

Testing the Metals Hypothesis in Spokane, Washington

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A 7-year, time-series, epidemiologic study is ongoing in Spokane, Washington, to examine the associations between ambient particulate constituents or sources and health outcomes such as emergency department (ED) visits for asthma or respiratory problems. One of the hypotheses being tested is that particulate toxic metals are associated with these health outcomes. Spokane is a desirable city in which to conduct this study because of its relatively high concentrations of particulate matter, low concentrations of potentially confounding air pollutants, variability of particulate sources, and presence of several potential particulate metals sources. Daily fine- and coarse-fraction particulate samples are analyzed for metals via energy-dispersive X-ray fluorescence (EDXRF) and instrumental neutron activation analysis. Particulate sources are determined using receptor modeling, including chemical mass balancing and positive matrix factorization coupled with partial source contribution function analysis. Principal component analysis has also been used to examine the influence of sources on the daily variability of the chemical composition of particulate samples. Based upon initial analyses using the EDXRF elemental analyses, statistically significant associations were observed between ED visits for asthma and increased combustion products, air stagnation, and fine particulate Zn. Although there is a significant soil particulate component, increased crustal particulate levels were not found to be associated with ED visits for asthma. Further research will clarify whether there is an association between specific health outcomes and either coarse or fine particulate metal species. **Key words:** aerosols, asthma, health effects, particulate matter, PM₁₀, PM_{2.5}, positive matrix factorization, receptor modeling, source apportionment. *Environ Health Perspect* 110(suppl 4):547–552 (2002).

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In response to new epidemiologic information regarding the associations between exposure to atmospheric particulate matter (PM) and increased health risks, including both mortality and morbidity, the U.S. Environmental Protection Agency (U.S. EPA) recently adopted new ambient air quality standards for particulate matter with a mass median aerodynamic diameter less than 2.5 μm (PM_{2.5}). Even so, many questions remain regarding the mechanism(s) responsible for the adverse health effects associated with exposure to PM, and the causative components of PM. In 1998 the National Research Council (NRC) was given the tasks of identifying the most important research priorities and monitoring research progress toward improved understanding of the associations between mortality or morbidity and atmospheric PM (1). Included in the research priorities is identification of the roles of specific constituents of PM mixtures. The constituents hypothesized to play a role in adverse health effects associated with PM include particles of certain sizes (e.g., fine vs. coarse particles), high numbers of particles (i.e., the ultrafine particles present in very large numbers but that do not contribute significantly to the total particulate mass), and specific classes of chemicals, including, but not limited to, organic species, soot, acid aerosols, and transition metals. It is generally thought that the more important PM

constituents from a health standpoint are those that are anthropogenic (man-made) and that fall into the fine particulate size range (2), but the role of coarse PM in observed health effects has not been ruled out. On the one hand, the general consistency among epidemiologic studies across a number of cities may suggest that the particulate mass concentration is responsible for observed health effects (3). On the other hand, estimated relative risks vary considerably from one place to another, and this variation may be due to differences in toxicity of PM that arise from differences in chemical and size characteristics (1). PM_{2.5} includes a mixture of combustion aerosols, secondary products, and crustal components (i.e., generated from mechanical grinding of geologic materials, including dust from paved and unpaved roads, unpaved parking lots, agricultural operations, and windblown dust). Briefly, it is not known whether the fine particulate mass (PM_{2.5}) is the most appropriate indicator for particles (or other air pollutants) that present the health risks currently linked to PM, or whether certain components of the fine particle mass are differentially more toxic.

One hypothesis that the NRC is interested in examining is the possible role of particulate transition metals in particulate toxicity. This hypothesis arises because a number of toxicologic studies have shown that many transition metals have cytotoxic

and inflammatory properties [see Lighty et al. (4) and references therein]. Toxicologic studies that examined the effects of inhalation exposure to metals found that the respiratory tract was a major target for the toxicity [e.g., Kelleher et al. (5)]. Human health effects resulting from acute occupational exposure have included respiratory tract irritation, bronchitis, rhinitis, impaired lung function, emphysema, and asthma, depending upon the metal and the level of exposure (6). Beyond occupational exposure and laboratory animal exposure studies, however, few studies examine the metals hypothesis for explaining the association between observed health outcomes and ambient PM exposures. In a recent study conducted on human airway epithelial cells (7), extracts of total PM collected in Provo, Utah, generated biological responses that could be replicated by culturing cells with quantities of Cu²⁺ comparable with those found in Provo extracts. The authors then hypothesized that Cu ions are responsible for the sensitivity of asthmatic individuals to Provo PM that has been previously reported in epidemiologic studies [e.g., Pope (8,9)].

