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Trends in PM_{2.5} transition metals in urban areas across the United States

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Abstract

Using data from the Environmental Protection Agency's Chemical Speciation Network, we have characterized trends in PM_{2.5} transition metals in urban areas across the United States for the period 2001–2016. The metals included in this analysis—Cr, Cu, Fe, Mn, Ni, V, and Zn—were selected based upon their abundance in PM_{2.5}, known sources, and links to toxicity. Ten cities were included to provide broad geographic coverage, diverse source influences, and climatology: Atlanta (ATL), Baltimore (BAL), Chicago (CHI), Dallas (DAL), Denver (DEN), Los Angeles (LA), New York City (NYC), Phoenix (PHX), Seattle (SEA), and St. Louis (STL). The concentrations of V and Zn decreased in all ten cities, though the V decreases were more substantial. Cr concentrations increased in cities in the East and Midwest, with a pronounced spike in concentrations in 2013. The National Emissions Inventory was used to link sources with the observed trends; however, the causes of the broad Cr concentration increases and 2013 spike are not clear. Analysis of PM_{2.5} metal concentrations in port versus non-port cities showed different trends for Ni, suggesting an important but decreasing influence of marine emissions. The concentrations of most PM_{2.5} metals decreased in LA, STL, BAL, and SEA while concentrations of four of the seven metals (Cr, Fe, Mn, Ni) increased in DAL over the same time. Comparisons of the individual metals to overall trends in PM_{2.5} suggest decoupled sources and processes affecting each. These metals may have an enhanced toxicity compared to other chemical species present in PM, so the results have implications for strategies to measure exposures to PM and the resulting human health effects.

Introduction

Transition metals often contribute to atmospheric particulate matter (PM) mass, frequently at trace concentration levels. Transition metals in PM, which include V, Cr, Mn, Fe, Co, Ni, Cu, Zn, are derived from numerous and diverse sources [1]. Wind-blown dust is the largest natural source of PM metals [2, 3]. Major anthropogenic sources of metals include motor vehicles (tailpipe and non-tailpipe emissions) [4–7], coal and fuel oil combustion [8, 9], biomass burning [10], municipal incinerators [11], metallurgical processes [12], and other industrial activities [9]. Knowledge of metal sources has led to the widespread

application of receptor modeling to apportion ambient PM to its sources [13, 14].

PM_{2.5} imparts numerous deleterious effects on human health [15, 16]. While this finding is now widely accepted, there is considerable uncertainty associated with the physiological mechanisms by which PM affects health, and differences in the toxicity of specific chemicals found in PM [17]. Despite their low abundance compared to other species, evidence suggests metals have an enhanced toxicity compared to other compounds [18–20]. Transition metals in PM have been extensively associated with reactive oxygen species (ROS) generation [5, 21–24]. Metals can catalyze ROS generation through mechanisms that involve

Table 1. Overview of AQI sites represented in this analysis.

City	City code	AQI site	AQIID
Atlanta, GA	ATL	South Dekalb	840130890002
Baltimore, MD	BAL	Essex	840240053001
Chicago, IL	CHI	Com Ed Maintenance Bldg.	840170310076
Dallas, TX	DAL	Dallas Hinton	840481130069
Denver, CO	DEN	Alsup Elementary School	840080010006
Los Angeles, CA	LA	LA—North Main Street	840060371103
New York City, NY	NYC	Queens College (2)	840360810124
Phoenix, AZ	PHX	JLG Supersite	840040139997
Seattle, WA	SEA	Seattle—Beacon Hill	840530330080
St. Louis, MO	STL	Blair Street	840295100085

both their soluble and insoluble forms [4, 22, 25–27]. Increased production of ROS within cells can lead to oxidative stress, which has been linked to numerous adverse health outcomes [28–31]. This offers a plausible explanation for why transition metals, although they make a minor contribution to PM_{2.5} mass (e.g. Rees *et al* [32]), are frequently identified as elevated relative risk factors in epidemiological studies [33].

PM_{2.5} concentrations in the United States have steadily decreased over the past 30 years in response to regulations that have limited emissions of PM and its precursors [34]. Energy pricing that has shifted substantial electricity generation from coal to natural gas has also contributed to regional and national air quality improvements [35, 36]. Many studies have characterized temporal trends in sulfate, nitrate, ammonium, and carbonaceous compounds—the major components of PM_{2.5} mass—across different regions of the US [37–44]. However, due to their typically minor contribution to PM mass, atmospheric trends in transition metals have not been closely studied. Spada *et al* [45] characterized the effects of a recent regulation that reduced marine fuel-S content on emissions of V and Ni. Since their focus was on shipping emissions of V, their analysis compared coastal and inland sites, but only for two years (2011 versus 2015) that represent periods before and after the fuel regulations were in place. Although their study only compares two years, Spada *et al* [45] demonstrate that sources that may have a minor effect on total PM_{2.5} concentrations can impart a large effect on atmospheric metals.

