of control samples were prepared, lab controls (CA-L), which were spiked with isotopes but stored in freezer immediately after spike, and field controls (CA-F), which were spiked with isotopes but were exposed to outdoor environment during the sampling period. The differences in recovery and conversion of Cr species between CA-L and CA-F indicate the influence of exposure to outdoor environment on Cr stability. The differences in recovery and conversion of Cr species between BS and CA-F indicate the influence of sampling process on Cr stability, while the differences between AS and CA-L indicate the effects of PM matrix on Cr stability. A Davis Weather Monitor II system (Hayward, CA) was used to record temperature and RH.

2.3. Sample and data analysis

All samples were extracted with 5 mL pH = 4 HNO₃ solution and analyzed for ⁵⁰Cr(VI), ⁵³Cr(VI), ⁵⁰Cr(III) and ⁵³Cr(III) by IC-ICPMS. The detailed extraction and analytical conditions are given by Meng et al. [18]. We want to note that the final pH of the extraction solution was actually ~9.0 due to basic NaHCO₃-impregnated MCE filters. The Cr(VI)-Cr(III) inter-conversion in both the chamber and field tests was assessed using the SIDMS method. Table 2 and Table 3 present the ratios of measured ⁵³Cr(VI)/spiked ⁵³Cr(VI), measured ⁵³Cr(III)/spiked ⁵³Cr(VI), measured ⁵⁰Cr(III)/spiked ⁵⁰Cr(III) and measured ⁵⁰Cr(VI)/spiked ⁵⁰Cr(III) in the chamber and the field tests. The measured ⁵³Cr(VI)/spiked ⁵³Cr(VI) represents the fraction of ⁵³Cr(VI) that remained in the hexavalent state under the experimental conditions, and is called the ⁵³Cr(VI) recovery. These ratios show the extent of Cr(VI) reduction, which would result in negative error in Cr(VI) measurement. The measured ⁵⁰Cr(VI)/spiked ⁵⁰Cr(III) ratio shows the fraction of ⁵⁰Cr(III) that was converted from trivalent to hexavalent state under these experimental conditions, and is the ⁵⁰Cr(III) to ⁵⁰Cr(VI) conversion. These ratios show the extent of Cr(III) oxidation, which would result in positive error in Cr(VI) measurement. A significant portion of ⁵³Cr(III) that was converted from ⁵³Cr(VI) would precipitate in the basic MCE filters, and the precipitated ⁵³Cr(III) is resistant to conversion [17]. Therefore, the sum of the measured ⁵³Cr(VI) and ⁵³Cr(III) was lower than the spiked amount. Similarly, the sum of the measured ⁵⁰Cr(III) and ⁵⁰Cr(VI) was also lower than the spiked amount due to precipitation of ⁵⁰Cr(III). Given such, the measured ⁵³Cr(III)/spiked ⁵³Cr(VI) and ⁵⁰Cr(III)/spiked ⁵⁰Cr(III) are not equivalent to conversion from ⁵³Cr(VI) to ⁵³Cr(III) and recovery of ⁵⁰Cr(III), respectively.

The ⁵⁰Cr(III) spike used in our tests is soluble Cr(III) (chemical form: Cr(NO₃)₃). Cr(III) in ambient air have different chemical forms. Werner et al. [36] and Tirez et al. [16] reported insoluble Cr(III), such as Cr₂O₃, Cr-Fe spinel and aged Cr(OH)₃, constituted the majority of the Cr(III) in ambient PM collected in their studies. Insoluble Cr(III) compounds are resistant to oxidation under environmental and our extraction conditions [5, 22]. Thus, the conversion from ⁵⁰Cr(III) to ⁵⁰Cr(VI) can only occur for soluble Cr(III) in airborne PM. Ambient PM contains trace Cr(VI) and Cr(III), including ⁵⁰Cr(III) and ⁵³Cr(VI). However, the ⁵⁰Cr(III) and ⁵³Cr(VI) that are originally in airborne PM will not affect the calculation of Cr(VI)-Cr(III) inter-conversion using isotope spikes in our study because those levels are much lower than the amount spiked on the filters (explanation shown in Supporting Information).