Sources of particulate metals include industrial point sources (e.g., mineral processing), dusts, and combustion processes such as those found in Spokane, Washington. Ambient PM in Spokane is unique in that it has a large

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crustal component as well as high levels of particulate combustion products. This airshed then provides an opportunity to sort out the effects of fine particulate mass as well as specific particulate components, including metals, combustion products, and crustal materials. Spokane is a semiarid, western city with a medium-sized urban population of approximately 200,000, and over 400,000 who live in the Spokane Valley. The area experiences periodic violations of the air quality standards for particulate matter with a mass median aerodynamic diameter less than 10 μm (PM_{10}) and is currently classified as a nonattainment area for PM_{10} . There are several particulate "seasons" that lead to greatly differing particulate chemical characteristics and concentrations (10). In the winter, the Spokane Valley is prone to inversions, and in addition to vehicular exhaust, residential wood burning contributes significantly to particulate pollution. In the fall, prescribed agricultural burning of myriad acres of bluegrass seed and wheat stubble fields takes place. In the late summer, during hot, dry periods, Spokane experiences high PM_{10} because of re-entrainment of dust from unpaved roads and parking lots, and during windy periods, wind-blown dust storms may occur (11). In contrast to many urban areas in the Eastern United States, the sulfur dioxide (SO_2) concentration, the fraction of secondary PM mass (including both sulfates and nitrates), and the level of particulate acidity are relatively low in Spokane PM (12). Major point sources of particulate pollution include a municipal waste incinerator and an aluminum smelter and there are several smaller potential particulate metal sources from metals processors and electronics manufacturing. The major point sources are on the outskirts of town, with the incinerator located southwest of the city and the aluminum smelter located to the northeast.

Toxic or transition metals potentially of concern in Spokane could include those that would derive from anthropogenic sources, such as oil-fired generating stations that would emit V, Fe, Zn, Pb, Cu, As, Co, Cr, Mn, and Sb. The municipal waste incinerator in Spokane would be expected to be a potential source of Zn, Fe, Hg, and Pb, in particular, with trace amounts of some of the other metals. The aluminum smelter, and other smaller metal processing facilities, would be sources of particulate metals, including Cu, Mn, Zn, and Cr. Natural crustal sources are also sources of many metals, such as (in order of decreasing abundances) Fe, Mn, Zn, Pb, V, Cr, Ni, Cu, Co, Hg, Cd, and possibly As from agricultural soils treated with pesticides. Many of these metals have already been detected via energy-dispersive X-ray fluorescence (EDXRF) in at least some of the Spokane particulate samples, including As, Cd, Cr, Co, Pb, Mn, Hg, V, and soluble Fe

(via inductively coupled plasma emission spectroscopy). As a final note, during the course of this study in Spokane, because of union labor strikes and high energy costs that have enabled the aluminum smelter to sell its energy allotment at a profit over actual aluminum production, the aluminum smelter was temporarily shut down in mid-December 2000 and remains shut down as of May 2002.

The implication of these sources of PM in a city classified as nonattainment for PM_{10} is that it is possible to examine associations between adverse human health effects and primary PM chemical constituents without some of the major confounding species (ozone, acids, sulfates, nitrates) present in high concentrations. These are described in the following sections [see also Norris et al. (13)]. Moreover, it is possible, in the Spokane data, to isolate effects associated with exposure to ambient PM from combustion sources from those associated with PM from other sources.

Spokane study. An extensive epidemiologic study examining the associations between health outcomes and specific chemical constituents of PM is currently being conducted in Spokane, with daily $\text{PM}_{2.5}$ as well as coarse-fraction PM [between 2.5 and ~ 8 μm in diameter ($\text{PM}_{8-2.5}$)] having been collected and chemically characterized from January 1995 to 15 May 2002. In Spokane, SO_2 concentrations are trivial, so confounding by this co-pollutant is not a factor.

Spokane was the location of a previous epidemiology study (14) in which the associations between short-term changes in air pollution and hospital admissions for pneumonia and chronic obstructive pulmonary disease (COPD) were examined. That study found that the magnitude of the PM_{10} effect was similar to that reported for other locations in the eastern United States and in Europe that would be subject to confounding by weather and by other co-pollutants such as SO_2 .

In summary, Spokane represents a suitable city in which to conduct an epidemiologic study on airborne PM and its associations with health effects, because of relatively high particulate levels; low levels of confounding air pollutants, including ozone, SO_2 , acids, sulfates, and nitrates; good variability of particulate sources; and the medium size of the catchment area (400,000 persons). The shutdown of the aluminum smelter may also represent an unusual opportunity to examine the relationship between health outcomes and this specific source of particulate pollution.

