A Literature Review of Concentrations and Size Distributions of Ambient Airborne Pb-Containing Particulate Matter

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ABSTRACT

The final 2008 lead (Pb) national ambient air quality standards (NAAQS) revision maintains Pb in total suspended particulate matter as the indicator. However, the final rule permits the use of low-volume PM_{10} (particulate matter sampled with a 50% cut-point of 10 μm) Federal Reference Method (FRM) monitors in lieu of total suspended particulate (TSP) monitors for some non-source oriented monitoring. PM_{10} FRM monitors are known to provide more reliable concentration measurements than TSP samplers because they are omnidirectional samplers and so are not biased by wind conditions. However, by design they exclude the upper tail of the particle size distribution. Hence, each monitor produces uncertainties about measured concentrations of Pb-bearing PM. Uncertainties in reported Pb data are also related to

spatiotemporal variation of the concentration and size distribution of Pb-bearing PM. Therefore, a comprehensive literature review was performed to summarize the current knowledge regarding the concentration and size distribution of Pb particles in the atmosphere. The objectives of this review were to compile data that could shed light on these uncertainties, to provide insights useful during future Pb NAAQS reviews, and to identify areas where more research is needed.

Results of this review indicated that Pb size distribution data are relatively limited and often outdated. Thirty-nine articles were found to have sufficiently detailed information regarding airborne Pb concentrations, study location, sample collection methods, and analytical techniques; only 16 of those papers reported Pb concentration data for multiple size fractions. For the most part, U.S. and European studies from the last forty years illustrate that the largest mode of the size distribution of airborne particle-bound Pb has shifted to larger sizes while airborne Pb concentrations have decreased in urban areas. This shift occurred as tetraethyl Pb additives in gasoline were phased out and industrial emissions and resuspended road dust became more important sources of Pb. Several studies also suggested the occurrence of long-range transport of Pb-bearing PM from industrial emissions. Uncertainties associated with these studies include influence of wind speed and direction on captured concentrations and variability in analytical techniques used to quantify Pb concentrations on the reported size distributions.

INTRODUCTION

Increased processing of lead (Pb) ore during the twentieth century increased airborne Pb emissions drastically. In particular, the introduction of tetraethyl Pb into gasoline as an antiknock additive in the 1920s contributed substantially to increased airborne Pb concentrations. By 1970, United States Pb emissions totaled 220,000 tons per year, of which on-road vehicles contributed 78% of total Pb emissions, far exceeding emissions from stationary sources (US EPA, 2009) (Figure 1).

The adverse health effects of tetraethyl Pb were discovered not long after the introduction of leaded gasoline (Shrader, 1925). The United States Environmental Protection Agency (US EPA) confirmed the health risks caused by exposure to Pb in particulate matter (PM) and issued regulations to protect human health (Federal Register, 1973). The legislation set a maximum limit on the Pb content of gasoline and initiated the phase-out of tetraethyl Pb in gasoline. The first national ambient air quality standard (NAAQS) for Pb was released by the US EPA in 1978 at a level of 1.5 $\mu g/m^3$, averaged quarterly (Federal Register, 1978).

Subsequently, ambient Pb concentrations in the U.S. decreased by 92% between 1980 and 2008 (US EPA, 2010a) (Figure 2). Total Pb emissions dropped to 3,300 tons per year by 1999 and included less than 0.5% from on-road vehicles. From 1995 through 2008, the average Pb concentration has fluctuated between 0.07 to 0.12 $\mu g/m^3$ with the 90^{th} percentile concentration ranging from 0.10 to 0.43 $\mu g/m^3$ (Figure 2). Because these statistics subsume monitors that have recently been designated as source or non-source-oriented monitors, the reported concentrations are heavily weighted by concentrations obtained in the vicinity of Pb sources. Non-source-oriented Pb concentrations in 2008 averaged 0.026 $\mu g/m^3$, while source-oriented Pb concentrations averaged 0.40 $\mu g/m^3$ during the same year. The decrease in airborne

Pb emissions from automobiles increased the relative contribution of industrial stationary sources such as metals processing and piston engine aircraft (Figure 3), changed the spatial distribution of ambient Pb concentrations, and altered the size distribution of Pb containing particles in the atmosphere.

An important source of Pb emissions, aircraft engines, is included in the data that comprise Figures 1 to 3. Pb emissions from air taxis and general aviation planes have been included in the 2008 National Emission Inventory (NEI). Aviation emissions are included in the "off-highway" emissions category and comprise roughly 50% of total Pb emissions for 2008. However, no studies are available in the literature to characterize the ambient air Pb concentrations or size distributions of Pb concentrations in the immediate vicinity of airports for the time period (1968-2009) covered by this review. Therefore, ambient air Pb concentrations related to aviation emissions are not included in this review.

The Pb NAAQS review process completed in 2008 resulted in the level of the NAAQS being reduced to 0.15 $\mu g/m^3$ on a rolling three-month average based on findings regarding public health impacts at low concentrations of Pb (Federal Register, 2008). Considering that the 90^{th} percentile concentration was 0.28 $\mu g/m^3$ in 2008, a substantial percentage of ambient air Pb measurements exceed the new NAAQS. A review of the EPA Air Quality System data suggests that concentrations exceeding these values occur in locations associated with Pb industry activities (e.g., mining, milling, smelting, recycling).

The final 2008 Pb NAAQS rule permits the use of low-volume PM_{10} (particulate matter sampled with a 50% cut-point of 10 μm) Federal Reference Method (FRM) monitors in lieu of total suspended particulate (TSP) monitors for some non-source oriented monitoring (Federal Register, 2008). PM_{10} FRM monitors provide less biased concentration measurements than TSP

samplers because representative PM_{10} samples can be obtained independent of wind speed and direction, and because the PM_{10} FRM has stricter design and performance specifications (Tolocka et al., 2001). PM_{10} FRM monitors are allowed to be used if two criteria are met. First, three-month average TSP Pb concentrations over three years cannot exceed 0.1 $\mu g/m^3$. Also, the ultra-coarse (operationally defined as particles that could be collected by a TSP sampler but not by a PM_{10} sampler) contribution to the Pb concentration must be minimal. These conditions are expected to be met for non-source oriented sampling sites that are required at NCore network stations located in core-based statistical areas with populations of 500,000 or more. The ruling specifically did not allow for site-specific scaling factors to be applied to converting Pb concentration in PM_{10} samples to that from TSP samples because the size distribution can change in time and with different source contributions. At non-required monitoring sites, PM_{10} monitors can be used without restrictions. Furthermore, the ruling stated that data from either TSP or PM_{10} monitors can be used to demonstrate violation of the NAAQS, although only data from TSP monitors can be used to demonstrate compliance with the NAAQS. However, changes in the implementation of the NAAQS raise questions about the interpretation of Pb concentration data in the Air Quality System (AQS) database. Variability of performance efficiency in TSP samplers and underestimation of the ultra-coarse PM in PM_{10} data would make it difficult to relate the TSP and PM_{10} data. Demonstrating compliance with the NAAQS using PM_{10} data would be also greatly challenged at sites near Pb sources where a low, but not zero-level of ultra-coarse PM is expected, and non-required monitoring sites where the TSP precondition data are not required. Uncertainties in these reported data are related to spatiotemporal variation of the concentration and size distribution of Pb-bearing PM. Therefore, understanding Pb particle size distribution is important to select the type and location of PM samplers for Pb NAAQS

compliance monitoring. In this study, a comprehensive literature review was performed to summarize the current knowledge regarding the concentration and size distribution of Pb particles in the atmosphere. Attention was given to the impacts of different sources, as well as the monitoring and analysis methodology. The objectives of this review were to compile data that could shed light on these uncertainties, to provide insights useful during future Pb NAAQS reviews, and to identify areas where more research is needed.