Non-parametric Kruskal-Wallis one-way analysis of variance (ANOVA) was conducted to examine the effects of exposure conditions and PM type on Cr stability in the chamber study as well as the impacts of sample type and seasonal change on Cr stability in the field study. All statistical analyses were performed with SAS (v 9.0, Cary, NC).

3. Results and Discussion

The recovery of $^{53}\text{Cr(VI)}$ varied from 31% to 90% in the chamber tests (Table 2 and Figure S1) and from 51% to 100% in the field study (Table 3). The conversion from $^{50}\text{Cr(III)}$ to $^{50}\text{Cr(VI)}$ varied from 9.5% to 68.8% in the chamber (Table 2 and Figure S2) and from 11% to 27% in the field (Table 3). The effects of different factors on Cr conversion are discussed below.

3.1 Effects of tested factors on the stability of Cr species: chamber study

a. PM type—The clean air in the chamber contained nothing that can react with the Cr. Therefore, any redox transformation due to exposure to clean air + 40% RH + 20°C was promoted by PM matrix. As shown in Table 2, the recoveries of $^{53}\text{Cr(VI)}$, which was spiked on the DPM and SOA filter samples and was exposed to clean air + 40% RH + 20°C for 24 hours, were $63.8 \pm 6.5\%$ (Mean $\pm$ SD, N = 3) and $57.0 \pm 6.9\%$ (N = 4), respectively. The two values were significantly ($p < 0.01$) lower than the corresponding control samples (CA) ($83.3 \pm 4.5\%$ for the DPM control (N = 5), $82.1 \pm 6.5\%$ for the SOA control (N = 7)). Thus, the DPM and SOA matrix were observed to reduce Cr(VI). The Cr(VI) reduction reactions involving particle-phase substances primarily occurred in liquid layer of DPM and SOA [37]. The use of basic filter, however, could not prevent Cr(VI) reduction that was promoted by PM matrix.

The conversion of $^{50}\text{Cr(III)}$ in SOA significantly ($p < 0.01$) increased after exposure to clean air + 40% RH + 20°C ($50.0 \pm 4.5\%$, N = 3) when compared to the SOA control samples ($30.0 \pm 9.3\%$, N = 7). The conversion from $^{50}\text{Cr(III)}$ to $^{50}\text{Cr(VI)}$ in the DPM matrix, however, did not increase significantly. In addition, the conversion from $^{50}\text{Cr(III)}$ to $^{50}\text{Cr(VI)}$ for the SOA samples in our study was significantly ($p < 0.01$) greater than the DPM samples. The Cr(III) oxidation in SOA was probably due to the presence of reactive oxygen species (ROS) in SOA. It was reported that ROS contribute to between 47% and 85% of SOA mass [26, 27, 30, 31]. Terpene- O_3 generated ROS contain hydroxyl, hydroperoxyl and epoxyl functional groups [25, 30], which oxidized Cr(III) to Cr(VI) [25]. Given that the SOA samples were stored frozen (-10°C) for 4 days before the exposure experiments, the residual ROS were the stable ones (e.g. organic peroxides and hydroperoxides) rather than the short-lived and unstable ROS such as $\cdot\text{OH}$ [26, 27].