The overall goal of the Spokane studies has been to examine the relationship between certain health outcomes and components of particulate pollution. The objective of the ongoing study in Spokane is specifically to test the hypothesis that health effects are associated with atmospheric particulate transition

metals species. The approach is a long-term (>7 years), time-series, epidemiologic study. Specific health outcomes of interest include asthma and respiratory emergency department (ED) visits and admissions for asthma and respiratory problems (including pneumonia, COPD, acute upper respiratory tract infections not including colds, and pediatric and adult asthma) and hospital admissions for respiratory or cardiovascular events. A secondary objective is to examine associations between specific source contributions of PM in Spokane and health outcomes. We realize that different health outcomes will not necessarily have the same mechanism for causation attributed to air pollution components. In this article we outline the methods for the overall study, then focus on asthma and summarize the findings to date from these studies conducted in Spokane, as well as discuss the intended future analyses.

Materials and Methods

Data Collection

Since 1995, daily fine ($\text{PM}_{2.5}$) and coarse ($\text{PM}_{8-2.5}$) particle samples have been collected at a central monitoring site in Spokane. Samples have been collected using the Versatile Air Pollutant Sampler (VAPS, URG Corp., Carrboro, NC, USA), a dichotomous type of sampler that splits the fine-fraction flow into two streams, thus allowing two separate fine-fraction samples to be collected, along with one coarse-fraction sample. Fine particulate samples have been chemically characterized for a variety of species, including elemental carbon (EC) and organic carbon (OC) via thermal manganese oxidation and the thermal optical transmission analysis based upon National Institute for Occupational Safety and Health method 5040 (15), ionic species sulfate and nitrate via ion chromatography and ammonium via automated colorimetry, >40 elements via EDXRF, and additional elements and metals via instrumental neutron activation analysis (INAA). Coarse particulate samples have also been analyzed via EDXRF and INAA. Metals of interest for the present study include several detected by EDXRF (Mn, Cd, Ni, Pb, Hg, V, Ti, Zn, and Fe), and several detected by INAA (As, Co, Cr, Sb, and Se as well as Fe and Zn). In addition to the 24-hr integrated particulate samples, continuous PM_{10} , $\text{PM}_{2.5}$, and PM_1 have been measured using tapered element oscillating microbalance technology (TEOM; Rupprecht and Patashnik Inc., Albany, NY, USA). Supporting measurements also include hourly wind speed, wind direction, ambient pressure and temperature, and carbon monoxide and SO_2 levels. Ozone is also measured regularly in Spokane during the ozone season but not at the same

monitoring site. NO₂ has been measured periodically in Spokane and is currently measured at the same site. Averaged 3-hr relative humidity data are available from the Spokane International Airport.

Health data have also been collected since 1994, and health outcome measures include ED visits and admissions (both childhood and nonelderly) at the four Spokane hospitals for asthma and respiratory problems including COPD, pneumonia, bronchitis, and upper respiratory infections but not including colds or sinusitis; hospital admissions (both childhood and nonelderly) for respiratory events; and total respiratory mortality. Gastroenteritis is used as a control.

Statistical Methods

Statistical approaches include standard ecologic time-series Poisson regression using a generalized additive model. Smoothing for time, day of week, and weather is performed. Single or multiple pollutants are used as linear terms for exposures, and short-term (e.g., 0-, 1-, 2-, and 3-day) lags are tested. Associations tested to date have included those between both nonelderly (defined as younger than 65 years) and childhood (younger than 18 years) ED visits for asthma and regularly monitored U.S. EPA criteria air pollutants, as well as PM size fraction and chemical composition (12). In the statistical analyses yet to be conducted, various transition metals will be tested directly, as well as source contributions from a source apportionment model. Also, outcomes to be tested will eventually include total respiratory hospital admissions and mortality.

Receptor Modeling

The influence of sources on the daily variability of the chemical data obtained from the elemental analyses, as well as the other chemical measurements, has been examined using principal component analysis (PCA) (12,13), and positive matrix factorization combined with partial source contribution function analysis (PMF/PSCF) (16). Current source apportionment studies use the chemical mass balance (CMB) method (17). PCA and PMF use the ambient measurements taken at the receptor site to identify the sources, rather than taking selected chemical profiles of sources from a source library, as is required

for CMB. In other words, in PCA and PMF, it is not necessary to identify the sources *a priori*, but rather it is possible to extract them as multivariate features that underlie the measurements. PCA and PMF differ from each other in the criteria they use to extract the source features. PCA attempts to capture the maximum amount of variation in the data set, whereas PMF tries to solve the mass balance equation with positive constraints on the mass contributions. PMF also accounts for the uncertainty in each data point as opposed to the overall uncertainty of the fitted model (18). In summary, the PCA and PMF features are not the same. The Spokane data have been analyzed via both these techniques as well as by CMB.