The purpose of this study is to examine the trends in PM_{2.5} transition metals in urban areas across the United States. We focus on transition metals that are abundant in PM, have well-known sources, exhibit toxicity and/or catalyze ROS formation. These elements include V, Cr, Mn, Fe, Ni, Cu, and Zn. We have selected ten urban areas for this analysis, each with at least a 15-year record of metal speciation in PM_{2.5}. The urban areas have broad diversity in geographic location, climatology, and source influences: Atlanta, GA (ATL), Baltimore, MD (BAL), Chicago, IL (CHI), Dallas, TX (DAL), Denver, CO (DEN), Los Angeles, CA (LA), New York City, NY (NYC), Seattle, WA (SEA),

St. Louis, MO (STL), and Phoenix, AZ (PHX). We focus on trends within individual cities, trends by region, proximity to major shipping port, and trends by metal.

Methods

The concentrations of many elements in ambient PM_{2.5} are measured as part of the Speciation Trends Network (<https://epa.gov/amtic/chemical-speciation-network-csn-general-information>). All of the data in this study were taken from PM_{2.5} collected onto Teflon® filters and analyzed by x-ray Fluorescence (XRF) [46] according to AQI methods 811, 821, and 831. The AQI methods differ only in the manufacturer of the filter collection system (811—MetOne; 821—Andersen; and 831—URG). The focus of this study are the transition metals, which are emitted in high quantities and are regularly measured in atmospheric particles [1]. The XRF analysis has a lower limit of detection for each element of 0.001 µg m⁻³. All data were accessed from the US Environmental Protection Agency's Ambient Air Quality Database (<https://aqs.epa.gov/api>).

The cities for this study were selected to provide a wide geographical distribution and were limited to cities with nearly continuous data coverage from 2001–2016. The selected cities are listed in table 1 and figure S1 is available online at stacks.iop.org/ERL/14/104006/mmedia. Five of the cities are part of the National Air Toxics Trends Station Network (<https://www3.epa.gov/ttnamti1/natts.html>). For each city, the sampling frequency was approximately every three days (table S1).

Results

Trends by metal

Table 2 gives the average annual change in transition metal concentrations and PM_{2.5} for each city. Among all transition metals analyzed through this study, concentrations of V decreased more dramatically from 2001 to 2016 than for any other metal. Relative to 2001 levels, V concentrations decreased by ~70%, on

Table 2. Average annual change (2001–2016) in $\text{PM}_{2.5}$ transition metal concentrations in each city. Units for individual metals are $(10^{-5}) \times \mu\text{g m}^{-3} \text{yr}^{-1}$. Bolded numbers represent trends that are statistically significant at the 95% confidence level ($p < 0.05$).

	Cr	Cu	Fe	Mn	Ni	V	Zn	^a $\text{PM}_{2.5}$
ATL	18	26	−14	−3	3	−6	−25	−0.57
BAL	8	−13	−329	−11	−8	−22	−88	−0.59
CHI	9	−1	−118	−3	2	−4	−70	−0.45
DAL	15	6	488	9	3	−4	−11	−0.29
DEN	0	−12	176	0	−4	−6	−48	−0.18
LA	−1	−18	−487	−11	−19	−62	−65	−0.65
NYC	12	4	−188	−9	−95	−47	−44	−0.49
PHX	−1	7	−861	−5	1	−22	−19	−0.14
SEA	−5	10	−163	−18	−8	−26	−31	−0.22
STL	1	−88	−381	−37	−2	−6	−137	−0.39

^a Units: $\mu\text{g m}^{-3} \text{yr}^{-1}$.