These results suggested competing redox reaction pathways for Cr in basic filter medium, i.e. some SOA matrix components (e.g. organic carbons) could promote Cr(VI) reduction whereas some others (e.g. stable ROS) could induce Cr(III) concurrent oxidation. Two recent studies [24, 25] reported similar pathways, although different environmental processes were studied and the PM compositions were very different. Nico et al. [24] reported bidirectional Cr reactions in ultrafine PM comprised of transition metals (e.g. Cr, Fe, and Mn) during simulated atmospheric aging. Torkmahalleh et al. [25] reported similar competing redox reaction pathways when exposing basic filters spiked with Cr(VI) and Cr(III) to O_3 or α -pinene generated ROS under dry conditions. Given the prevalence of SOA in atmosphere, the competing redox reaction pathways could affect Cr in ambient PM during sampling. As a result, a critical part of ambient Cr(VI) measurements would be the simultaneous assessment of Cr(VI) reduction and Cr(III) oxidation, the advantage of the SIDMS technique.

b. SO_2 —Exposure to 160 ppb SO_2 resulted in the largest reduction of $^{53}\text{Cr(VI)}$, with recovery of $31.7 \pm 15.8\%$ (N = 3) for DPM samples and $42.0 \pm 7.9\%$ (N = 4) for SOA samples. The two values were significantly ($p < 0.01$) lower than those from exposure to clean air. The effect of SO_2 on $^{53}\text{Cr(VI)}$ reduction was still significant even at exposure to the lower SO_2 concentration (50 ppb), with only $42.0 \pm 7.0\%$ recovery of the $^{53}\text{Cr(VI)}$

spiked on SOA. Dose-response relationship was not observed at the two exposure levels of SO₂. This is because only Cr(VI) atoms on the surface of the crystals formed when the spike solution dried can react, so that the extent of reduction is dependent on the availability of Cr(VI) atoms to react and not on the reductant concentration. An analogous situation occurred in Torkmahalleh et al. [25], which showed that reaction of Cr spiked on a filter achieved a maximum level of conversion within a few hours.

These results suggested that SO₂ can reduce Cr(VI) in airborne PM during sampling. The Cr(VI)-S(IV) redox reaction occurred under basic conditions (pH ~ 9.0) in our study. Thus, the reaction mechanisms governing the redox reactions may be different from that suggested for typical atmospheric aerosol with pH values < 6, which involves the production of SO₄²⁻ and S₂O₆²⁻ (Equation 1) [22, 37]:

The major forms of Cr(VI), S(IV) and converted Cr(III) should be CrO₄²⁻, SO₃²⁻ and Cr(OH)₃, respectively, under basic conditions based on Equations 2 to 5 [22, 37]:

The standard electrode potentials (E⁰) for the related reaction couples under basic conditions [38] are:

The E⁰ for the S₂O₆²⁻/SO₃²⁻ couple is greater than the CrO₄²⁻/Cr(OH)₃·n H₂O couple, and the E⁰ of the SO₄²⁻/SO₃²⁻ couple is lower than the CrO₄²⁻/Cr(OH)₃·n H₂O couple. Therefore, SO₄²⁻ is likely the oxidized product of S(IV) under our test conditions. Thus, the possible mechanism behind the Cr(VI) – S(IV) redox reaction in our study is:

The Gibbs free energy change at standard state (ΔG⁰) for Equation 9 was calculated as -246.3 kJ/mol from the Gibbs free energy of formation at standard state (ΔG_f⁰) for each

component in Equation 9 [39]. The negative ΔG^0 indicates that this reaction is spontaneous at standard state conditions. Given the large negative value of ΔG^0 , the changes of pH and concentrations of each component in Equation 9 within a reasonable range would not alter the reaction direction. Thus, the Cr(VI) reduction in ambient PM during sampling, induced by SO₂, cannot be completely prevented through the use of a weak basic filter medium.

c. O₃ and NO₂—Exposure to 150 ppb NO₂ or 100 ppb O₃ + clean air + 40% RH + 20°C in our chamber study did not result in any significant redox transformations of ⁵³Cr(VI) or ⁵⁰Cr(III), when compared to clean air + 40% RH + 20°C. The results suggested that NO₂ and O₃ alone could not promote the redox transformations of Cr species in airborne PM in the dark under our sampling conditions. This finding agreed with the RTI study with respect to O₃ effect, in which simultaneous exposure to O₃ and KMnO₄ without illumination did not induce the oxidation of Cr(III) that was sprayed on PVC filters [21]. However, a small amount of Cr(III) oxidation when exposed to very high O₃ was observed by Torkmahalleh et al. [25].