Results

PM Climatology in Spokane

Table 1 shows the range of conditions for various meteorologic and pollution measurements in Spokane for the period of January 1995 through 1997. Figure 1 shows a summary of the fraction of particulate samples collected from January 1995 through December 1997, with levels of selected elements and metals of interest above their detection limits for EDXRF and INAA. These two methods are complementary, with EDXRF detecting a higher percentage of Mn, Hg, Cd, Ti, and V on Spokane samples; INAA detecting a higher percentage of Cr, Co, As, and Sb on Spokane samples; and both methods detecting comparable percentages in Spokane for Zn, Fe, Ni, and Se.

To determine whether the metals concentrations will be intercorrelated, multivariate methods were applied to the EDXRF data that have been collected. Table 2 shows correlation coefficients for the various metals detected by EDXRF, along with some other particulate characteristics. Ti, Fe, and Mn are significantly correlated to reconstructed fine soil, with correlation coefficients greater than 0.90. There appear to be small but possibly significant correlations between vanadium and titanium ($r = 0.36$), and between vanadium and chromium ($r = 0.42$). Of the rest of the toxic metals of interest, it appears that only lead is correlated to other characteristics of atmospheric PM, with correlation coefficients for PM₈, PM_{2.5}, and OC greater than 0.30.

Although the data in Table 2 suggest that the various metals are not intercorrelated, this might be expected to some extent because of the low concentrations of metals species in fine PM. The incorporation of INAA along with EDXRF analysis provides better resolution for certain metal species such as As, Cr, Co, Se, and Sb (Figure 1) (17).

Receptor Analyses: PCA

To examine the major sources of variability in PM_{2.5} composition in Spokane, Norris (12) included several daily meteorologic indices in a PCA. A stagnation index was characterized by the number of hours during which stagnant conditions (i.e., hourly wind speed < 50th percentile value of the hourly wind speeds) existed. A "cold and foggy" index was characterized by cool temperatures and high relative humidity (i.e., reported foggy conditions, corresponding to near 100% relative humidity). The third meteorologic index was the aridity index, characterized by the number of hours in a day during which the relative humidity is less than 40%.

Norris (12) incorporated these meteorologic indices into a PCA of all pollutant measurements. Fine and coarse soil components were reconstructed using a mass attribution model (19) based upon the particulate mass concentrations of Si, Ca, Fe, and Ti. For Spokane, the factor analysis resulted in four factors accounting for 65.8% of the variation in the data set. The first factor (29.5% of variation) included loadings over 0.5 for the stagnation parameter, plus CO, particulate OC, and EC. The second factor (15.1%) included the cold and foggy indicator, plus NH₄⁺ and SO₄²⁻. The third factor (11.9%) was composed of coarse soil and particle number, and the fourth factor (9.3%) included the aridity index and the fine soil (12). The PM_{2.5} composition was also analyzed using PCA, which revealed three factors explaining 60.2% of the variability in the PM_{2.5} data set. These factors were represented by the three meteorologic indices as discussed above, and indicated that products of incomplete combustion were associated with stagnation; secondary aerosols were associated with cold, foggy conditions; and fine particulate soil was associated with low relative humidity (12).

Table 1. Meteorologic conditions and pollution measures for 1995–1997 in Spokane, Washington.

Percentile	RH (%)	T (°F)	T _d (°F)	SO ₂ (ppb)	PM _{10t} (µg/m ³)	PM _{8v} (µg/m ³)	PM _{2.5t} (µg/m ³)	PM _{2.5v} (µg/m ³)	TC (µg/m ³)	NO ₃ (µg/m ³)	SO ₄ ²⁻ (µg/m ³)	NH ₄ ⁺ (µg/m ³)
25 th	54.6	35.7	29.5	1.1	13.7	9.8	7.2	6.1	2.6	0.0	0.5	0.1
50 th	69.6	46.4	36.5	1.9	19.8	14.7	9.7	9.6	3.9	0.2	0.8	0.2
75 th	86.0	60.6	43.5	3.2	27.7	22.4	13.9	14.9	5.6	0.6	1.1	0.4
99 th	99.0	77.4	55.7	8.3	68.4	60.1	30.5	41.9	13.7	2.9	3.4	1.3

Abbreviations: RH, relative humidity; T, temperature; T_d, dew point; TC, total particulate carbon. Subscript "t" denotes particulate measurements from TEOM continuous monitors; subscript "v" denotes particulate measurements from 24-hr VAPS samplers. Ionic species are particulate components as well.

