Elemental composition of PM_{10} and $PM_{2.5}$ in ambient air downwind of agricultural operations in California's San Joaquin Valley

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Abstract

Fugitive dust emissions from soil are thought to constitute a large fraction of the PM_{10} and $PM_{2.5}$ inventory in California's San Joaquin Valley (SJV) and other western air basins, especially during dry periods. The major sources of these emissions are paved and unpaved roads, construction sites, windblown dust, and agricultural activities. Furthermore, PM_{10} and $PM_{2.5}$ are considered to be among the most harmful of all air pollutants. When inhaled these particles evade natural defenses of the respiratory system and lodge deep in the lungs causing serious health problems. Some heavy metals in small particles have the tendency to donate electrons and to form basic oxides. Biologically, many metals are essential to living systems and are involved in a variety of cellular, physiological, and structural functions. But at high doses, many metals become toxic. The route of exposure may affect the dose and the site where the metal concentrates, and thus the observed toxic effect.

In California's San Joaquin Valley, agricultural operations are highly complex and potentially significant sources of PM_{10} and $PM_{2.5}$, especially during late summer and fall. A series of experiments was conducted to measure PM_{10} and $PM_{2.5}$ emissions with traditional array sampling from agricultural operations in San Joaquin Valley. The elemental analysis of PM_{10} and $PM_{2.5}$ collected in the field samples was conducted using Proton Induced X-Ray Emissions (PIXE), Proton Elastic Scattering Analysis (PESA) and X-Ray Fluorescence (XRF) analytical techniques available in our laboratory.

The composition of PM_{10} dust collected downwind of agricultural operations is different from the composition of the $PM_{2.5}$ dust collected at the same time. The smaller particles are enriched in sulphur and in heavy metals.

Keywords: PM_{10}, $PM_{2.5}$, fugitive dust, agriculture, particle speciation, elemental composition.

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1 Introduction

California's San Joaquin Valley is one of the most productive agricultural regions in the United States. The dominance of fugitive dust from mobile and agricultural sources in the fall has lead to the hypothesis that agricultural operations may contribute significantly to the exceedance of PM_{10} concentrations in the valley.

Carvacho, et al. [1, 2] documented a strong relationship between soil texture as measured by the amount of sand, silt, and clay in the soil and the amount of PM_{10} and $PM_{2.5}$ that could be generated from it (the PM_{10} or $PM_{2.5}$ Index). They also showed that the $PM_{2.5}$ that could be generated from a soil was approximately 10% of the PM_{10} that could be generated from the same soil. Carvacho, et al. [3] examined the composition of PM_{10} and $PM_{2.5}$ from resuspended soil samples collected in the San Joaquin Valley. Finally, Carvacho et al. [4] documented the presence of heavy metals in $PM_{2.5}$ that may be hazardous to human health.

In this study, we document the elemental composition of the ambient PM_{10} and $PM_{2.5}$ dust collected downwind of agricultural operations on a variety of soil textures, and the elemental enrichment of metals and other elements in $PM_{2.5}$ versus PM_{10} dust.

2 Materials and methods

All samples were collected on a single farm near Stratford, CA between July 26 and September 11, 1999. All measurements were made under actual field conditions. A combination of upwind/downwind source isolation and vertical profiling were used to quantify PM_{10} and $PM_{2.5}$ concentrations, as described in Holmén et al. [5], and shown in Figure 1. We collected ambient PM_{10} and $PM_{2.5}$ on Teflon filters using IMPROVE samplers [6, 7] for gravimetric and elemental analyses.

The aerosol mass concentrations were calculated using the gravimetric method. The elemental composition (22 elements) was determined using three analytical methods: PIXE (Proton Induced X-ray Emissions) for elements with atomic mass less than Fe, XRF (X-Ray Fluorescence) for Fe and above, and PESA (Proton Elastic Scattering Analysis) for hydrogen. Further details of these techniques are described elsewhere [7–9]. PIXE and PESA were conducted using 4.5 MeV protons produced by the 76" cyclotron at the Crocker Nuclear Laboratory of the University of California in Davis. XRF analysis used a General Electric grounded anode diffraction type X-ray tube with molybdenum anode.

2.1 Composite variables

A SOIL parameter was calculated using the IMPROVE formula by adding the concentrations of five major soil elements in their typical oxide form [10] as shown in eqn (1).

$$SOIL = 2.20*[Al] + 2.49*[Si] + 1.63*[Ca] + 2.42*[Fe] + 1.94*[Ti] \quad (1)$$

The hydrogen concentration is useful as an estimate of organic mass. Sulphur was used to calculate the sulphate aerosol component, which is assumed to be ammonium sulphate. Organic mass and sulphate were calculated following the IMPROVE formulas [10, 11], shown in eqns (2) and (3).

$$Organic(byH) = 13.75 * ([H] - 0.25 * [S]) \tag{2}$$

$$SO_4^{=} = 4.125 * [S] \tag{3}$$

Figure 1: Photograph of downwind sampling array and meteorological measurement tower in a land preparation field study.