d. Temperature and RH—The recoveries of ⁵³Cr(VI) in both DPM and SOA after exposure to clean air + 31°C + 70% RH were not significantly different from clean air + 20°C + 40% RH. The conversion of ⁵⁰Cr(III) in SOA after exposure to clean air + 31°C + 70% RH, was $68.8 \pm 6.1\%$ (N = 3), significantly (p = 0.02) higher than exposure to clean air + 20°C + 40% RH, $50.0 \pm 4.5\%$ (N = 3). The difference in ⁵⁰Cr(III) conversion between the two conditions, however, was not significant on DPM. The greater conversion of ⁵⁰Cr(III) in SOA was primarily due to increased humidity. The deliquescence relative humidity (DRH) of Cr(NO₃)₃ (the chemical form of ⁵⁰Cr(III) spike) is 52% at room temperature (25°C) [17]. At 70% RH, ⁵⁰Cr(III) may deliquesce. The resulting water would facilitate ⁵⁰Cr(III) reactions [17]. As previously discussed, the stable ROS in SOA likely promoted the observed conversion of ⁵⁰Cr(III) in SOA. The DRH of K₂Cr₂O₇ (the chemical form of ⁵³Cr(VI) spike) is 94% at room temperature [17]. Thus, limited deliquescence was expected to occur for Cr(VI), and such RH increase would not lead to aqueous Cr(VI) reactions. As a result, no significant further ⁵³Cr(VI) reduction was observed when RH was increased from 40% to 70%.

However, some PM matrix components could indirectly facilitate the inter-conversion between Cr(VI) and Cr(III) in basic sampling medium by enhancing PM deliquescence. For instance, the RH (i.e. 40% and 70%) in our study was lower than the DRH of Cr(VI). However, significant reduction of ⁵³Cr(VI) was still observed after the 24-hour exposure to clean air when compared to control samples. Some of the oxidized organic species in DPM and SOA, such as carboxylic acids, could enhance the hygroscopicity of airborne PM [17, 40-42]. Enhanced hygroscopicity in turn facilitate reduction of Cr(VI) by reductants in the airborne PM. The absence of PM matrix in the RTI study [21] resulted in limited hygroscopicity. The lack of an aqueous phase resulted in no Cr(VI) reduction under neutral sampling condition even in the presence of SO₂, formaldehyde, m-xylene and propylene. Given such, humidity control is a potential measure that will stabilize Cr(VI) and Cr(III) under basic sampling condition.

3.3 Stability of Cr species in the field

⁵³Cr(VI) recoveries for the field controls (CA-F), i.e. $67.4 \pm 6.6\%$ (Mean $\pm$ SD, N = 4) in summer and $80 \pm 12.0\%$ (N = 7) in winter, were significantly (p < 0.01) lower than the lab control (CA-L) for the field study (~100%, Table 3). As explained previously, this difference indicated that the reduction of Cr(VI) occurred when Cr(VI) was exposed to the ambient environment. The recovery of ⁵³Cr(VI) spiked on the blank filters prior to sampling (BS), i.e. $51.5 \pm 16.1\%$ (N = 7) in summer and $68.0 \pm 17.1\%$ (N = 7) in winter, were

significantly ($p < 0.01$) lower than the recovery of $^{53}\text{Cr(VI)}$ spiked on the ambient PM samples post sampling (AS) ($63.2 \pm 8.1\%$ ($N = 7$) in summer and $82.0 \pm 18.0\%$ ($N = 7$) in winter) and the $^{53}\text{Cr(VI)}$ recovery for CA-F. As previously discussed, the differences in Cr(VI) recovery between BS and AS, between BS and CA-F, indicated that ambient sampling process led to significant Cr(VI) reduction. Based on the chamber and the field results, a basic filter collection medium cannot prevent Cr(VI) in ambient PM from being reduced during air sampling.