Receptor Analyses: PMF/PSCF

To further distinguish sources in Spokane, Kim et al. (16) used PMF on the EDXRF analyses on a portion of the PM_{2.5} data set (January 1995 through December 1997). Using PMF, seven sources were hypothesized: vegetative burning, automobiles, diesel exhaust, secondary PM, the municipal incinerator, soil, and a metal processing or copper source. As a result, PMF/PSCF identified both point sources and area sources, and the distinctions between these two types of sources are apparent. Area sources either exhibit seasonal behavior or a “background” value, whereas point sources tend to exhibit randomly occurring spikes that are usually correlated to wind direction. In Spokane,

the two major pollutant point sources are on the outskirts of town: the municipal waste incinerator, which is at the southwest corner of the airshed, and the Kaiser aluminum plant, which is at the northeast corner of the airshed. Although point sources would not be expected to uniformly impact a community because (depending upon wind direction) both point sources are occasionally upwind of the major population centers, the particulate measurements taken from the central monitoring site may provide a reasonable measure of the exposure of the community to particulate emissions from these sources. For testing the metals hypothesis, we believe we can take advantage of this capability of PMF/PSCF to distinguish

point sources because point sources may represent significant sources of metals.

Further examination of the secondary aerosol contribution identified by PMF was conducted using PSCF, which suggested that secondary aerosol, determined by a combination of sulfur, ammonium, and some iron, seems to be high when the wind direction is from the northeast, which is also the direction of the aluminum smelter. We speculate that when further elemental analyses from the ongoing INAA analyses are incorporated into the PMF receptor model, we may further resolve this source, currently identified as secondary aerosol, into a secondary aerosol plus the aluminum smelter.

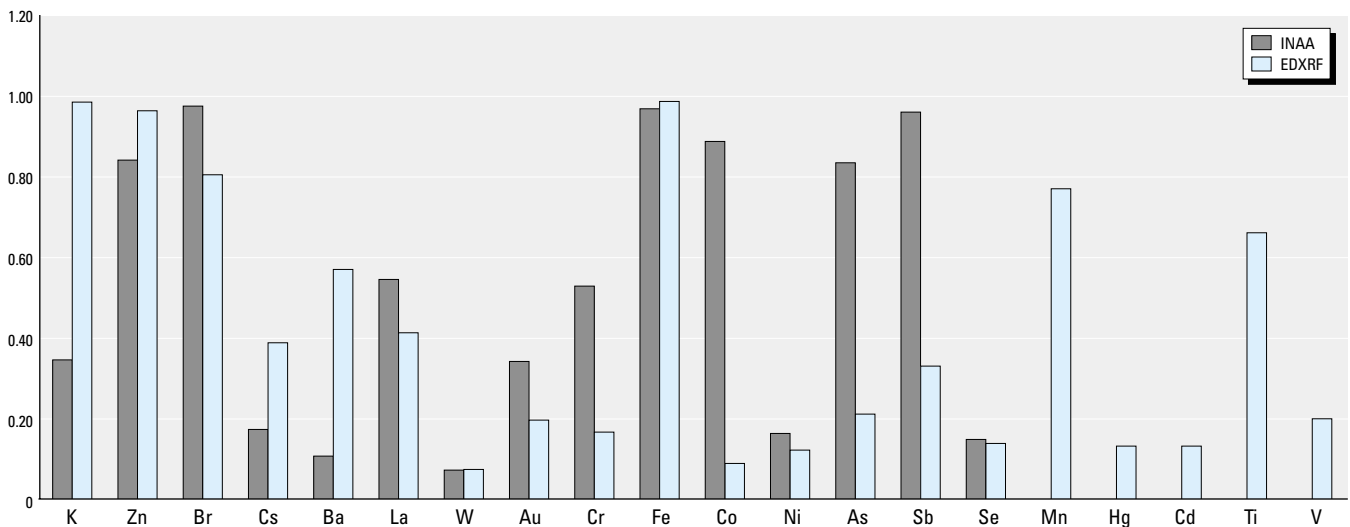


Figure 1. Comparison of EDXRF and INAA data for 698 ambient, fine particulate samples collected in Spokane from January 1996 through December 1997. Bars indicate the fraction of samples with amounts of indicated metals above the detection limit for each method.

Table 2. Pearson correlation coefficients for selected particulate components from 4 years of daily samples collected in Spokane, Washington.^a