LITERATURE SEARCH METHODS

A thorough literature search for peer-reviewed published articles on airborne Pb-containing particles in the United States was conducted to obtain information about particle concentration and size distribution at varying spatial and temporal conditions. Web-based research database services and search engines, including Web of Science, EBSCOhost, Google Scholar, ScienceDirect, and Wiley InterScience, were used to locate all relevant articles including government publications and peer-reviewed scientific research papers. A global search was conducted using search terms for various Pb emission sources, major EPA air monitoring programs and networks, and specific types of analytical techniques (Table 1). Certain topics and publication types (Table 1) were excluded from the search to constrain the scope of topic area. Electronic search of the article title and abstract identified publications with a focus on atmospheric Pb data; studies of other media or biological matrices were thereby excluded. Finally, full text articles were obtained and reviewed in detail to extract Pb concentration and size distribution data. Additional data such as Pb sources, monitoring method, analytical technique, and spatial and temporal conditions were also collected if available. The literature

search focused on studies conducted in the US, but research conducted in Europe and Asia were also included if the presented data supported the review objectives.

RESULTS

The literature search identified more than 20,000 published peer-reviewed articles and government publications that contained Pb data in air, water and soil environmental media or biological matrices such as human blood, hair, and plants. Among these, 41 articles had detailed information on Pb concentrations in airborne particulate matter, study location, sample collection methods, and analytical technique that were desired for this review (Table 2). The publication chronology of the 41 papers fell into three categories: 9 used Pb concentration data collected prior to implementation of the tetraethyl Pb phase-out in 1976, 3 used data collected between 1976 and 1986 during the bulk of tetraethyl Pb phase-out, and 29 presented data obtained after 1986.

Eighteen papers reported Pb concentration data in multiple size fractions (Table 3). These papers provided an indication of the change in the Pb particle size distribution. The other 23 papers reported concentrations in a single size fraction. For easy comparison between studies, concentration unit originally presented as ng/m^3 or mg/m^3 were converted to $\mu g/m^3$. By accounting for the cutpoints of the impactor stages, concentrations from cascade impactor stages not aligned with 1 μm, 2.5 μm, or 10 μm cut-points were interpolated to calculate PM_1, $PM_{2.5}$, and PM_{10} concentrations. Furthermore, concentration data and size fraction ratios reported in Table 3 were extracted from graphs in several of the studies (Holsen et al., 1993; Dorn et al., 1976; Zota et al., 2009; Yi et al., 2006; Dall'Osto et al., 2008; Chang et al., 2000; Harrison et al.,

2003; Bruggemann et al., 2009; Sabin et al., 2006; Lee et al., 1972; Zereini et al., 2005; Wang et al., 2006; Singh et al., 2002).

DISCUSSION

The long-term, continuous decline in ambient Pb concentrations from 1976 to 1995 is well documented by EPA monitoring data (Figure 2) (US EPA, 2010a). Until tetraethyl Pb in gasoline was reduced to 0.1 g per gallon in 1986, automobile emissions were the primary source of Pb emissions, especially submicron Pb particles (Figure 1). Figure 3 shows that piston engine aircraft and industrial sources were the two largest sources in 2008 (U.S. EPA, 2011). This section begins with a discussion of uncertainties associated with sampling and analysis of Pb-bearing PM to provide context for subsequent review of the literature regarding observations of Pb concentrations and size distributions of Pb-bearing PM.

Uncertainties

The sample collection methods used should be considered when comparing data from multiple studies conducted over extended time periods (for this review, ~40 years). Sample collection methods have evolved during that period. The studies described in Table 2 collected Pb particle samples in various size ranges using multiple samplers in a variety of meteorological conditions. The difference in particle collection principles and instrument designs implies that the overall sampling efficiencies among different samplers could vary. Authors did not consistently report or cite characterization of or data correction for inlet aspiration efficiency internal losses, separation efficiency, or other performance characteristics that possibly affected

reported concentrations. The influence of wind direction and speed on the aspiration efficiency of the sampler inlet probably had the greatest impact on the reported concentrations.

Cascade impactors were frequently used in metals speciation and concentration studies. When used for ambient air monitoring, the upper stages of cascade impactors have been shown to have poor efficiency at moderate wind speeds (Hangal and Willeke, 1990; Howell et al., 1998). Moreover, none of these studies reported using an omni-directional inlet, therefore it is probably safe to assume that one was not used. Sampler aspiration efficiency for coarse mode or larger particles is influenced by wind speed, with a decrease in efficiency as particle size or wind speed increases. As a result, in studies that involve ambient aerosols with a significant fraction of Pb particles in the coarse fraction (e.g., Dorn et al., 1976), Pb mass concentration measured for larger particles may be negatively biased.

The collection efficiency of coarse mode or larger particles with the Hi-Vol sampler is also dependent upon wind speed and direction (Wedding et al., 1977; McFarland et al., 1979). The Hi-Vol TSP sampler is the current instrument deployed in the EPA monitoring network. The few studies that reported Hi-Vol data (Hudson et al., 1975; Ragaini et al., 1977; Pirrone et al., 1995; Pekney and Davidson, 2005; Wojas and Almquist, 2007) did not provide sufficient information to assess how wind speed and direction would affect their data.

Analytical techniques used to quantify Pb concentrations have evolved since the 1970s. Atomic absorption spectrometry (AAS) was the primary analytical method used in the 1970s and 1980s (Lee et al., 1968; Purdue et al., 1973; Hudson et al., 1975; Dorn et al., 1976; Kleinman et al., 1980) . Non-destructive x-ray fluorescence (XRF) analysis became available in the late 1970s (e.g., Ragaini et al., 1977). As Pb concentrations decreased after the 1996 ban of tetraethyl Pb, ICP-MS analysis of air samples became more prevalent because it has a lower limit of detection

(LOD) (e.g., Wu et al., 1994). Among the papers reviewed, two studies compared atmospheric Pb concentrations measured by XRF and ICP-MS. Pekney and Davidson (2005) measured comparable Pb concentrations via XRF and ICP-MS, although the higher LOD of XRF introduced additional error in the measured Pb concentrations. Herner et al. (2006) compared trace element concentrations measured by XRF and ICP-MS. The authors found ICP-MS to be the superior analytical method. The ICP-MS LOD was at least a factor of 10 lower than XRF, 1 ng per filter versus 10 ng per filter, respectively. The precision of replicate measurements was also better for ICP-MS (RMS < 10%) than XRF (RMS > 10%).

Pb Concentrations

Individual studies provide evidence that the reduction in atmospheric Pb concentrations from 1976 to 1995 at different locations matched the national trend. Sheets et al. (1997) monitored the steady decline in annual average TSP Pb concentration from 0.4 ng/m^3 in 1975 to 0.01 μg/m^3 in 1993 for Springfield, MO. Pirrone et al. (1995) observed a similar reduction at multiple sites in Detroit, MI between 1982 and 1992. Seasonal average TSP Pb concentrations at suburban, commercial, and industrial locations decreased from 0.33 μg/m^3 to 0.04 μg/m^3 during that period.