The PM matrix played an important role in the observed Cr(VI) reduction. The $^{53}\text{Cr(VI)}$ recovery for AS was significantly ($p < 0.01$) lower than CA-L. As discussed above, this difference indicated the effects of PM matrix on Cr(VI) reduction. The results were in agreement with the chamber study with respect to the effects of the PM matrix on the Cr(VI) stability,

These results also agree with Tirez et al. [16] and Meng et al. [18] with respect to sampling-induced reduction. The recoveries of Cr(VI) in Meng et al. [18] were $57 \pm 9\%$ for spike prior to sampling and $67 \pm 23\%$ for spike post sampling. The average recoveries of Cr(VI) in Tirez et al. [16] were 75%, with a range of 33 - 103%. Seasonal differences were not reported in these two studies. The Cr(VI) recoveries varied in our study, Meng et al. [18] and Tirez et al. [16]. This is because environmental factors affecting Cr(VI) reduction, e.g., SO_2 , PM matrix and humidity identified in the chamber, varied largely day-by-day. As a result, in-situ monitoring of Cr(VI) reduction is needed to obtain accurate concentration values.

The conversion from $^{50}\text{Cr(III)}$ to $^{50}\text{Cr(VI)}$ was in the range of 19.4% - 27.1% in the summer and 11.0% - 21.0% in the winter, and there was no significant difference in $^{50}\text{Cr(III)}$ conversion among the 3 types of samples (i.e. CA-F, BS and AS). The results implied that ambient sampling process had minor effects on Cr(III) conversion. The average conversion from Cr(III) to Cr(VI) in Meng et al. [18] was $17 \pm 9\%$ for spike prior to sampling and $11 \pm 5\%$ for spike post sampling, which are similar to the values in the present study. It is within expectation as a) the same sampling and extraction conditions were used and b) aerosol properties would be similar given geographic proximity between Rahway and Paterson where Meng et al. [18] implemented the fieldwork. The Cr(III) conversions are much lower in Tirez et al. [16], i.e. 0.4 - 3.1%. Differences in aerosol properties, sampling and extraction conditions may result in the differences in the observed Cr(III) conversion.

Seasonal effects on the $^{53}\text{Cr(VI)}$ recovery and $^{50}\text{Cr(III)}$ conversion were significant ($p < 0.01$). The $^{53}\text{Cr(VI)}$ recoveries for CA-F, AS and BS obtained in summer were significantly lower than in winter; while the conversions from $^{50}\text{Cr(III)}$ to $^{50}\text{Cr(VI)}$ for CA-F, AS and BS obtained in summer were also greater than in winter. These observations may have several causes. First, most chemical reactions proceed faster at higher temperature. Second, water vapor in atmosphere may condense during summer nights when ambient temperature drops below the dew point. Ambient PM deliquesces under condensing conditions, and the resulting aqueous phase facilitates Cr reactions. Water in atmosphere may freeze during winter nights when the ambient temperature is below the frost point. The lack of a liquid layer stabilizes Cr species [1]. Third, more intense photochemical activities in the summer produce elevated O_3 and other oxidants in the atmosphere [23, 26, 27, 32, 43]. Our chamber study, as well as Nico et al. [24], Werner et al. [23] and Torkmahalleh et al. [25], suggested that ROS can promote the inter-conversion between Cr(III) and Cr(VI). Therefore, the inter-conversion between Cr(III) and Cr(VI) would be more active in summer.