	PM ₈	PM _{2.5}	OC	EC	NO ₃	SO ₄	NH ₄	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Cd	Sb	Hg	Pb	Soil	
PM ₈	1.00																							
PM _{2.5}	0.85 ^b	1.00																						
OC	0.66 ^b	0.77 ^b	1.00																					
EC	0.41 ^b	0.44 ^b	0.59 ^b	1.00																				
NO ₃	0.30 ^b	0.48 ^b	0.27	0.31 ^b	1.00																			
SO ₄	0.47 ^b	0.58 ^b	0.30 ^b	0.23	0.49 ^b	1.00																		
NH ₄	0.33 ^b	0.53 ^b	0.27	0.18	0.65 ^b	0.64	1.00																	
Ti	0.46 ^b	0.29	0.15	0.08	-0.04	0.23	0.01	1.00																
V	0.07	0.07	0.01	-0.08	0.01	0.10	0.07	0.36 ^b	1.00															
Cr	0.06	0.06	0.02	-0.04	0.01	0.04	0.04	0.18	0.42 ^b	1.00														
Mn	0.48 ^b	0.32 ^b	0.20	0.13	-0.06	0.23	-0.02	0.85 ^b	0.10	0.12	1.00													
Fe	0.51 ^b	0.35 ^b	0.20	0.11	-0.05	0.24	0.00	0.93 ^b	0.11	0.08	0.93 ^b	1.00												
Co	0.01	-0.01	-0.05	-0.01	0.04	0.03	0.02	0.05	0.04	0.01	0.01	0.03	1.00											
Ni	-0.01	0.01	0.00	-0.02	0.03	-0.03	0.03	0.06	0.00	0.10	0.07	0.06	0.03	1.00										
Cu	0.15	0.18	0.14	0.04	0.09	0.08	0.09	-0.02	0.02	0.02	0.01	0.00	-0.10	0.09	1.00									
Zn	0.55 ^b	0.64 ^b	0.55 ^b	0.31 ^b	0.29	0.31 ^b	0.34 ^b	0.21	0.04	0.08	0.26	0.27	-0.02	0.20	0.23	1.00								
As	0.22	0.27	0.22	0.14	0.16	0.22	0.16	0.07	0.03	0.02	0.06	0.08	-0.03	0.02	0.07	0.24	1.00							
Se	0.05	0.08	0.05	0.03	0.09	0.05	0.06	0.01	-0.03	0.00	0.04	0.03	0.07	-0.03	-0.02	0.08	0.13	1.00						
Cd	0.01	-0.02	-0.01	0.02	-0.06	-0.01	-0.01	0.02	-0.06	-0.03	0.04	0.04	0.02	-0.04	0.00	-0.03	0.02	0.02	1.00					
Sb	0.06	0.05	0.11	0.07	0.03	0.04	0.03	-0.02	-0.15	-0.09	0.07	0.03	-0.06	0.03	0.07	0.04	0.03	0.02	0.00	1.00				
Hg	-0.05	-0.03	-0.05	-0.05	-0.03	-0.04	0.00	0.02	0.02	0.02	-0.02	-0.01	0.06	-0.03	-0.04	-0.05	-0.09	0.05	0.02	-0.06	1.00			
Pb	0.32 ^b	0.41 ^b	0.31 ^b	0.17	0.16	0.26	0.24	0.17	0.00	0.00	0.22	0.22	0.02	0.07	0.10	0.50 ^b	-0.02	0.05	0.04	0.01	0.02	1.00		
Soil	0.48 ^b	0.32 ^b	0.16	0.09	-0.06	0.24	0.01	0.93 ^b	0.13	0.09	0.92 ^b	0.99 ^b	0.04	0.07	-0.02	0.23	0.09	0.03	0.03	0.02	-0.01	0.20	1.00	

^aMetals analyses were all determined using EDXRF. The soil component was determined using a mass attribution model (10,14). OC and EC were determined using thermal manganese oxidation, which does not include an optical correction for pyrolytic char. ^bCorrelation coefficient ≥ 0.30.

Health Studies

Epidemiologic studies completed to date for the Spokane data set have examined the relationships between ED visits for asthma and various pollution measures, including the PCA indices described above. Results to date are summarized below.

Associations with air pollution measures and meteorologic indices. Norris et al. (13) evaluated the associations between ED visits for asthma and several air pollutants and the meteorologic index for stagnation. A 27-month data set was used for this study (January 1995 through March 1997). Air pollution measures included PM₁₀, ozone, carbon monoxide, and SO₂. Nonelderly ED visits for asthma were significantly associated [95% confidence interval (95% CI), 1.05–1.19] with an increase in the interquartile range in the stagnation parameter, which was associated with products of incomplete combustion. Nonelderly ED asthma visits were significantly associated with an interquartile increase in PM₁₀ mass concentration during the spring and winter

only (95% CI, 1.05–1.26 and 1.01–1.16, respectively) (13).

The associations between ED visits for asthma and specific PM components from the same 27-month data set were further examined by Norris (12). PM exposure variables for this examination included several sizes, including PM₁, PM_{2.5}, PM₁₀, and coarse-fraction PM. Reconstructed soil PM_{2.5}, nonsoil PM_{2.5}, and coarse soil PM were examined. Chemical species examined included soil-corrected K (total K minus soil K), Zn, Cu, and S. Of the chemical constituents examined (Cu, OC, EC, S, Zn), Zn was the only one for which a statistically significant association with nonelderly ED asthma visits was observed (95% CI, 1.01–1.10, for an increase of 9 ng/m³). Zn was found to be associated with combustion sources; in the factor analysis of this 27-month data subset, the first factor, accounting for 34.6% of the variability, included the stagnation parameter as well as CO, OC, EC, and Zn. The association between particulate Zn and observed health outcomes is intriguing—it is not known whether Zn is a causative agent or an indicator for some other causative species. The role of Zn in the observed health outcomes associated with PM exposures is under further investigation.