3 Results and discussion

Figure 2 shows the mass concentration and fractional composition of the PM_{10} dust collected from ambient samples downwind of agricultural operations. For all the soil types examined, mineral soil (i.e. the SOIL parameter) accounts for 77% to 87% of the PM_{10} mass in downwind ambient samples. Organic matter comprises 12% to 22% of the PM_{10} mass for all soil types, with sulphate, metals, and other elements accounting for 1% or less.

Figure 3 shows the mass concentration and fractional composition of the $PM_{2.5}$ dust collected from ambient samples downwind of agricultural operations. The $PM_{2.5}$ mass is 6% to 7% of the PM_{10} mass for all soil types except loam, where it is 12% of the PM_{10} mass. Mineral soil accounts for 37% to 66% of the $PM_{2.5}$ mass for all soil types. Organic matter accounts for 32% to 41% of the $PM_{2.5}$ mass, and sulphate is 2% to 21%. Metals and other elements account for 3% or less of $PM_{2.5}$ mass.

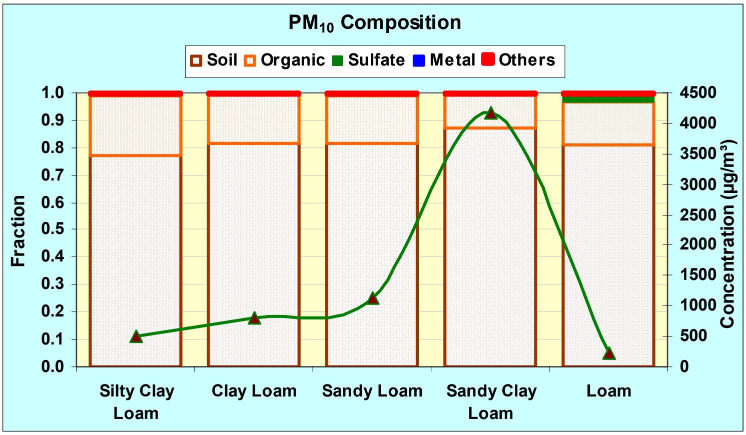

Figure 2: Concentration and composition of PM_{10} soil dust from ambient samples.

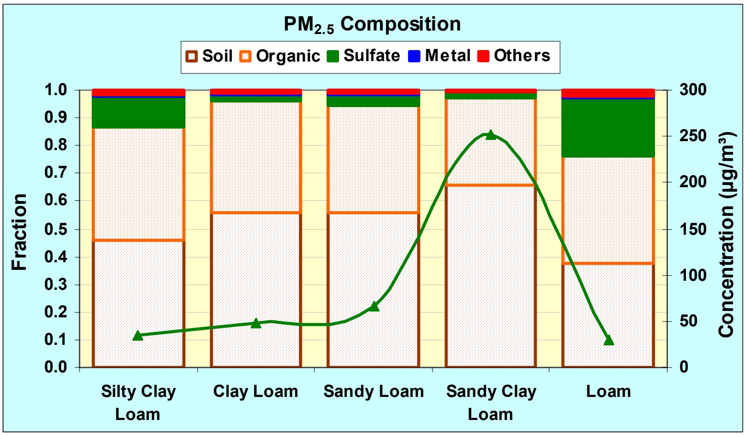

Figure 3: Concentration and composition of $PM_{2.5}$ soil dust from ambient samples.

In general, the elemental composition of the ambient samples collected during agricultural operations suggests the dust is mostly local soil. Exceptions are for sulphate, metals, and organic mass. This is possibly because the ambient samples contain sulphate and metals from San Joaquin Valley air that are not present, or are present in very small amounts, in the underlying soil. The contribution from ambient background particulate matter was subtracted from the downwind samples, though, so the contribution from agricultural equipment may be a major source of these components.

We calculated enrichment factors (Table 1) relative to silicon using eqn (4) for elements in $PM_{2.5}$ compared to elements in PM_{10} samples.

$$EF = \frac{\left([E_{2.5}]/[Si_{2.5}]\right)}{\left([E_{10}]/[Si_{10}]\right)} \tag{4}$$

In eqn (4) EF is the enrichment factor, $[E_x]$ is the elemental concentration in the $PM_{2.5}$ or PM_{10} fraction, and $[Si_x]$ is the silicon concentration in the $PM_{2.5}$ or PM_{10} fraction.

Table 1: Enrichment factors for elements in $PM_{2.5}$ versus PM_{10} relative to silicon.