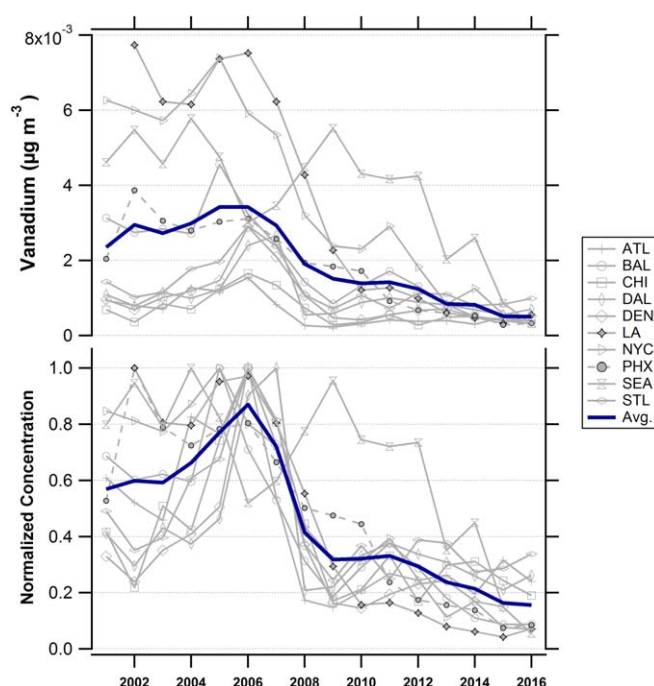


Figure 1. Annual trends in the absolute mass concentration (top) and normalized concentration of V (bottom) in $\text{PM}_{2.5}$. The normalized trend for each city is relative to the maximum average V concentration in each city from 2001 to 2016. On average, the V concentration has fallen by $\sim 72\%$ over this time.

average, across the study period (figure 1). A distinct peak in the average annual V concentration occurred in 2006, which was $\sim 65\%$ higher than the average concentration in 2001. The decrease was even more dramatic ($\sim 85\%$) when compared to the 2006 level. In five of the ten cities (BAL, LA, NYC, PHX, SEA), the average annual V concentration decreased by over 90% from its peak level. Even in the city that had the lowest relative decrease (STL), the average V concentrations decreased by 67% from its peak level. Further, if the analysis started with the year that the average V concentration peaked within each city (2006 at the latest), the decreasing trend is statistically significant in all ten cities (95% confidence level). Mann-Kendall nonparametric regression analysis was performed on the V trends in all ten cities (Igor Pro v. 8.03 software

package). The nonparametric regression analysis yielded identical information about the trend direction (increasing/decreasing) and statistical significance as the least squares linear regression analysis (bold values in table 2).

Concentrations of Zn also decreased in all ten cities, but the decreases were not nearly as dramatic as they were for V. On average, annual Zn concentrations have fallen by $\sim 25\%$ from 2001 to 2016 (figure 2). The most significant decrease ($\sim 55\%$) occurred in STL, while the smallest decreases ($\sim 5\%$ – 10%) were observed in ATL and DAL. In contrast to the trends in V, Zn did not show a distinct peak in any given year, but was nearly constant from 2001 to 2005. The Zn decrease from 2001 to 2016 was statistically-significant (95% confidence level) in seven cities; however, if the

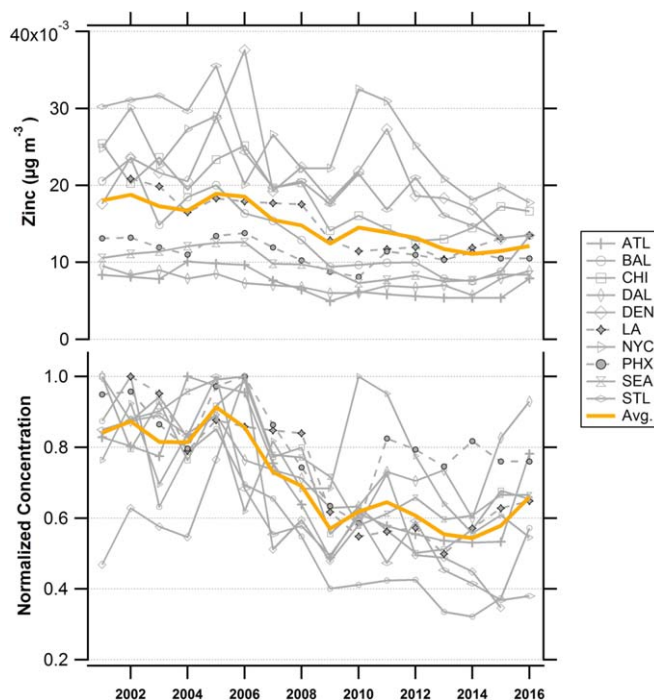


Figure 2. Annual trends in the absolute mass concentration (top) and normalized concentration of Zn (bottom) in $PM_{2.5}$. The normalized trend for each city is relative to the maximum average Zn concentration in each city from 2001 to 2016. On average, the Zn concentration has fallen by $\sim 25\%$ over this time.