Dust and soil PM. Norris (12) also examined the associations between ED visits and reconstructed soil. Reconstructed soil in the fine particle range (i.e., in PM_{2.5}) was not found to be associated with increased ED asthma visits in Spokane (95% CI, 0.89–0.97) (12). The associations between PM of crustal origin and other health end points have also been examined for Spokane. Schwartz et al. (20) found no association between total mortality and dust storm occurrences in Spokane. Given these observations, coarse-fraction (vs. fine-fraction) metal species would not be expected to be associated with either ED visit or mortality health outcomes. As mentioned above, particulate metal species from crustal sources could include Fe, Mn, Zn, Ti, and trace amounts of many other metals. Table 3

summarizes the range of metals concentrations found to date on coarse-fraction filters. Over 80% of the coarse-fraction samples contained detectable quantities of Fe, Mn, Ti, Cu, and Zn. With the particulate data set being amassed for Spokane, it will be possible to test for toxicity of several coarse-fraction metal species such as Fe, Mn, Zn, Cu, and Ti.

Ongoing studies. Currently, we are examining the relationships between specific particulate sizes (TEOM measurements of PM₁₀, PM_{2.5}, and PM₁) and certain health outcomes such as ED admissions for asthma or respiratory events using a larger data set (January 1995 through June 2001). Specific fine and coarse particulate metals will also be independently examined for any associations with health outcomes. Particulate metals that have been found in over 50% of the fine particulate samples analyzed to date include Cr, Co, As, and Sb (INAA); Mn and Ti (EDXRF); and Fe and Zn (both methods). Other toxic metals that have been detected but not in the majority of the Spokane samples include Hg, Cd, V, Ni, and Se. The relatively high number of these samples that contain below-detection concentrations of these metals will reduce the statistical power in any statistical analyses of these species. Sources of PM as determined using PMF/PSCF will also be used as exposure variables in further statistical analyses. This raises the question of whether any feature extractions in Spokane are correlated with any of the metals. Table 4 summarizes the correlations between fine particulate metals and the source features determined from PMF/PSCF. As expected, Fe and Mn are strongly correlated (correlation coefficients > 0.90) with soil. Co is also strongly correlated with soil and is detected in more than 90% of the INAA samples. Zn, As, and Sb are somewhat correlated with vegetative burning (correlation coefficients between 0.60 and 0.70), but the reasons for these associations are not known. This is consistent with the finding of Norris (12) that a correlation exists between Zn and the stagnation parameter, which in turn is linked to combustion sources.

Table 3. Coarse particulate metal species concentrations detected via EDXRF in PM_{8-2.5} samples collected in Spokane from January 1995 through March 1999.^a

Element	Mean concentration (ng/m ³)	Standard deviation	Samples > DL n	%
Fe	242.1	234.7	1,581	98.8
Mn	5.2	5.2	1,452	90.8
Ti	33.2	30.8	1,390	86.9
Cu	4.9	8.2	1,388	86.8
Zn	4.2	4.7	1,382	86.4
Cr	1.5	1.5	1,035	64.7
Ni	1.2	0.9	721	45.1
Pb	1.6	1.1	565	35.3
V	1.7	0.9	557	34.8
Sb	4.8	5.0	429	26.8
As	0.7	0.3	268	16.8
Hg	1.2	0.9	258	16.1
Co	1.7	0.9	242	15.1
Se	0.5	0.2	151	9.4

^aData are listed in order of decreasing frequency of observation at levels above detection limit (DL).

Table 4. Pearson correlation coefficients between fine particulate metals and particulate sources in Spokane, Washington.^a

	Ti	V	Mn	Fe	Ni	Cu	Zn	Cd	Hg	Pb	Sb	Se	As	Co	Cr
Diesel exhaust	0.00	-0.13	0.03	0.04	-0.11	-0.08	0.04	0.00	-0.03	0.10	0.00	0.12	0.18	0.05	0.02
Soil	0.95 ^b	0.47 ^c	0.93 ^b	0.98 ^b	-0.01	-0.04	0.18	0.01	-0.03	0.16	0.09	0.05	0.11	0.83 ^c	-0.07
Incinerator	-0.08	-0.03	-0.07	-0.06	0.05	0.02	0.19	0.03	-0.02	0.15	0.18	-0.02	0.21	-0.09	-0.01
Cu/metal	-0.04	0.20	0.01	-0.02	0.55 ^c	0.99 ^b	0.22	-0.15	0.04	0.08	0.08	0.00	0.08	0.01	0.00
Secondary	0.00	-0.05	-0.07	-0.03	0.01	0.05	0.31 ^d	0.11	-0.03	0.15	0.32 ^d	0.19	0.35 ^d	-0.11	-0.03
Motor	-0.05	-0.02	0.01	-0.03	0.02	0.05	0.18	-0.14	0.11	0.08	0.34 ^d	0.27 ^d	0.28 ^d	0.09	-0.12
Vegetative	0.10	0.15	0.13	0.20	0.01	0.07	0.66 ^c	0.01	0.00	0.37	0.63 ^c	0.37 ^d	0.66 ^c	0.18	-0.08
No. XRF	725	213	907	1,126	318	1,093	1,102	178	169	898					
XRF (%) ^e	64	19	81	100	28	97	98	16	15	80					
No. NAA											668	105	581	617	369
NAA (%) ^e											99	16	86	92	55