National Air Surveillance Network (NASN) data collected in six US cities (Chicago, IL; Cincinnati, OH; Denver, CO; Philadelphia, PA; St. Louis, MO; and Washington DC) with high traffic volumes between 1968 and 1970 were documented by Lee et al. (1972) to vary from 1.3 to 3.2 μg/m^3 and by Purdue et al. (1973) to vary from 1.2 to 5.1 μg/m^3. Kleinman et al. (1980) measured similar Pb levels in TSP in high traffic areas of New York City from 1968 through 1975. The average TSP Pb concentrations at the NYU Medical Center decreased from 2.11

223 μg/m^3 to 1.07 μg/m^3 over the period from 1968 to 1975. Average Pb concentrations in Bronx,
224 NY decreased from 3.82 to 1.58 μg/m^3 over the same period. TSP Pb levels measured in
225 Queens, NY in 1974 and 1975 were 0.80 and 0.70 μg/m^3, respectively.
226 TSP Pb concentrations in urban locations exhibited a decrease of approximately two
227 orders of magnitude since 1986. Several studies reported TSP Pb concentrations less than 0.010
228 μg/m^3 at locations not impacted by industrial sources. A Speciation Trends Network (STN)
229 monitor located near St. Louis, MO, roughly 5 km west of a coal fired power plant and 18 km
230 north of a Pb smelter, measured average $PM_{2.5}$ Pb concentration of 0.019 μg/m^3, while a STN
231 site sited approximately 30 km northeast of the power plant and 45 km northeast of the smelter
232 reported average $PM_{2.5}$ Pb concentrations of 0.013 μg/m^3 from 2000 to 2003 (Lee and Hopke,
233 2006). Ondov et al. (2006) investigated industrial-urban sources in the vicinity of three
234 monitoring locations (one near-source monitor, two urban monitors within 5-10 km of industrial
235 sites) within the Baltimore Supersite in 2001-2003 using the Reference Ambient Air Sampling
236 System (RAAS, Andersen Instrument Company, Inc., Smyrna, GA) and Semi-continuous
237 Elements in Aerosol Sampler (SEAS, Ondov Enterprises, Inc., Clarksville, MD). The industrial
238 site had an annual average Pb concentration of 0.083 μg/m^3, but the two receptor sites measured
239 Pb concentrations in the range of 0.0019 to 0.0024 μg/m^3 and 0.0060 to 0.0072 μg/m^3,
240 respectively. Melaku et al. (2008) collected multi-stage cyclone impactor samples in
241 Washington, D.C. in 2006-2007. Pb concentrations ranged from 0.0029 to 0.137 μg/m^3, with a
242 summer average of 0.103 μg/m^3 and a winter average of 0.0057 μg/m^3.
243 Prior to the tetraethyl Pb phase-out, rural areas had substantially lower Pb concentrations
244 than their urban counterparts. Hi-Vol TSP-measured Pb concentrations in suburban and rural
245 locations in Urbana-Champaign, IL in 1973-1974 were less than 0.200 μg/m^3 (Hudson et al.,

246 1975). Dorn et al. (1976) collected cascade impactor samples at a rural location in southeast
247 Missouri in 1972. Their TSP Pb concentrations, calculated as the sum of all impactor stages,
248 varied from 0.080 to 0.120 $\mu g/m^3$. These concentrations were comparable to NASN TSP Pb
249 concentrations that varied from 0.100 to 0.500 $\mu g/m^3$ in non-urban areas from 1966-1974 (U.S.
250 EPA, 1977).
251 Few recent studies describe ambient Pb concentrations in rural areas. Goforth et al.
252 (2006) is the only study that provided an assessment of TSP Pb concentrations. They measured
253 an average Pb concentration of 0.015 $\mu g/m^3$ in a rural area of South Carolina during February
254 and March of 2003. Two additional studies presented PM_{10} Pb concentrations. Holsen et al.
255 (1993) used a dichotomous sampler with an omni-directional inlet and measured average PM_{10}
256 Pb concentrations of 0.0052 $\mu g/m^3$ and 0.0112 $\mu g/m^3$ in a rural location in southeastern
257 Michigan and over Lake Michigan, respectively. Holsen et al. estimated total Pb concentrations
258 using a Noll Rotary Impactor, but the Pb concentrations were poorly correlated with the PM_{10}
259 data from all sites. PM_{10} Pb concentrations in a Finnish forest averaged 0.010 $\mu g/m^3$ over several
260 days in 2006 (Makkonen et al. 2010). Finland banned tetraethyl Pb in the late 1980s, so current
261 ambient concentrations in rural areas could be considered similar to U.S. conditions.
262 The difference in Pb concentration reductions between urban/suburban and rural areas is
263 likely attributed to a paucity of sources in rural areas. Moreover, differences between land use
264 types with respect to the number of vehicle miles traveled may contribute to the quantity of Pb in
265 soils and the amount of Pb resuspended. Prior to the ban on tetraethyl Pb in gasoline, direct
266 urban Pb emissions were substantially higher than rural Pb emissions (Mielke et al., 2011; Alpert
267 and Hopke, 1981; Berstein et al., 1979; Kleinman et al., 1980). Subsequent to the ban, higher
268 urban traffic levels had the potential to re-entrain greater quantities of historically deposited Pb

in soil. Urban and suburban areas historically average 50 to 100% more vehicle-miles traveled per year than rural areas (U.S. Department of Transportation, 1997).

Pb Size Distributions

Prior to 1976, monitoring locations in urban areas were dominated by traffic sources and measured up to 75% of the Pb particles smaller than 2 μm, with a mass median diameter less than 0.8 μm (Lee et al., 1972). Locations with a mix of industrial and traffic sources indicated an enrichment of Pb in the fine fraction. In 1972, Ragaini et al. (1977) used a Hi-Vol sampler and XRF analysis to measure airborne Pb levels in the vicinity of a Kellogg, ID Pb smelting complex. For samples collected about 2.4 km downwind from the main smelter complex, they indicated that Pb enrichment occurred predominantly in the particles smaller than 3 μm. Dorn et al. (1976) found a smaller percentage of the Pb particles in the fine fraction and more Pb particles in the coarse fraction at their monitoring locations than were typically measured at the high traffic, urban locations. Their site 0.8 km from a Pb smelter found about 60% of the Pb mass of 1.04 $\mu g/m^3$ in particles greater than 2.1 μm, compared to about 47% of the Pb mass of 0.112 $\mu g/m^3$ at the rural control site 40 km away. Dorn et al. (1976) attributed the large percentage of Pb particles between 2.1 and 11 μm to the lack of adequate control equipment on the Pb smelter or on a coal-fired power plant near the second location.

Most studies conducted after 1986 indicated a shift in the Pb size distribution from the fine fraction to the coarse fraction. This shift occurred because the source of atmospheric Pb particles shifted from mobile sources to industrial facilities. As an example, stack sampling of waste incinerator emissions measured a bimodal Pb particle size distribution, with the first peak at 2 μm and the second peak at 6.8 μm (Chang et al., 2000). A limitation of the recent ambient

292 studies, however, is that few provided an estimate of TSP that allowed easy comparison with
293 pre-1976 studies. Most recent studies used sampling equipment with a 10 μm 50% upper limit,
294 either specified by the size selectivity of the inlet or cut-point of the largest impactor stage.
295 However, more data are available to compare $PM_{2.5}/PM_{10}$ ratios pre- and post-1986.
296 Several recent studies allow for comparison of pre- and post-1986 size distributions of
297 Pb-bearing PM using size-specific concentrations or ratios of PM_{10}/TSP and $PM_{2.5}/PM_{10}$. Sabin
298 et al. (2006) used open-faced cassettes to collect TSP and used a Noll Rotary Impactor to obtain
299 size segregated Pb concentration data at near an interstate freeway 10 m, 150 m, and 450 m
300 downwind and upwind locations; data presented in Table 3 are from the upwind and 10 m
301 downwind sites. The calculated Pb concentrations showed an enrichment of Pb in particles
302 smaller than 6 μm at the background site compared to the near-road location. Although the
303 PM_{10}/TSP ratios were similar to pre-1976 studies, their data indicated the near-road site was a
304 source of Pb particles larger than 6 μm; opposite of the trend reported by Lee et al. (1972). Yi et
305 al. (2006) used a MOUDI in their 2001-2002 study of Pb concentrations in an industrial area in
306 New York and within 0.5 km of an interstate highway and an urban area within 2 km of a major
307 highway in New Jersey. Their measured PM_{10}/TSP ratios of 0.73 and 0.93 at the industrial and
308 roadway conditions, respectively, agreed with the Dorn et al. (1976) and Lee et al. (1972) results,
309 but their measured $PM_{2.5}/PM_{10}$ ratio at the roadway site was slightly smaller (0.82 versus 0.90),
310 which may suggest a shift in the Pb particle size distribution to the coarse mode. Likewise,
311 Lough et al. (2005) measured size distributions of Pb emissions within two tunnels located in
312 Milwaukee, WI. They observed a PM_{10}/TSP ratio of 0.85, and a $PM_{2.5}/PM_{10}$ ratio of 0.17-0.46,
313 depending on the measurement technique. The lower $PM_{2.5}/PM_{10}$ ratio supports the notion of the
314 size distribution shifting towards the coarse mode. These findings suggested that most emissions