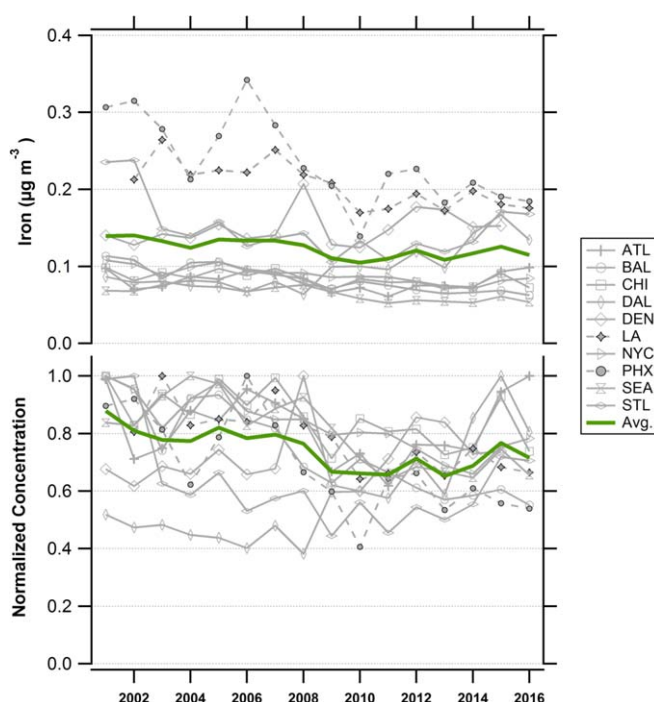


Figure 3. Annual trends in the absolute mass concentration (top) and normalized concentration of Fe (bottom) in $PM_{2.5}$. The normalized trend for each city is relative to the maximum average Fe concentration in each city from 2001 to 2016. On average, the Fe concentration has fallen by $\sim 15\%$ over this time.

analysis started with the peak Zn average, the decrease was statistically-significant in all of the cities except DAL.

Fe is often the most abundant transition metal in $PM_{2.5}$ [47]. Fe concentrations in $PM_{2.5}$ have decreased

by $\sim 15\%$, on average, across the ten cities in this study's domain; however, Fe has exhibited mixed trends in many cities. For example, average Fe concentrations have decreased by 40%–50% from 2001 to 2016 in ATL and PHX, while average Fe

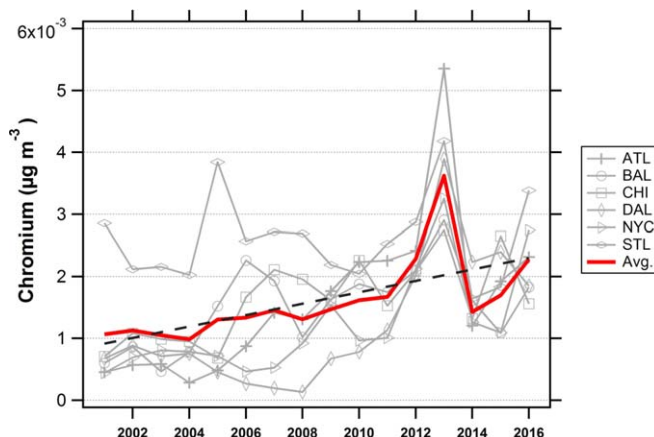


Figure 4. Annual trends the mass concentration of Cr in $PM_{2.5}$ in cities where the concentration increased from 2001 to 2016.

concentrations have actually increased in DAL and DEN during the same time (figure 3).

In contrast to the decreasing trends in the above metals, the average concentrations of Cr in $PM_{2.5}$ have risen significantly from 2001 to 2016 in many cities. The average Cr concentration in the six easternmost cities has increased by more than a factor of three from 2001 to 2016 (figure 4). Also evident from figure 4 is the distinct spike in Cr concentrations in 2013. This was observed in all six cities represented in figure 4. This is notable since the distance separating these cities ranges from ~ 250 km on the low end (BAL to NYC) to ~ 2200 km (DAL to NYC) at the high end. In the three westernmost cities (LA, PHX, and SEA), the average Cr concentration has decreased by $\sim 30\%$ over this same time period (supporting information figures S2–S21).

The other metals analyzed (Cu, Mn, and Ni) had trends that ranged from moderate increases to moderate decreases, with no consistent trends across cities. For each city, the trends for all metal concentrations are presented in table 2 and in the supplemental information (figures S2–S21).

Geographic trends

Similar to the results across all seven metals, there was substantial city-to-city variability in the PM transition metal trends. In LA, the concentrations of all seven metals decreased from 2001 to 2016 (table 2, figure S12). In BAL, SEA, and STL, the concentrations of six out of seven metals decreased during the same time period. On the other hand, the concentrations of four metals (Cr, Fe, Mn, and Ni) had statistically-significant increases in DAL from 2001 to 2016. Figure S8 shows that the metal concentrations in DAL were relatively flat from 2001 to 2008, but steadily increased from 2009 to 2016.

