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Concentration, size distribution, and dry deposition rate of particle-associated metals in the Los Angeles region

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## **Authors**

Lim, Jeong-Hee H Sabin, L D Schiff, K C <u>et al.</u>

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7	Jeong-Hee Lim <sup>a*</sup> , Lisa D. Sabin <sup>b</sup> , Kenneth C. Schiff <sup>b</sup> , and Keith D. Stolzenbach, <sup>a</sup>
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13	<sup>1</sup> Department of Civil and Environmental Engineering, University of California, 5/32J Boelter
14 15	<sup>b</sup> Southern California Coastal Water Research Project 7171 Ferwick Lane Westminster CA
16	92683 USA
17	92003; 0511
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21	Manuscript Submitted to
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32	
33	
34	* Please address correspondence regarding this manuscript to: Jeong-Hee Lim, Department of
35	Civil and Environmental Engineering, University of California, 7809 Boelter Hall,
36	Los Angeles, CA 90095, USA. Tel: (310) 267-5465. Fax: (310) 206-2222.
27	Email Addrass: ihlim@uala adu

Email Address: jhlim@ucla.edu 37

#### 1 Abstract

2 Daily averaged atmospheric concentrations and dry deposition fluxes of particulate 3 metals were measured seasonally at six urban sites and one non-urban coastal site in the Los 4 Angeles region using a conventional total suspended particulate matter (TSP) filter, surrogate 5 surface deposition plates, and a Noll Rotary Impactor (NRI), which provides information about 6 particle size distribution in four size ranges above 6 microns. With the exception of the non-7 urban site, particulate metal concentrations and deposition fluxes were remarkably uniform 8 spatially and temporally. At all sites there were significant metal concentrations on particles 9 greater than 10 microns, a commonly used upper limit for many air quality monitoring studies, 10 and these large particles were estimated to be responsible for most of the deposited mass of 11 metals. Annual averaged values of deposition rates measured with a surrogate surface were in 12 good agreement with values estimated using theoretical deposition velocities in conjunction with 13 measured size- segregated particle concentrations. Image analysis of particles deposited on NRI 14 stage A, which collects all particles greater than 6 µm, indicated nighttime metal concentrations 15 and deposition at the non-urban coastal site was higher than in the day time due to offshore 16 advection of urban air associated with the diurnal land breeze. Measured enrichment of crustal 17 and metals was correlated, indicating efficient mixing of natural and anthropogenic material from 18 different sources, hypothesized to be the result of cyclical resuspension and deposition of dust by 19 moving vehicles and wind.

20 Keywords: NRI; Dry Deposition Velocity; Resuspension; Image Analysis; Enrichment Factor

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#### 1. Introduction

2 Atmospheric deposition has long been recognized as a potentially significant non-point 3 source of contaminants and nutrients to water bodies (Davis et al., 2001; Van Metre and Mahler, 4 2003). Recent studies have identified the importance of atmospheric deposition for organic 5 compounds such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls 6 (PCBs) (Simcik et al., 1998; Franz et al., 1998), metals (Zufall et al., 1998; Shahin et al., 2000; 7 Yi et al., 2001), and nitrogen (Paerl, 1995; Scudlark et al., 1998). Typically, the dry deposition 8 flux has been calculated indirectly from measured particle concentrations and a modeled dry deposition velocity (Holsen and Noll, 1992; Caffrey et al., 1998; Stolzenbach et al., 2001). 9 10 Several studies, however, have been conducted to measure dry deposition directly and to 11 characterize the deposited material using artificial collectors (Paode et al., 1999; Tai et al., 1999; 12 Shahin et al., 2000). Many of these studies concluded that dry deposition was primarily the result 13 of deposition of relatively large particles, greater than 10 microns in size, that were present in the 14 atmosphere.