were in the coarse fraction, and the authors attributed these observations to resuspension of road dust that may potentially contain wheel weights thrown from moving vehicles and then pulverized by traffic. The dichotomous sampler data collected by Holsen et al. (1993) had average Pb $PM_{2.5}/PM_{10}$ ratios of 0.69 in Chicago, 0.81 over Lake Michigan, and 0.92 at a rural location. Zota et al. (2009) measured average Pb $PM_{2.5}/PM_{10}$ ratios less than 0.63 at three sites in rural Oklahoma. Harvard impactor data yielded the lowest Pb $PM_{2.5}/PM_{10}$ ratio at the location nearest mine waste piles, with increasing ratios as distance from the source increased.

Atmospheric Pb concentration studies in the European Union, which banned all tetraethyl Pb in gasoline in 2000, report similar results. Harrison et al. (2003) measured airborne Pb with a 4-stage MOUDI 9 m from a major highway during fall and winter of 2001. Their average Pb $PM_{2.5}/PM_{10}$ ratio was 0.9, with 80% of the Pb mass in particles smaller than 1 µm. Birmili et al. (2006) collected samples near the same highway using a cascade impactor and reported a higher average Pb concentration (0.0012 $\mu g/m^3$) in 1.5-3.0 µm particles compared to 0.004 $\mu g/m^3$ in particles smaller than 0.5 µm. The observed shift in Pb size distribution over time was attributed to metallurgical industries and waste incinerators becoming the dominant source of Pb emissions instead of automobile exhaust. Zereini et al. (2005) reported variable Pb concentrations at three sites with different traffic densities in Frankfurt, Germany in 2001-2002. The Pb $PM_{2.5}/PM_{10}$ ratios measured by cascade impactors were lowest in an urban area where the majority of Pb mass was found in particles greater than 5.8 µm. Pb $PM_{2.5}/PM_{10}$ ratios were highest at a side street and rural site. At these locations, Pb comprised a larger proportion of the mass of particles smaller than 2.1 µm, with the proportion of Pb in PM increasing with decreasing particle size to 29% for a rural site, 25% for a side street, and 18% for a main street for particles smaller than 0.43 µm. The higher Pb concentrations and smaller $PM_{2.5}/PM_{10}$ ratio in the urban area suggested

a large contribution of re-suspended road dust. Singh et al. (2002) conducted a study in the Los Angeles Basin that does not follow the trend of increasing Pb $PM_{2.5}/PM_{10}$ ratio as distance from roads increases and sampling locations become more rural. Their MOUDI data provided an average Pb $PM_{2.5}/PM_{10}$ ratio of 0.86 near two major highways and multiple industrial sources, whereas a ratio of 0.60 was measured at the downwind rural location.

Taken together, these studies suggest the largest mode of the Pb particle size distribution has shifted from submicron particles to particles larger than 2.5 μm since the phase-out of tetraethyl Pb in gasoline. Locations impacted by re-suspended roadway dust or near industrial sources exhibit the lowest Pb $PM_{2.5}/PM_{10}$ ratios and typically the highest TSP or PM_{10} Pb concentrations, ranging from 0.0045-0.0326 $\mu g/m^3$ (Holsen et al., 1993; Zereini et al., 2005; Sabin et al., 2006; Wang et al., 2006; Zota et al., 2009). Background monitoring locations for these studies had Pb concentrations ranging from 0.0030-0.0116 $\mu g/m^3$.

$PM_{2.5}/PM_{10}$ ratios greater than 0.8 observed in rural downwind locations suggest that fine PM may be transported over distances of tens of kilometers. Pekney and Davidson (2005) measured particle-bound Pb concentration with $PM_{2.5}$ and PM_{10} Hi-Vol samplers at the Pittsburgh Supersite and four satellite sites in the Pittsburgh area in July 2001 and January 2002. Overall, Pb concentrations at these sites were less than 0.040 $\mu g/m^3$. PM_{10} and $PM_{2.5}$ Pb concentrations between all five sites were significantly correlated. Bein et al. (2005) identified steelworks as the largest source of Pb emissions. Given the variety of urban, suburban, and rural locations monitored, regional transport of Pb particles from the steelworks is the most likely cause of the strong correlation (Wittig et al., 2004). Although $PM_{2.5}/PM_{10}$ ratios were not reported, Kim et al. (2007) also suggests that long range transport of Pb-bearing PM occurs. Kim et al. (2007) collected $PM_{2.5}$ FRM samples at a rural location near Athens, OH during 2004-2005

as part of a source apportionment study. The average Pb concentration was 0.0042 $\mu g/m^3$ and matched an industrial source profile. Since industrial sources of Pb were not nearby, the authors suspected that regional transport from Pittsburgh, PA, more than 300 km to the east, occurred.

CONCLUSIONS

The ban of tetraethyl Pb in gasoline significantly reduced the airborne Pb concentrations and altered the Pb particle size distribution. Between 1980 and 2008, the level of the maximum three month average ambient airborne Pb in TSP dropped 92% at 19 national sites (Figure 1). During that period, the primary source of ambient Pb particles shifted from automobile exhaust to industrial sources and near-road resuspension of Pb-containing dust. *This change shifted the primary mode of the Pb particle size distribution from less than 2.5 μm to sizes between 2.5 and 10 μm.* However, recent studies of industrial and traffic sources reported varying degrees of Pb enrichment in coarse particles depending on the distance from the source and the type of industrial process.

The revised NAAQS monitoring requirement expanded the number of Pb monitoring sites to 236 and allowed the use of TSP for source-oriented monitoring and TSP and PM_{10} FRM monitors (in certain instances) for non-source-oriented sample collection. The final rule acknowledges that monitoring locations near industrial sources may have some ultra-coarse particles that contribute a significant portion of the mass collected. Lough et al. (2005), Sabin et al. (2006), and Yi et al. (2006) data showing PM_{10}/TSP ratios of 0.66-0.93 support this rationale. *However, results of this review indicated that Pb size distribution data are relatively limited and outdated. Moreover, insufficient data have been collected to quantify the importance of ultra-coarse Pb particles on compliance with the NAAQS.*

This review did not cover urban-scale spatial variability in air Pb concentration because insufficient data are available for such an assessment. The spatial variability of air Pb concentration is influenced by the local Pb emission characteristics and meteorology. Analysis of the spatial variability is especially complex in airsheds with multiple industrial and roadway sources, and often cities do not possess more than one ambient Pb monitor. This spatial analysis is further hampered by lack of studies using sampling inlets that are wind-speed and direction independent for the particle size of interest. Additional studies to characterize the differences between the various FRMs, in addition to other available monitors such as the Hi-Vol TSP monitor and the Wide Range Aerosol Classifier (Burton and Lundgren, 1987) are needed for sound assessment of new multisite study data, as well as for interpreting data from the existing monitoring network and previous research studies.