Element	Silty Clay Loam	Clay Loam	Sandy Loam	Sandy Clay Loam	Loam	Average all soils
H	4.1	3.8	3.7	3.6	7.1	4.5
Al	1.1	1.1	1.0	0.8	0.8	1.0
Si	1.0	1.0	1.0	1.0	1.0	1.0
Ca	2.4	1.7	2.1	1.7	1.8	2.0
Ti	0.5	1.7	1.5	1.6	1.5	1.3
Fe	1.3	1.3	1.2	1.4	1.4	1.3
S	36.5	11.5	13.1	13.0	17.6	18.4
V	40.0	16.3	4.0	5.7	8.1	14.8
Cr	8.9	12.4	18.3	4.3	11.2	11.0
Mn	5.1	3.8	2.4	2.1	2.0	3.1
Ni	9.3	8.5	7.7	6.5	7.2	7.8
Cu	46.1	21.8	43.9	14.3	12.4	27.7
Zn	15.4	8.0	10.7	9.4	3.5	9.4
Ga	16.2	11.6	13.2	9.6	12.1	12.6
Hg	17.5	11.8	15.1	9.8	7.8	12.4
As	6.9	7.7	4.9	3.8	13.1	7.3
Pb	17.4	16.4	24.6	11.7	4.4	14.9
Se	17.6	13.7	16.1	11.3	11.4	14.0
Br	17.9	15.4	28.7	5.3	17.4	16.9
Rb	2.0	2.0	1.7	1.3	2.7	1.9
Sr	1.6	1.9	1.4	1.2	1.3	1.5

Table 1 shows the enrichment factors for all five soils and for the average of all soils. The enrichment factors are also shown graphically in Figure 4. Four of the five soil elements (Al, Si, Ti, and Fe) are very similar in the $PM_{2.5}$ and PM_{10} fractions for all soil types. Calcium is enriched in the $PM_{2.5}$ fraction by a factor of two. Rubidium and strontium are also slightly enriched (by less than a factor of two) in the $PM_{2.5}$ fraction. Hydrogen, manganese, nickel, and arsenic are enriched by factors of 3-8. Other metals, including V, Cr, Ga, Hg, Pb, Se, and Br are enriched by factors of 11 to 17 on average, with a wide variation for individual soil types. Sulphur is enriched by a factor of 18 on average with a range of 11.5 to 36.5. Finally, copper is enriched by a factor of nearly 28 on average, with a range of 12 to 46 for different soil types. It's not clear whether the source of these metals is the underlying soil, background $PM_{2.5}$ concentrations in the San Joaquin Valley atmosphere, or the emissions of the agricultural equipment used in the operations being sampled. The background concentrations were subtracted from these measurements, though, so it's unlikely that ambient levels are the source.

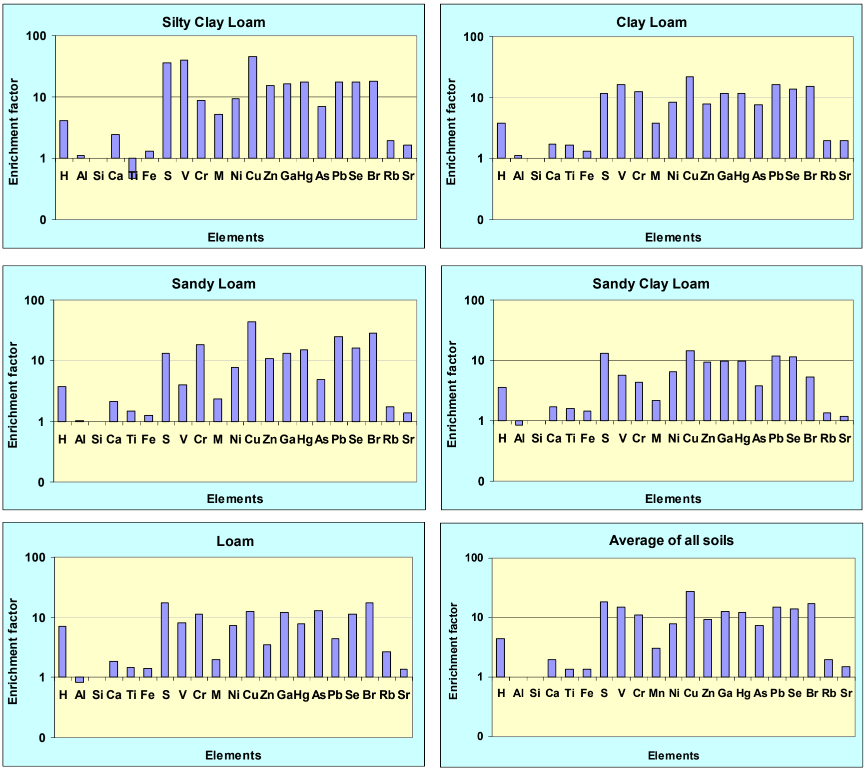

Figure 4: Enrichment factors, relative to silicon, of elements in $PM_{2.5}$ versus PM_{10}.