^aData were determined from PMF/PSCF analyses for January 1995 through December 1997 (EDXRF analyses) and for January 1996 through December 1997 (INAA analyses). ^bCorrelation coefficients > 0.90. ^cCorrelation coefficients between 0.40 and 0.90. ^dCorrelation coefficients between 0.20 and 0.40. ^ePercentage of samples that is above the detection limit.

Conclusions

Particulate studies conducted to date have shown that particulate pollution in Spokane occurs as a result of several factors, including stagnation periods during which concentrations of combustion products are high; arid conditions during which crustal PM is prevalent, and occasionally during which wind-blown dust storms occur; and cold and foggy conditions during which secondary aerosols occur. Seven major sources of ambient fine PM have been identified using PMF/PSCF, including both area and point sources. These sources are soil, automobiles, diesel exhaust, residential wood/biomass combustion, secondary aerosols, waste incineration, and a Cu or nonferrous metal processing source. The two major point sources in Spokane that may affect the airshed and contribute to particulate concentrations are a municipal waste incinerator located to the southwest of the airshed and an aluminum smelter located to the northeast. The source apportionment studies conducted to date have not included the ongoing INAA analyses; it is anticipated that the addition of INAA may help better resolve particulate sources such as the metal processing source and combustion sources.

Epidemiologic studies conducted to date on a subset of the data collected in Spokane have focused primarily on ED visits for asthma. Increased ED visits for asthma have been found to be associated with combustion products and air stagnation. These analyses will be more thoroughly examined with the full data set, which will span more than 7 years. ED visits have also been found to be significantly associated with fine particulate Zn, which is also associated with combustion products (specifically, biomass burning) and stagnation. It is not known whether exposure to particulate Zn represents a health risk, or whether Zn serves as an indicator of another pollutant(s) responsible for the observed health outcomes. Another possible explanation for the Zn effect is that it occurred as significant by chance and there is no underlying association. Analysis of longer time series will help clarify these findings.

Although PM₁₀ and PM_{2.5} in Spokane both have a significant soil component, the soil component in either particulate fraction is not associated with increased ED visits for asthma. Although particulate metals species are hypothesized to contribute to the toxicity of ambient PM, based upon these

observations we hypothesize that metals in the coarse fraction (i.e., those from soils) will not be associated with health outcomes, whereas metals in the fine fraction will be associated with health outcomes. Potential sources of fine-fraction particulate metals in Spokane include the incinerator and aluminum smelter in addition to combustion sources such as mobile sources.

These findings provide a good foundation for further hypotheses to be tested. Future analyses will test for associations between health outcomes and particulate Zn, as well as OC and EC, which are all associated with combustion products. The addition of INAA to the chemical analyses of particulate samples has increased the number of samples with detectable amounts of some of the toxic metals of interest, thus allowing additional statistical analyses to examine the role of toxic metals, including the coarse-fraction metals. Finally, specific particulate source contributions as identified from PMF/PSCF analyses will be examined.

As statistical tests proceed from an examination of PM mass to specific metal species, there will be some loss of statistical power because of the percentage of values below detection, although for some metals there is a large fraction of values that are above detection limits (e.g., Zn, Fe, Co, As, Sb, and Mn are detectable in >75% of the samples analyzed to date via EDXRF, INAA, or both). As statistical analyses proceed further to sources of particles, as identified by PMF/PSCF, we hypothesize that the health effects will be larger and therefore there will be greater statistical power for the analyses. In CMB-type receptor models, it is necessary to select the source profiles *a priori* from a source library. This means that the sources selected may not actually represent the particulate constituents to which the people are exposed. By contrast, in PMF/PSCF (and in PCA), the features are developed from the actual ambient measurements, which do represent the PM constituents to which the community is exposed. Testing for associations between specific source contributions as developed from PMF, therefore, may have less loss of power due to measurement error. Our previous work has already demonstrated that health effects are associated with the combustion feature determined from PCA but not the other features. An interesting

question that will be pursued is whether the same relationship will show up with any of the PMF/PSCF combustion features.

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