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TABLES

Table 1. List of global search and exclusion terms used for the literature review.

Table 2. Summary of the 38 articles that provided atmospheric Pb data and research details that satisfied the objectives of this review.

Table 3. TSP and size fractionated Pb concentrations reported in the literature used to evaluate the shift in Pb particle size distribution since 1986.

FIGURES

Figure 1. Trends in Pb emissions between 1970 and 2008, by source sector. Note that the "fuel combustion" sector contains the NEI categories "fuel combustion industrial", "fuel combustion electrical utilities", and "fuel combustion other"; the "miscellaneous/ industrial processes" sector contains the NEI categories "other industrial processes", "chemical and allied manufacturing", "petroleum and related industries", "solvent utilization", "storage and transport", and "miscellaneous". Source: U.S. EPA National Emissions Inventory (U.S. EPA, 2011).

Figure 2. Trends in annual maximum quarterly average of Pb concentration levels at 20 monitoring sites between 1980 and 2009. The average Pb concentration is shown with the solid black line, while the 10^{th} and 90^{th} percentiles are indicated by the dashed lines. Red dashed and solid lines indicate the National Ambient Air Quality Standards before and after the 2008 revision, respectively. Source: U.S. EPA Trends Report (U.S. EPA, 2010a).

578 Figure 3. Total ambient air Pb emissions from various source sectors in the U.S. in 2008. Source:

579 U.S. EPA National Emissions Inventory (U.S. EPA, 2011).

Figure 1.

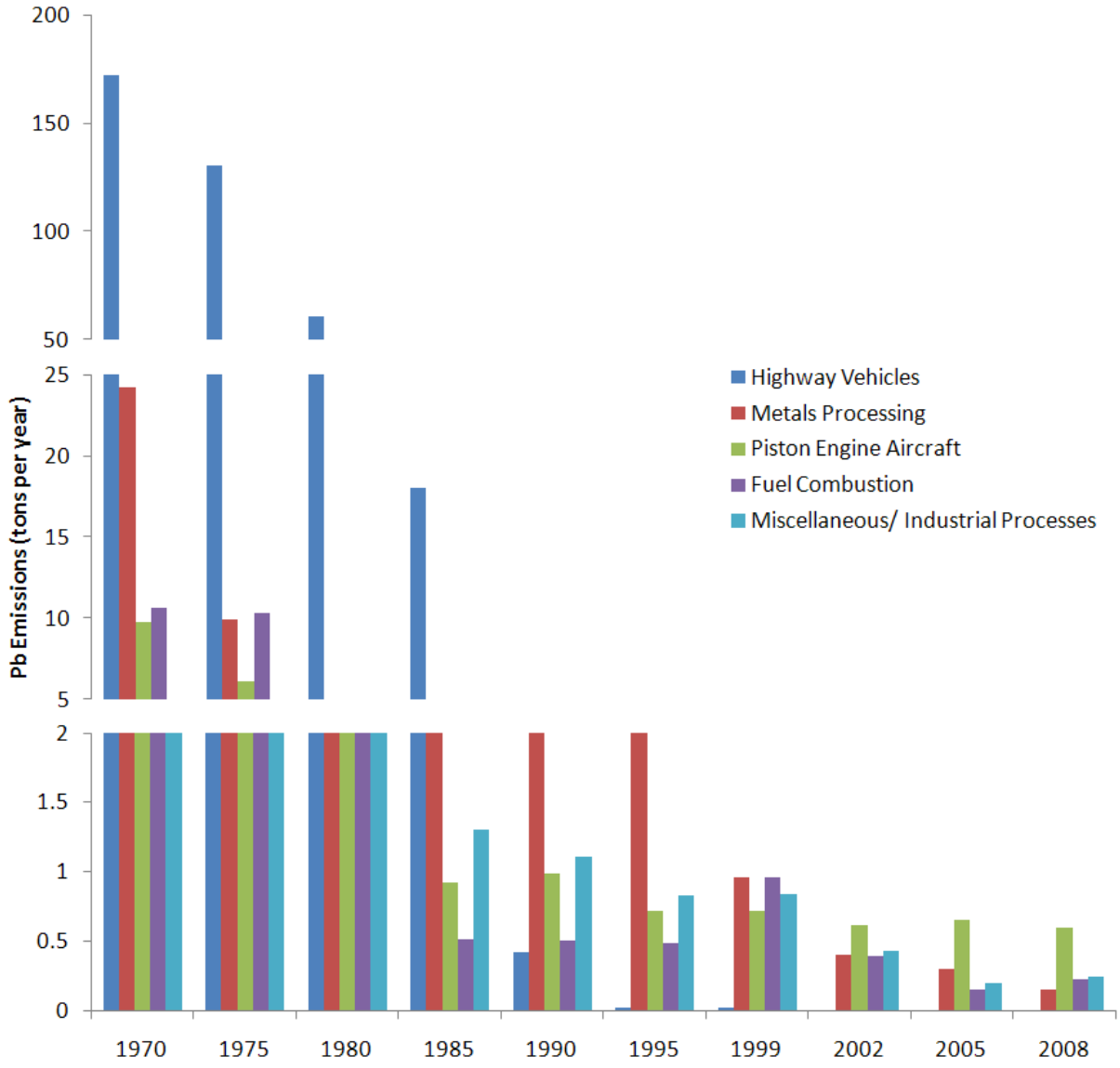
Pb Emissions (tons per year)
200
150
100
50
25
20
15
10
5
2
1.5
1
0.5
0
1970
1975
1980
1985
1990
1995
1999
2002
2005
2008
Highway Vehicles
Metals Processing
Piston Engine Aircraft
Fuel Combustion
Miscellaneous/ Industrial Processes

Figure 2.

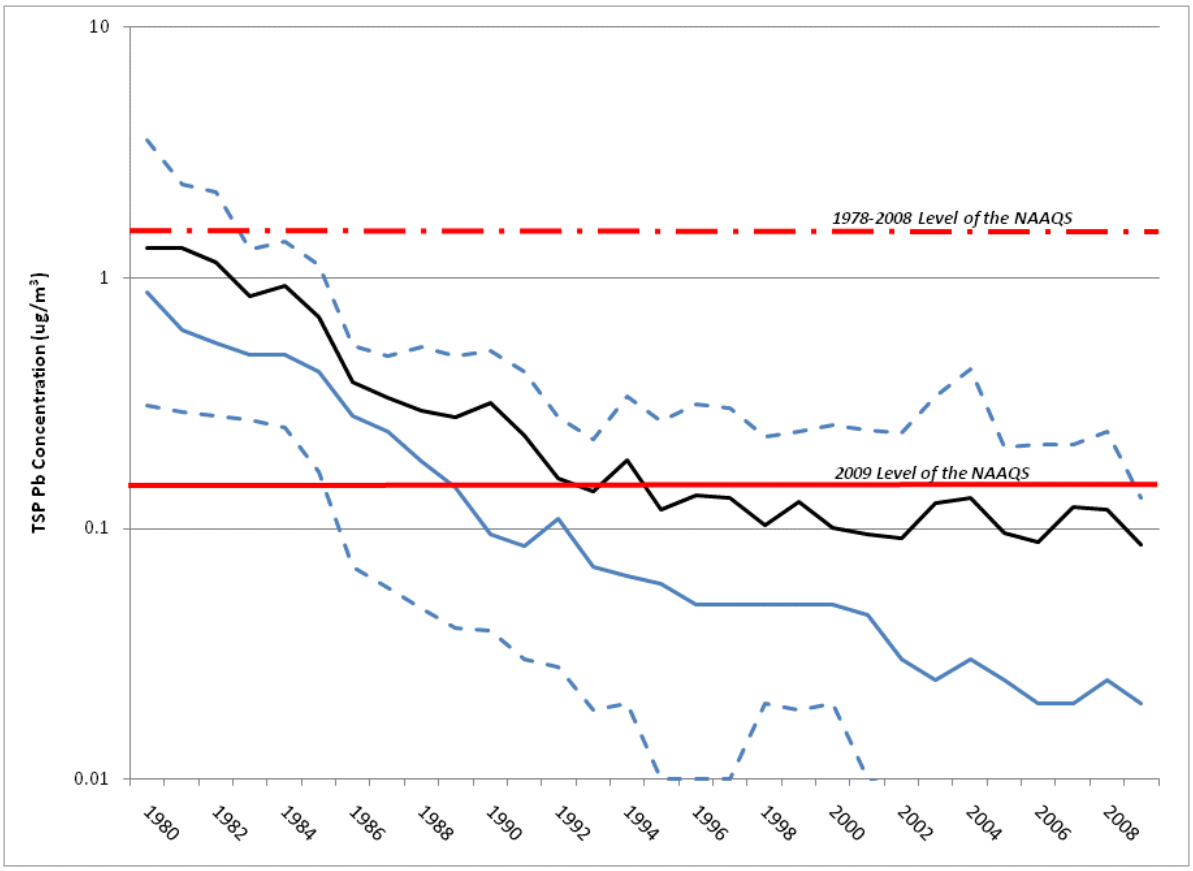
10
1
0.1
0.01
TSP Pb Concentration (ug/m³)
1978-2008 Level of the NAAQS
2009 Level of the NAAQS
1980
1982
1984
1986
1988
1990
1992
1994
1996
1998
2000
2002
2004
2006
2008