When grouped into port (BAL, LA, NYC, and SEA) and non-port cities (ATL, CHI, DAL, DEN, PHX, STL), several interesting trends emerge. Port cities were identified as those in which the measurement station was within 30 km of a major shipping

port. The trends for five metals (Cr, Cu, Fe, Mn, and Zn) were quite similar in port and non-port cities (figure 5). However, the trends for Ni and V show distinct differences between these cities. In 2001–2003, the concentrations of both metals were higher by about a factor of five in port cities, suggesting a strong source from marine shipping. Ni and V concentrations have decreased precipitously in the past decade, to the point that there is now no practical difference in the levels of either metal in port and non-port cities.

Although the similarities between Ni and V in figure 5 suggest a common source, possibly marine oil combustion [45], further analysis by grouping eastern (ATL, BAL, NYC), central (CHI, DAL, STL) and western (DEL, LA, PHX, SEA) cities highlights important differences. Figure 6 shows that the concentrations of V in eastern and western cities have followed a nearly identical trend. By contrast, Ni concentrations in eastern cities were significantly higher than in central or western cities in 2001–2003. Concentrations of Ni in eastern cities have experienced a dramatic decrease compared to the trends in central or western cities. Further, correlation analysis suggests that shipping emissions were not likely the major source of both Ni and V in port cities. From 2001 to 2005, Ni and V were moderately-to-strongly correlated in port cities (figure S23). Starting in ~ 2005 , the Ni–V coefficient of determination (R^2) decreased significantly in BAL, LA, and NYC. In 2016, the Ni–V R^2 was <0.05 in these three cities. In SEA, the Ni–V R^2 remained quite high from 2001 through 2014, but decreased significantly in 2015 and again in 2016. The recent Ni–V trend in SEA likely reflects regulations on the S content of heavy fuel oil, which took effect in 2015 [45].

Discussion

While transition metals in PM are often dominated by local sources [48–50], our analysis shows broad, consistent trends across multiple cities and regions for several metals. V and Zn had decreasing

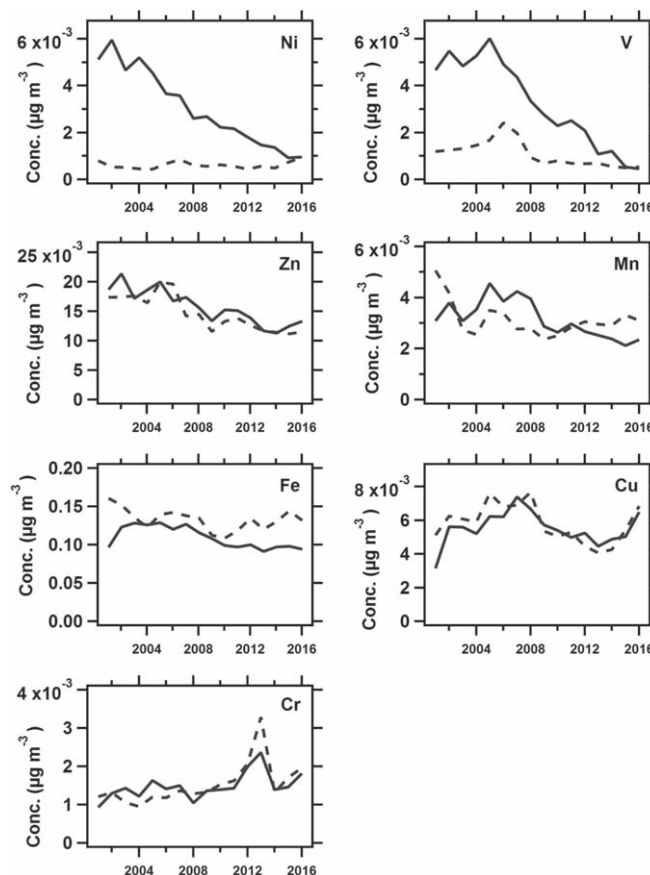


Figure 5. Comparison of metal concentrations in port cities (solid lines; BAL, LA, NYC, SEA) and non-port cities (dashed lines; ATL, CHI, DAL, DEN, PHX, STL).

concentrations in all ten cities analyzed. The V concentration decreases indicate a disconnect between total emissions on a national level and the sources that most affect population exposures. Soil and dust sources collectively represent >60% of V emissions (mass basis) across the US [1]. However, the 70%–85% decrease in $PM_{2.5}$ V in urban areas is most likely associated with combustion and changes in fuel-S reformulations, sources which account for <15% of total V emissions in the 2001 NEI [1]. The urban hotspots are captured by the NEI (see figure S5(b) in Reff *et al* [1]), suggesting that regulations targeting relatively minor sources—e.g. as a fraction of the total—can have a dramatic effect on population exposures.