4. Implications and recommendation

Both Cr(VI) and Cr(III) are reactive even in basic sampling medium under typical sampling conditions. Our chamber study characterized concurrent, competing Cr reactions that affect speciation during sampling with basic filters, i.e. one pathway drives Cr(VI) reduction while the other drives Cr(III) oxidation. A suite of interrelated environmental factors that affect competing Cr speciation was identified in the chamber studies, including SO₂, stable ROS, oxidizable PM matrix components, temperature, and humidity. Cr speciation under basic matrix depends on the oxidative capacity of PM matrix: reducing components drive Cr(VI) reduction, whereas stable ROS such as organic peroxides drive Cr(III) oxidation. Oxidized organic species may enhance the hygroscopicity of the PM and facilitate Cr(VI)-Cr(III) inter-conversion even when RH is below DRH of the Cr compounds. This combination of factors lead to Cr(VI) reduction and Cr(III) oxidation with significant day-to-day and seasonal variations in the field. The use of basic, NaHCO₃-pretreated filter medium will not prevent Cr(VI) reduction under sampling conditions. Thus, optimization of the sampling method is needed to prevent conversion of Cr species during sampling process. For instance, installation of a dehumidifier to remove moisture, a cooling system to keep the filter sample at low temperature, and a denuder to remove reactive gases such as SO₂ could be considered.

The competing redox reactions of Cr(VI) and Cr(III) as well as significant day-to-day and seasonal variations of Cr(VI)-Cr(III) inter-conversion have two major implications on ambient Cr(VI) measurements: (1) simultaneous assessment of Cr(VI) recovery and Cr(III) conversion is necessary. However, the two issues were usually separately assessed in previous monitoring campaign; (2) in-situ assessment of Cr(VI) recovery and Cr(III) conversion is important. However, the two indices were not usually assessed on daily basis in previous monitoring programs. The SIDMS method would be one promising approach to improve the measurement accuracy since enriched isotope (⁵³Cr(VI) and ⁵⁰Cr(III)) can be applied to the samples to allow simultaneous monitoring of Cr(VI) reduction and Cr(III) oxidation.

However, there are still concerns regarding the use of the SIDMS method. The critical prerequisite for using this method is that the spiked isotope species should have the same chemical properties as the target elements in the samples such that the spiked species mimic the species in the air samples [6, 44]. Cr(III) in ambient PM may not be in the same chemical form as the spiked ⁵⁰Cr(III) as previously discussed. Cr(III) conversion is closely associated with its solubility [22]. Insoluble Cr(III) compounds are chemically inert and resistant to oxidation [5, 22]. As a result, conversion of the spiked soluble ⁵⁰Cr(III) may not reflect conversion of ambient Cr(III), which are mainly insoluble species. Composition of ambient Cr(III) and its conversion under sampling and extraction conditions need to be examined prior to Cr(VI) concentration correction via SIDMS method. The work about Cr(III) solubility on conversion will be reported in future publication .

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Table 1

Chamber test conditions

Experiment round	Exposure Condition ^a	<u># of sample filters^b</u>	
		SOA	DPM
1	150 ppb NO ₂	4	3
2	100 ppb O ₃	4	3
3	160 ppb SO ₂	4	3
4	50 ppb SO ₂	4	N/A ^c
5	Clean air	3	3
6	T = 31 °C, RH = 70%	3	3
CA	Control samples (Stored at -10 °C)	7	5
CAF	Filter control (Stored at -10 °C)	10	

^aT = 20 °C, RH = 40% was set for experiment 1-5.

^bSample filters with DPM/SOA particles were spiked with 50 µl 2 ng/µl ⁵³Cr(VI) and 50 µl 2 ng/µl ⁵⁰Cr(III).

^cNo further tests were conducted for Cr(VI) spiked on DPM at the SO₂ of 50 ppb condition.