Figure 3.

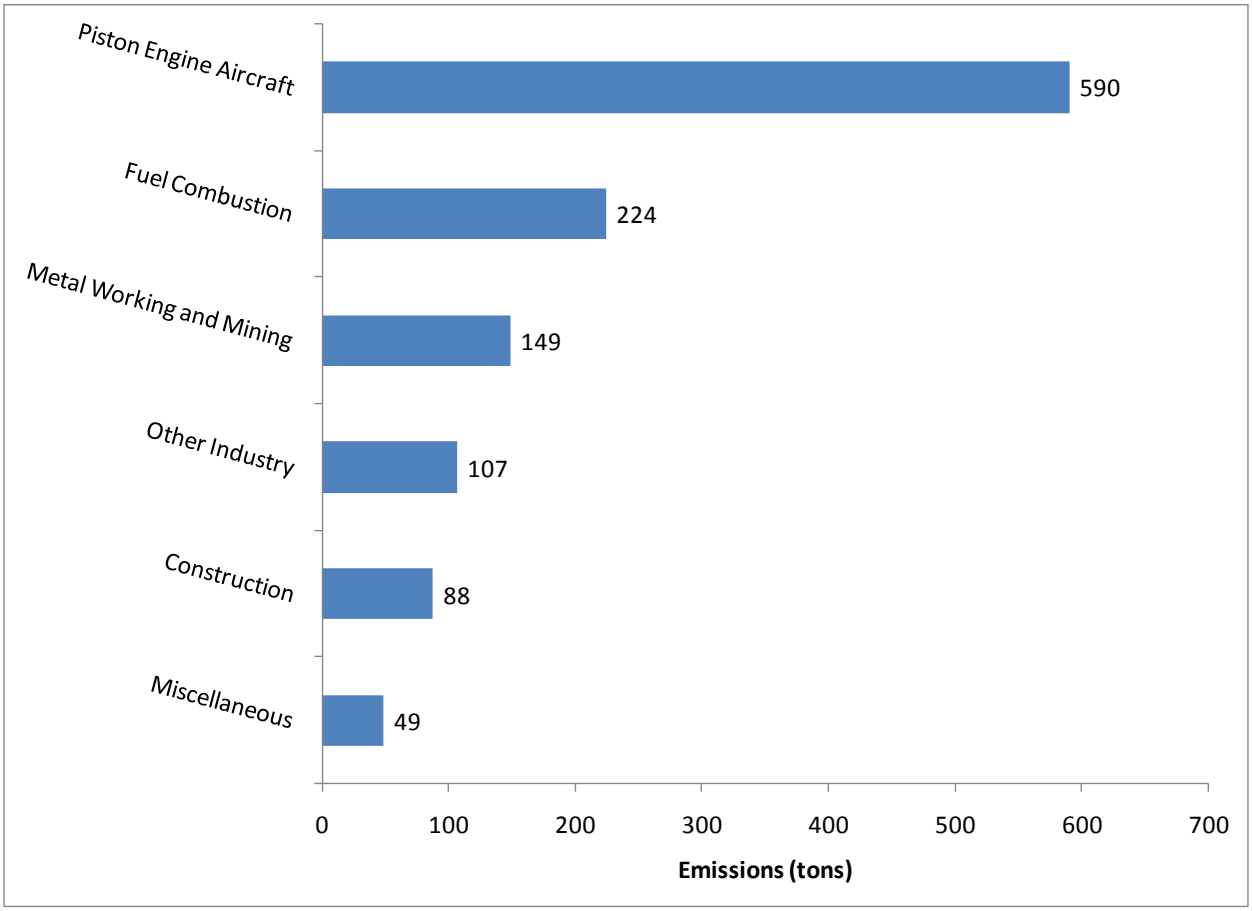
Piston Engine Aircraft
590
Fuel Combustion
224
Metal Working and Mining
149
Other Industry
107
Construction
88
Miscellaneous
49
0
100
200
300
400
500
600
700
Emissions (tons)

Table 1.

Global Search Terms: Pb AND		
Air	Federal Reference Method (FRM)	Resuspen*
Atmospher*	Gasoline	Road
Avgas	Highway	SLAMS
Aviation Fuel	IMPROVE	Smelt*
Aviation Gas	Industr*	Source Apportionment
Dispers*	Monitor	Spectrometry
Dust	NAMS	Total Suspended Particulate (TSP)
Environment	Particulate Matter (PM, PM_{10}, $PM_{2.5}$, $PM_{10-2.5}$)	Transport
Expos*	Regulatory network	Urban
Exclusion Terms		
AIDS	History	Pipe
Anesthesiology	Infectious Disease	Polymer Science
Anthropology	Information Technology	Produce Review
Astronomy	Jewelry	Psychiatry
Business/Economics	Legal Medicine	Radiology
Charm	Material Science	
Communicatin	Mathematics	Rehabilitation
Computer Science	Medical Ethics	Sociology
Critical Care Medicine	Medical Information	Solder
Crysallog*	Medical Laboratory Tech*	Social Issues
Demography	Microbiology	Sports Science
Education and Education Research	Microscopy	Steel
Electronic	Nursing	Substance Abuse
Engineering	Optics	Superconductor
Evolutionary Biology	Orthopedics	Surgery
E-waste	Parasitology	Telecommunications
Geology	Philosophy	Toy
Government Law	Physics	Transplantation
		Weapon

Table 2.