Spada *et al* [45] analyzed trends in Ni and V concentrations in the IMPROVE network. Based on substantial decreases in two coastal cities (New Orleans and Seattle), they hypothesized that the observed decreases were driven by reduced marine emissions (heavy fuel oil). By contrast, we saw dramatic reductions in V concentrations across all urban areas, including those with little shipping influence (e.g. DEN, PHX). Diesel vehicles represent a significant source of V emissions in urban areas [7, 51]. We propose that diesel fuel reformulations that reduced fuel-S also reduced fuel-V and resulted in the ubiquitous decreases shown in figure 1. Ni, however, did show a

more dramatic decrease in cities with busy ports (BAL, LA, NYC, and SEA) compared to the others, suggesting that heavy fuel oil is its dominant source (figure 6). A correlation analysis also supports this idea, as Ni–V correlations steadily decreased in port cities over 2001–2016 (figure S23). Peltier and Lippmann [48] showed through detailed measurements at multiple sites in NYC that Ni and V have different sources, even though both derive predominantly from heavy fuel oil combustion. The dominant source of Ni in NYC is boilers used for heating during winter while V appears to come predominantly from the port of NY, likely from marine engine emissions [48]. It should be noted that changing combustion conditions under constant fuel composition can dramatically alter the V:Ni emission ratios for marine engines [52]. The decreasing correlation shown in figure S23 is likely due to fuel-S regulations, which have the unintended benefit of also reducing transition metals (V) in the fuel [45].

The consistent trends in Zn concentrations observed across all ten cities are likely due to a combination of factors. Dust sources (paved and unpaved road dust, agricultural soil, and construction dust), which collectively contribute the largest fraction of Zn emissions nationally (25%) [1], are not likely responsible for the broad Zn decreases. Fe and Mn in $PM_{2.5}$ are also derived from soil and dust sources, explaining