Table 2Effects of O₃, NO₂, SO₂ and high T&RH on the stability of Cr species^{a,b}

Exposure Condition	⁵³ Cr(VI) ^c				⁵⁰ Cr(III) ^c			
	Measured ⁵³ Cr(VI)/Spiked ⁵³ Cr(VI) ^d		Measured ⁵³ Cr(III)/spiked ⁵³ Cr(VI)		Measured ⁵⁰ Cr(III)/Spiked ⁵⁰ Cr(III)		Measured ⁵⁰ Cr(VI)/Spiked ⁵⁰ Cr(III) ^e	
	DPM	SOA	DPM	SOA	DPM	SOA	DPM	SOA
CAF ^f	89.7±3.7		0.2±0.4		2.7±2.2		15.4±6.3	
CA ^f	83.3±4.5	82.1±6.5	1.4±0.3	1.2±0.9	5.2±2.4	3.7±1.6	9.5±2.5	30.0±9.3
Clean air	63.8±6.5	57.0±6.9	0.4±0.3	1.0±0.7	1.7±0.3	2.0±0.4	19.3±3.2	50.0±4.5
150 ppb NO ₂	57.3±2.3	63.3±5.7	1.5±0.6	2.2±1.2	2.5±0.3	2.5±0.3	23.7±5.1	59.4±11.0
160 ppb SO ₂	31.7±15.8	42.0±7.9	2.4±1.7	2.6±0.5	1.3±1.1	1.8±0.7	22.5±13.6	30.7±7.5
50 ppb SO ₂	N/A	42.0±7.0	N/A	7.1±1.6	N/A	6.0±0.0	N/A	23.6±1.8
100 ppb O ₃	67.2±1.3	50.0±6.4	2.0±0.5	3.4±1.8	3.3±2.5	3.0±1.0	20.9±2.9	27.2±6.0
High T/RH	60.7±2.6	64.7±4.6	1.3±0.1	2.0±0.5	4.3±0.6	2.3±0.1	22.4±0.8	68.8±6.1

^aThe concentration of NO₂, SO₂ and O₃ was 150, 160 and 100 ppb, respectively. The temperature was set as 20 °C and RH at 40% except the condition of high T&RH in which temperature and RH were set as 31°C and 70%.

^bAll values in Table 2 are expressed as Mean±SD

^cThe number of replicates for each type is presented in Table 1

^dThe values are also phrased as recovery of ⁵³Cr(III)

^eThe values are also phrased as conversion from ⁵⁰Cr(III) to ⁵⁰Cr(VI)

^fThe CAF samples were not pre-loaded with airborne particles, but the CA samples were pre-loaded with ~0.4 mg airborne particles

Table 3

The $^{53}\text{Cr(VI)}$ recovery and conversion from $^{50}\text{Cr(III)}$ to $^{50}\text{Cr(VI)}$ (Mean $\pm$ SD) in the field study

Season	Temperature (°C)	RH (%)	Sample type	Number	Recovery of $^{53}\text{Cr(VI)}$ (%)	Conversion from $^{50}\text{Cr(III)}$ to $^{50}\text{Cr(VI)}$ (%)
Winter	2.6 ± 5.4 (N = 7)	47.1 ± 15.4 (N = 7)	BS	14	68.0 ± 17.1	21.0 ± 8.7
			AS	14	82.0 ± 18.0	11.0 ± 5.9
			CA-F	7	80.0 ± 12.0	17.0 ± 4.6
			CA-L	6	100 ± 6	14.0 ± 2.0
Summer	21.9 ± 3.3 (N = 6)	59.5 ± 7.8 (N = 5)	BS	13	51.5 ± 16.1	19.7 ± 6.7
			AS	13	63.2 ± 8.1	27.1 ± 6.4
			CA-F	4	67.4 ± 6.6	21.9 ± 6.2
			CA-L	7	100 ± 11	19.6 ± 6.8

CAL: lab control samples, i.e. filters were pre-spiked with isotopes and stored in the freezer until analysis

CAF: field control samples, i.e. filters were pre-spiked with isotopes, taken to the field, loaded in cartridges but did not undergo sampling

AS: samples spiked with isotopes post field sampling

BS: samples spiked with isotopes prior to field sampling

Sampling dates: 08/20/2008, 08/25/2008, 09/03/2008, 09/08/2008, 09/15/2008, 09/17/2008, 09/22/2008, 2/9/2009, 2/11/2009, 2/16/2009, 2/18/2009, 2/23/2009, 2/25/2009, 3/2/2009