Paper	Purpose	Location (Date)	Sampling Method	Analysis
Lee *et al.* (1968)	Particle size distribution of metal components in urban air	Cincinnati, OH (urban) and Fairfax, OH (suburban) (Sep 1966-Feb 1967)	Modified 5-stage Andersen cascade impactor with backup filter. Use of an omni-directional inlet not reported.	Atomic absorption spectrophotometer (AAS)
Lee *et al.* (1972)	Metal concentration as a function of particle size	Six US metropolitan cities (Chicago, IL; Cincinnati, OH; Denver, CO; Philadelphia, PA; St. Louis, MO; Washington DC) (1970)	Modified 5-stage Andersen cascade impactor with backup filter. Use of an omni-directional inlet not reported.	X-ray spectrometry
MacLeod *et al.* (1973)	Diurnal trace metal pattern using spot samples with anodic stripping voltammetry technique	Chicago, IL and Washington DC (Nov-Dec 1968)	AISI spot tape sampler. Use of an omni-directional inlet not reported.	Anodic stripping voltammeter (ASV)
Purdue *et al.* (1973)	Atmospheric Pb in six US cities	Six US metropolitan cities (Chicago, IL; Cincinnati, OH; Denver, CO; Philadelphia, PA; St. Louis, MO; Washington DC) (1970)	Membrane filter (Millipore type HA: 0.45 micrometer pore). Use of an omni-directional inlet not reported.	AAS
Hudson *et al.* (1975)	Ambient lead concentration contributed from a traffic source	10 sites in the vicinity of Urbana-Champaign, IL (Aug 1973-Feb 1974)	Hi-Vol with 4 different particle sizing heads.	AAS
Dorn *et al.* (1976)	Metals concentrations and size near a Pb smelter and at a control site	Southeast, MO (Jan-Aug 1972)	8 stage Andersen impactor. 24 hour samples. Minimum 14 days sample collection per season per site. Use of an omni-directional inlets not reported.	AAS
Ragaini *et al.* (1977)	Metals concentrations near a Pb smelting complex	Kellogg, ID (Jan-Dec 1972)	24-hr Hi-Vol samples over 12-mos period with 8-day intervals. Use of omni-directional inlets not reported.	X-ray fluorescence (XRF)
Kleinman *et al.* (1980)	Chemical tracer concentrations in	5 sites in New York City (1968-1975)	7-day integrated air filter samples. Use of an omni-directional inlet not reported.	AAS

	airborne PM for source apportionment			
Alpert *et al.* (1981)	Trace elements for source apportionment	St. Louis, MO (Jul-Aug 1976)	Dichotomous sampler.	XRF
Dodd *et al.* (1991)	Metal concentration and size distribution of sub-micrometer particles	Deep Creek Lake, rural Maryland(Aug 1983)	Microorifice impactor (MOI) with a cyclone pre-collector (D_{50} of 2.5 μm). Use of an omni-directional inlet not reported.	XRF
Holsen *et al.* (1993)	Metal concentrations and dry deposition near Lake Michigan	Chicago, South Haven, and Lake Michigan, IL (Jul-Aug 1991)	Andersen I ACFM nonviable ambient particle-sizing sampler (AAPSS) with a pre-separator and 9 stages, Noll rotary impactor (NRI), and dichotomous sampler. Use of an omni-directional inlet on the AAPSS and NRI not reported.	AAS (AAPSS and NRI samples) and XRF (dichot samples)
Wu *et al.* (1994)	Trace elements for source apportionment	Chesapeake Bay, MD (Jun 1990-Apr 1991)	Dichotomous sampler with 10 μm impactor and Teflon filter.	Inductively coupled plasma – atomic emission spectrometer (ICP-AES)
Pirrone *et al.* (1995)	Trace metal trend in Detroit from 1982 to 1992	7 urban sites in Detroit, IL (1982-1992)	TSP Hi-vol sampler.	AAS
Sweet *et al.* (1998)	Trace metal concentrations and wet and dry deposition near Lake Superior, Lake Michigan, and Lake Erie	Eagke Harbor, MI (Lake Superior), Sleeping Bear Dunes, MI (Lake Michigan), Sturgeon Point, NY (Lake Erie)	Hi-vol dichotomous sampler with Teflon filter.	XRF
Singh *et al.* (2002)	Size distribution and diurnal pattern of metals in LA	Los Angeles Basin, CA (Sep 2000-Jun 2001)	Micro-orifice uniform deposit impactors (MOUDI). Use of an omni-directional inlet not reported.	XRF
Harrison *et al.* (2003)	Composition of size-fractionated PM in the roadside environment	Birmingham, United Kingdom (Oct 2000- Jan 2001)	Modified 4-stage MOUDI. Use of an omni-directional inlet not reported.	Inductively-coupled plasma – mass spectrometer (ICP-MS)
Newhook *et al.* (2003)	Review of metals concentrations near copper and zinc plants	Canada (1995-1998)	Mostly TSP samplers. Annual average data. . Use of omni-directional inlets not reported.	

Bein *et al.* (2005)	Ultrafine PM speciation for Pittsburgh Air Quality study	Pittsburgh, PA (Sep 2001-Sep 2002)	Rapid single particle mass spectrometer (RSMS-3). Analyzes submicrometer particles.	Ion mass spectrometer
Lough *et al.* (2005)	Trace metal analysis within two vehicular tunnels	Milwaukee, WI (Jul 2000-Jan 2001)	11-stage MOUDI. Use of an omni-directional inlet not reported. $PM_{2.5}$ and PM_{10} samplers built at the University of Wisconsin. Teflon filter media.	ICP-MS
Pekney *et al.* (2005)	Trace elements analysis for Pittsburgh Air Quality study	Pittsburgh, PA (Jul 2001-Sep 2002)	$PM_{2.5}$ and PM_{10} Hi-Vol samplers. Cellulose or Teflon filter media.	ICP-MS and XRF
Weitkamp *et al.* (2005)	Size and composition of particles from a coke production facility	Pittsburgh, PA (Aug-Sep 2002)	Semi-continuous element in aerosol sampler (SEAS: PM1.8), and Hi-Vol ($PM_{2.5}$)	AAS (SEAS samples) and ICP-MS (hivol samples)
Zereini *et al.* (2005)	Heavy metals in urban airborne PM in Germany	Frankfurt am Rhein, Germany (Aug 2001-Jul 2002)	Cellulose nitrate filter (PM_{22}) and an 8-stage Andersen impactor (PM_{10}). Use of omni-directional inlets not reported.	ICP-MS and total reflection x-ray fluorescence (TXRF)
Bein *et al.* (2006)	Sub-micrometer particle composition for source apportionment during Pittsburgh Air Quality study	Pittsburgh, PA (Jul 2001-Sep 2002)	Rapid single particle mass spectrometer (RSMS-3) analysis of submicrometer particles. Micro-orifice uniform deposit impactors (MOUDI); use of an omni-directional inlet not reported.	Ion mass spectrometer and ICP-MS
Birmili *et al.* (2006)	Composition of size-fractionated PM at a roadway, a road tunnel, and an urban background site	Birmingham, United Kingdom (Apr-Oct 2002)	Sierra-Andersen high-volume cascade impactor. Use of an omni-directional inlet not reported.	ICP-MS
Goforth *et al.* (2006)	Trace elements in rural area in the south eastern US	Tugaloo Arm of Lake Hartwell, GA (Feb-Mar 2003)	TSP with an open-face cassette. $PM_{2.5}$ with a cyclone separator. Membrane filters. Use of an omni-directional inlet not reported.	ICP-MS
Herner *et al.* (2006)	Analytical methods comparison for trace elements	Bakersfield, Bodega Bay, Davis, Modesto, Sacramento, and Sequoia, CA (Dec 2000-Feb 2005)	$PM_{2.5}$ Reference Ambient Air Sampler (RAAS) sampler and AIHL cyclone equipped MOUDI that collected particles smaller than 1.8 μm.	ICP-MS and XRF