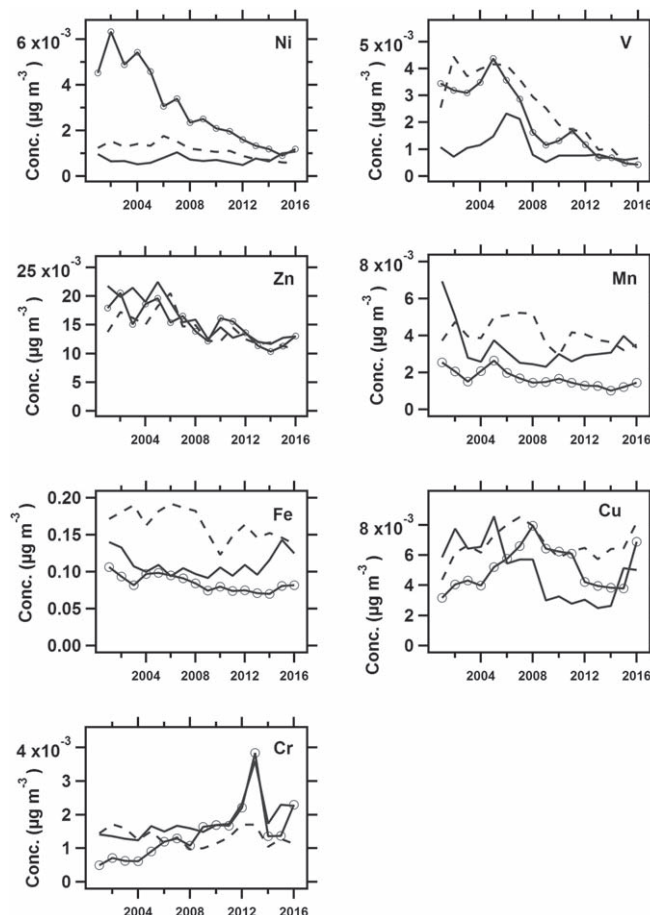


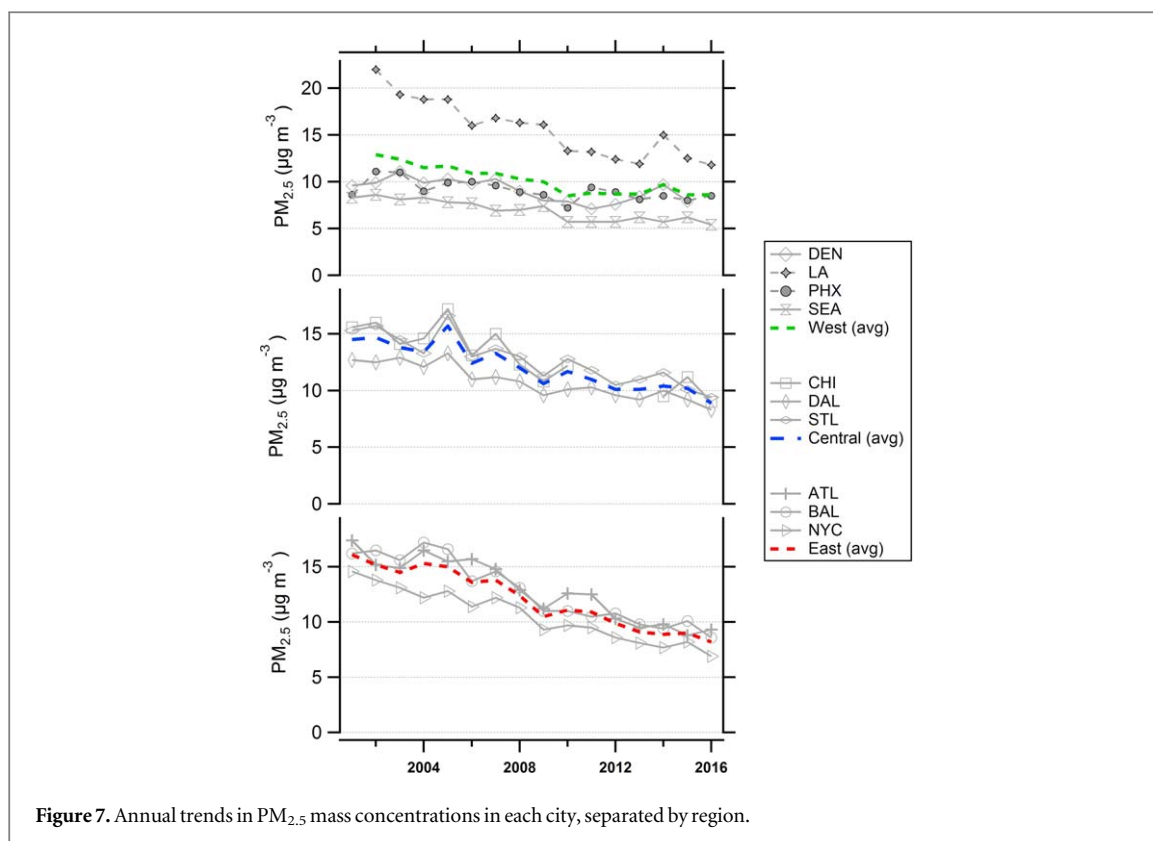
Figure 6. Comparison of metal concentrations in eastern (circles; ATL, BAL, NYC), central (solid lines; CHI, DAL, STL), and western (dashed lines; DEN, LA, PHX, SEA) cities.

their higher concentrations in central and western cities (figure 6). By contrast, Zn concentrations were much more regionally uniform (figure 6), pointing to a more ubiquitous source. The changes in Zn levels are more likely from decreases in emissions from mobile sources (HDDV and on-road gasoline emissions) and fossil fuel combustion, which together represent $\sim 20\%$ of Zn emissions [1]. Reductions in emissions from these sources have been well documented [39, 53, 54], and most likely underlie the Zn trends.

The Fe concentration decreases observed in BAL, CHI, LA, NYC, PHX, SEA, and STL are likely due to decreases in coal combustion and metallurgical processes, since these sources collectively contribute $\sim 20\%$ of Fe emissions nationally [1]. Other major Fe sources, such as soil, dust and brake wear (together represent 75% of Fe emissions nationally) [1], did not decrease during that time. Brake wear is the third largest source of Cu emissions nationally [1], but Cu concentrations did not exhibit a statistically-significant decrease (95th percent C.I.) in seven of the ten cities analyzed (table S2, figures S2–S20). Therefore, it is unlikely that the Fe trends were related to changes in brake wear emissions, since a decrease in emissions from such a ubiquitous source would also show in the Cu trends. The Cu decreases in STL were a factor of ~ 7

greater than in any of the other cities (figure S20), but were unrelated to motor vehicles. STL is one of the hotspots for Cu emissions (see figure S6(b) in [1]), and the decreases in Cu after 2008 were likely from reductions in industrial metallurgical operations [1]. The causes of the Fe trends in ATL, DAL, and DEN are not known, but may implicate changes in land use and development, since unpaved road dust and construction dust are two of the four largest Fe sources.