4 Conclusions

The composition of PM_{10} soil dust collected downwind of agricultural operations is primarily underlying mineral soil with a small fraction representing organic matter. The PM_{10} fraction is approximately 80% mineral soil (as calculated by the IMPROVE equation) and 20% organic matter, with only minor amounts of sulphate and metals.

The composition of $PM_{2.5}$ soil dust collected downwind of agricultural operations is enriched in sulphur and heavy metals as compared to the PM_{10} fraction. The $PM_{2.5}$ mass concentration is 6-7% of the PM_{10} concentration for operations on most soils, but is higher (12%) for operations on loamy soil. The $PM_{2.5}$ composition is more variable than the PM_{10} composition, with 37-66% mineral soil, 32-41% organic matter, up to 20% sulphate and less than 1% metals.

Sulphate and metals are enriched in the $PM_{2.5}$ fraction compared to the PM_{10} fraction by factors that vary depending on the soil type and test conditions. Calcium is enriched by approximately a factor of two, while rubidium and strontium are enriched by less than a factor of two. Other metals, particularly V, Cr, Cu, Zn, Ga, Hg, Pb, Se, and Br are enriched by about an order of magnitude in the $PM_{2.5}$ fraction relative to the PM_{10} fraction. Sulphur is enriched by a factor or 11-36 (18.4 on average).

References

[1] Carvacho, O. F., L. L. Ashbaugh, Brown, M. S., & Flocchini, R. G. Relationship between San Joaquin Valley soil texture and PM_{10} emission potential using the UC Davis Dust Resuspension Test Chamber. *Transactions of the ASAE* 44(6): 1603-1608, 2001.

[2] Carvacho, O. F., Ashbaugh, L. L., Brown, M. S., & Flocchini, R. G. Measurement of $PM_{2.5}$ emission potential from soil using the UC Davis resuspension test chamber. *Geomorphology*, 59(1-4), 75-80, 2004.

[3] Omar F. Carvacho, Ashbaugh, L. L., Brown, M. S., & Flocchini, R. G. Elemental Composition of PM_{10} and $PM_{2.5}$ from Resuspended Soil in California's San Joaquin Valley. *The First International Conference on Environmental Science and Technology*, Sponsored by American Academy of Science, Fairmont Hotel, New Orleans Louisiana, USA January 23 – 26, 2005.

[4] Carvacho, O. F., Ashbaugh, L. L., & Flocchini, R. G. $PM_{2.5}$ Metals in Ambient Air Downwind of Agricultural Operations in California's San Joaquin Valley. *International Society for Aerosol in Medicine. 15th International Congress*. Perth, Western Australia March 14 – 18, 2005. *Journal of Aerosol Medicine*, Vol. 18, Number 1, pages 100-101, 2005.

[5] Holmén, B. A., T. A. James, L. L. Ashbaugh, & R. G. Flocchini. Lidar-assisted measurement of PM_{10} emissions from agricultural tilling in California's San Joaquin Valley - Part II: emission factors. *Atmospheric Environment*, 35, 3265-3277, 2000.

[6] Eldred, R. A., Cahill, T. A., Pitchford, M., & Malm, W. C. IMPROVE – A new remote area particulate monitoring system for visibility studies. *Proceedings of the 81st Annual Meeting of the Air Pollution Control Association*, Pittsburgh, PA, 1988.

[7] Cahill, T. A., Eldred, R. A., Shadoan, D., Feeney, P. J., Kusco, B. H., Matsuda, Y. Complete Elemental Analysis of Aerosol - PIXE, FAST, LIPM and Mass. *Nuclear Instruments and Methods in Physics Research*, B3, 291-295. 1984.

[8] Morales, J., Dinator, M., Romo-Kroger, C. Caracterización del material particulado atmosférico en suspensión en Santiago de Chile. Parte VII: determinación elemental mediante PIXE. *Nucleotécnica* 15, 47 – 50. 1995.

[9] Rojas, M. C., Artaxo, P., Van Grieken R. Aerosol in Santiago de Chile: a study using receptor modeling with X-Ray fluorescence and single particle analysis. Atmospheric Environment B 24, 227 – 241, 1990.

[10] Eldred, R. A., Cahill, T. A., Feeney, P. J., Particulate monitoring at United-States National-Parks Using PIXE. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 22, 289-295, 1987.

[11] Eldred, R. A., Cahill, T. A., Wilkinson, K. L., Feeney, P. J., Particulate Characterization at Remote Sites Across the US: First year results of the NPS/IMPROVE Network. *Air Waste Management Assoc. 82nd Annual Meeting & Exhibition*, Anaheim, California June 25 – 30. Paper 89-151.3, 1989.