Lee and Hopke (2006)	PM2.5 constituents for source apportionment	St. Louis, MO (Feb 2000-Dec 2003)	$PM_{2.5}$ Reference Ambient Air sampler (RAAS) and $PM_{2.5}$ Spiral Aerosol Speciation Sampler	XRF
Ondov *et al.* (2006)	PM chemical constituents at an industrial/urban site	Baltimore Supersite, MD (May 2001-Mar 2003)	$PM_{2.5}$ Reference Ambient Air Sampler (RAAS) and $PM_{2.5}$ SEAS (Semicontinuous Elements in Aerosol Sampler)	Not described
Sabin *et al.* (2006)	Resuspended metals near a freeway	Los Angeles, CA (April-May 2003)	Open-face cassette for TSP for 8 hours per event. Use of an omni-directional inlet not reported. Noll Rotary Impactor with 6, 11, 20, 29 μm stages. 2 to 8 hour samples, total of 3 sampling events.	ICP-MS
Wang *et al.* (2006)	Trace metals in size-fractionated PM	Kanazawa, Japan (May-Jun 2003)	Andersen 9-stage cascade impactor. Use of an omni-directional inlet not reported.	ICP-MS
Yi *et al.* (2006)	Trace elements in urban and industrial areas	2 sites near NY/NJ harbor (Sep 2001-Jun 2002)	Micro-orifice uniform deposit impactor (MOUDI) and coarse particle rotary impactor (CPRI). Use of an omni-directional inlet not reported.	ICP-MS
Kim *et al.* (2007)	PM2.5 chemical constituents for source apportionment for a rural Ohio River Valley site	Athens, OH (Mar 2004-Nov 2005)	FRM PM2.5 sampler	ICP-MS
Wojas *et al.* (2007)	PM concentrations and metal speciation of various PM fractions in urban and suburban areas	Oxford, OH (suburban) and Cincinnati, Middletown, and Hamilton, OH (Jan-Dec 2005)	$PM_{2.5}$ Reference Ambient Air sampler (RAAS) Andersen PM_{10} Hi-Vol sampler, and TSP Hi-Vol sampler.	Inductively coupled plasma (ICP)
Dall'Osto *et al.* (2008)	Size and chemical composition of PM near a large steelwork site	Port Talbot, UK (Apr-May 2006)	ATOFMS and 8-stage MOUDI. Use of omni-directional inlets not reported.	ICP-MS
Melaku *et al.* (2008)	Seasonal variation of heavy metals in Washington DC	Washington D.C. (Jul 2006-Jan 2007)	Multi-stage cyclone impactor and glass fiber filter. Use of an omni-directional inlet not reported.	AAS
Brüggemann *et al.* (2009)	Composition of size-fractionated PM at a curbside of a busy street	Dresden, Germany (Sep 2003- Aug 2004)	5-stage Berner type low-pressure impactor. Use of an omni-directional inlet not reported.	Proton-induced x-ray emission (PIXE)
Zota *et al.* (2009)	Metal concentrations in	Ottawa County	PM_{10} and $PM_{2.5}$ Harvard impactors for 7-day	EDXRF, SEM,

	two size fractions of ambient PM near mine waste and a control site	(Northeastern), OK (Jul 2005-Sep 2006)	integrated samples. Inlets are not omni-directional.	CCSEM/EDX
Makkonen *et al.* (2010)	Size distribution and chemical components of PM in background air in a forest	Virolahti, Finland (Feb 2006-Mar 2007)	Teflon filter samples with omni-directional inlets collecting PM_{10}, $PM_{2.5}$ and PM_1	ICP-MS

Table 3.

Study	Location or Site Type	TSP ($\mu g/m^3$)	PM_{10} ($\mu g/m^3$)	$PM_{2.5}$ ($\mu g/m^3$)	PM_1 ($\mu g/m^3$)	PM_{10}/TSP	$PM_{2.5}$/TSP	PM_1/TSP	$PM_{2.5}$/PM_{10}
Lee *et al.* (1968)	Urban Suburban							0.75 0.65	
Lee *et al.* (1972)	Chicago, IL Cincinnati, OH Denver, CO Philadelphia, PA St. Louis, MO Washington D.C.					0.93 1.00 0.99 0.98 0.98 0.99	0.83 0.88 0.88 0.87 0.81 0.90	0.59 0.72 0.70 0.70 0.62 0.74	0.89 0.88 0.89 0.89 0.83 0.91
Dorn *et al.* (1976) [a,b]	Near a Pb smelter Year Winter Summer Control site Year Winter Summer	 1.04 1.76 0.78 0.11 0.10 0.08	 0.91 1.69 0.54 0.09 0.10 0.08	 0.47 0.84 0.32 0.06 0.07 0.04	 0.27 0.46 0.18 0.04 0.04 0.03	 0.88 0.96 0.69 0.83 0.93 0.94	 0.45 0.48 0.41 0.52 0.70 0.51	 0.26 0.26 0.23 0.32 0.36 0.34	 0.51 0.50 0.59 0.63 0.75 0.54
Alpert *et al.* (1981)	Urban	0.913		0.720			0.79		
Holsen *et al.* (1993)	Urban Rural Lake Michigan		0.0257 0.0052 0.0112	0.0189 0.0043 0.0091					0.69 0.92 0.81
Sweet *et al.* (1998)	Lake Erie Lake Michigan Lake Superior		0.9 1.4 1.3	7.0 2.1 3.1					
Singh *et al.* (2002)	Traffic+Industrial Receptor		0.0069 0.0039	0.0059 0.0021	0.0051 0.0017			0.67[c] 0.41[c]	0.86 0.60
Harrison *et al.* (2003)	9m from a highway		0.0274			0.98	0.89	0.80	0.90
Lough *et al.* (2005)	Traffic Tunnel					0.85[d]	0.39[d]	0.20[d]	0.46[d] 0.17[e]

Study	Location or Site Type	TSP ($\mu g/m^3$)	PM_{10} ($\mu g/m^3$)	$PM_{2.5}$ ($\mu g/m^3$)	PM_1 ($\mu g/m^3$)	PM_{10}/TSP	$PM_{2.5}$/TSP	PM_1/TSP	$PM_{2.5}/PM_{10}$
Zereini *et al.* (2005)	Main street Side street Rural	0.0326[f] 0.0126[f] 0.0116[f]						0.45[c] 0.60[c] 0.64[c]	0.59 0.78 0.82
Yi *et al.* (2006)	Traffic+Indus. Traffic	0.0097 0.0066	0.0071 0.0061	0.0040 0.0051	0.0028 0.0038	0.73 0.93	0.42 0.77	0.29 0.57	0.57 0.82
Goforth *et al.* (2006)	Rural	0.0150		0.0061			0.41		
Sabin *et al.* (2006)[◊]	10m from hwy Urban bkg	0.0200 0.0110	0.0132 0.0091			0.66 0.83			
Wang *et al.* (2006) [a]	Traffic + Industrial	0.0045	0.0044	0.0031	0.0017	0.99	0.69	0.37	0.69
Dall'Osto *et al.* (2008)[a,g]	Near a large steelwork site + major motorway	0.0306	0.0290	0.0245	0.0140	0.95	0.80	0.46	0.84
Brüggemann *et al.* (2009)	curbside of a busy street		0.0169	0.0154	0.0120			0.71[c]	0.86
Zota *et al.* (2009)	Near mine waste Traffic + Mine waste Upwind		0.0114 0.0052 0.0030	0.0035 0.0022 0.0019					0.31 0.42 0.63
Makkonen *et al.* (2010)	Rural bkg No wildfire Wildfire		 0.0099 0.0153	 0.0055	 0.0035 0.0097			 0.35* 0.64*	 0.55

a TSP calculated as a sum of all size fractions
b PM > 0.43 μm
c PM_1:PM_{10}
d Estimated from mass emissions distribution measured using MOUDIs
e U. of Wisconsin samplers
f PM < 22 μm
g 0.10 μm <PM< 75 μm