The Cr concentration increases, including the spike in 2013, are somewhat puzzling. Cr has not increased in the westernmost cities, and did not exhibit a spike in 2013 in LA, PHX, or SEA. The pronounced spike in 2013 was due to a four-week period between mid-September and mid-October when elevated Cr concentrations were observed in the six eastern-most cities (figure S24). According to the 2001 EPA National Emissions Inventory (NEI), the major sources of Cr emissions are steel production (28%), agricultural soil (15%), and metallurgical processes (heat treating, 14%) [1]. There were not increases in US steel production or coal use in 2013, nor in the fraction of bituminous and subbituminous coal produced (US EIA, https://eia.gov/coal/annual/pdf/table_es1.pdf (<https://eia.gov/coal/annual/>)). The simultaneous Cr spike in the eastern-most cities was



also not likely caused by widespread fire emissions, as aerosol K^+ concentrations did not show a simultaneous increase in 2013 (figure S25). Seasonal analysis of Cr concentrations in 2012 and 2014 (not shown) did not exhibit a similar peak as in 2013. The reason for the spike in 2013 is unclear.

The trends in transition metals are interesting to contrast with the overall trends in $PM_{2.5}$ mass concentrations, which have decreased steadily from 2001 to 2016 in most of the cities included in this analysis (figure 7). By region, $PM_{2.5}$ concentrations have decreased most dramatically in eastern cities (avg. decrease = 49%, $7.9 \mu\text{g m}^{-3}$), followed by central (avg. decrease = 39%, $5.6 \mu\text{g m}^{-3}$) and western cities (avg. decrease = 34%, $4.3 \mu\text{g m}^{-3}$). In some cases, trends in transition metal concentrations followed the overall trends in $PM_{2.5}$. For example, DEN and PHX had the smallest absolute (and relative) decreases in $PM_{2.5}$ and also had the fewest metals declining from 2001 to 2016 (figures S10, S16). However, in many cases, the transition metal trends were quite different than those for $PM_{2.5}$. In DAL, four metals increased in concentration from 2001 to 2016 even though $PM_{2.5}$ decreased by 35% ($4.4 \mu\text{g m}^{-3}$) over that same time. Trends in Cr are also more pronounced when compared with the $PM_{2.5}$ trends. In the six cities represented in figure 4, the Cr concentration increases have occurred while overall $PM_{2.5}$ levels have decreased. This has increased the Cr/ $PM_{2.5}$ ratio by more than a factor of three from 2001 to 2016 (figures S2–S21). Differences in the $PM_{2.5}$ trends compared to those of the individual metals are consistent with predictions

of ultrafine particle concentrations ($PM_{0.1}$) in urban areas across the US [55]. Similar to PM metals, ultrafine particles are dominated by primary emissions in urban areas, especially during pollution episodes, whereas major contributors $PM_{2.5}$ (e.g. organics, sulfate, nitrate, ammonium) are predominantly secondary in origin [55]. A separate study similarly concluded that metals exhibit much greater spatial variability than $PM_{2.5}$ mass across the US due to the high contribution and regional nature of secondary PM formation [56].

Conclusions

Overall, we have characterized the trends in $PM_{2.5}$ transition metals in ten urban areas across the US for the period of 2001–2016. Many interesting trends emerged, with unique insight provided when the analysis was performed by metal, by city, or by region. The concentrations of all seven transition metals have decreased in STL and LA, while concentrations of six metals decreased in BAL and SEA. Conversely, the concentrations of four metals have increased in DAL over the time period analyzed, predominantly over the past ~8 years. A comparison of port and non-port cities showed striking differences in Ni concentrations, pointing to major decreases in Ni emissions from marine engine sources. Cr levels in $PM_{2.5}$ increased significantly in eastern and midwestern cities, a trend not observed in the three westernmost cities. The concentrations of V decreased in all ten cities, likely

due to fuel-S regulations that targeted on-road mobile source emissions. Zn concentrations also decreased over 2001–2016 in all ten cities, though the reductions were much more modest than they were for V.

The population of urban areas continues to grow [57], indicating the increasing importance of this work. Chemical components in PM show different trends in urban and rural areas across the US [58]. Here, we have focused on urban areas, so the trends in PM transition metals in rural areas may be quite different, but would also need to be assessed. Seasonal analyses within individual cities may also reveal interesting trends and provide further insight into major sources [48].

These results have potentially important implications for PM exposure and human health effects. The oxidative stress induced by PM has been proposed as an explanation for the link between PM exposures and numerous disease outcomes with which PM has been associated. Transition metals likely affect human health differently than other chemical species present in PM due to their disproportionately (high) contribution to measures of oxidative stress [4, 22, 23]. Our results suggest that measures to control overall PM mass concentrations are decoupled from transition metals. For example, Cr in many cities has increased while overall PM levels have decreased. Likewise, multiple transition metals have increased in DAL, and other cities, while overall PM_{2.5} mass concentrations have declined. The health effects of such disparate trends have not been analyzed.


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Data availability statement

The data that support the findings of this study are openly available at <https://epa.gov/outdoor-air-quality-data>.

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