15 The air quality in the Los Angeles metropolitan area ranks among the worst in the United 16 States. Particles in the ambient air of greater Los Angeles are known to contain concentrations of 17 toxic constituents, as well as potentially eutrophying nutrients (Young et al., 1976; Arey et al., 18 1989). Although the Los Angeles basin has been extensively studied with regard to priority air 19 pollutants and, to a lesser extent, acid rain and fog (e.g. Russell et al., 1993) and metals (Cass 20 and McRea, 1986; Lyons et al., 1993), little information currently exists for assessing the relative 21 contribution to runoff from atmospheric deposition of toxic contaminants and nutrients compared 22 to other, better-characterized sources. Stolzenbach et al. (2001) used a regional air quality model 23 to estimate that atmospheric deposition accounted for between 13 % and 99% of the total mass

loading of metals to Santa Monica Bay. They also determined that dry deposition of large
particles accounted for more than 80% of the total for most metals studied. These results are
consistent with earlier studies of deposition in the Los Angeles region (Kaplan and Lu, 1993;
Eaganhouse and Venkatesan, 1993; Lankey et al., 1998), but were limited by the absence of
confirming measurement of contaminant concentrations on large particles and atmospheric
deposition.

The objective of this study was to make measurements of metal concentrations on particles and dry deposition in the Los Angeles region. This paper describes the methodologies used to make these measurements and reports results relating to the size distribution of particles contributing to deposition and to measured and calculated deposition fluxes. A companion paper (Sabin et al., 2006) discusses the relative importance of atmospheric deposition to storm water runoff in the Los Angeles region.

13 2. METHODOLOGY

14 2.1. Sampling sites

15 Sampling took place over a 24-hour period during each of four seasons at six urban sites 16 (Fig. 1) from August 2002 through June 2003. These included three sites in the Los Angeles 17 River watershed (LA1, LA2, LA3), one in the Dominguez Channel watershed (DC), one in the 18 Ballona Creek watershed (BC), and one in the lower Santa Ana River watershed (SA). Two sites, 19 LA1 and LA2, were located at existing air monitoring stations operated by the South Coast Air 20 Quality Management District (SCAQMD). Both BC and SA were located on rooftops, while 21 LA3 was located within the grounds of a water reclamation facility, and DC was located on the 22 grounds of a university. We also sampled at one non-urban coastal site at Malibu Lagoon State 23 Beach within the Malibu Creek watershed (MA). Specific site selection criteria for all sites

incorporated the recommendations of the National Atmospheric Deposition Program (NADP,
 2000).

3 2.2. Instrumentation

4 Atmospheric concentrations and coarse particle size distributions of metals were 5 measured over a 24-hour period using a Noll Rotary Impactor (NRI), which consisted of a multi-6 stage rotary impactor that operates by simultaneously rotating four rectangular collector stages of 7 different widths through the air. This instrument has been used successfully to measure air 8 concentrations on coarse particle size fractions in other studies and is described elsewhere (Lin et 9 al., 1994; Yang et al., 1999). The instrument was operated at 320 rpm, producing cut diameters 10 of 6µm (stage A), 11 µm (stage B), 20 µm (stage C), and 29 µm (stage D). Mylar strips, sized 11 according to the desired cut point, were coated with a thin layer of Apezion L grease (M&I 12 Materials Ltd., UK) and mounted onto each of the four collector stages. To prevent saturation of 13 the strip surfaces, strips on stage A were changed at 2-hour intervals during the day and 4-hour 14 intervals at night during the 24-hour collection period. Stage B strips were changed every 4 15 hours during the day and every 8 hours at night. Stage C and D were not changed during the 24-16 hour collection period.

17 Dry deposition fluxes were measured over a 24-hour period using surrogate surfaces. 18 Surrogate surfaces for this study were comprised of a circular PVC deposition plate, 33 cm in 19 diameter, with a sharp edge (< 10 ° angle), covered with a Mylar® sheet coated with a thin 20 (average thickness of 10  $\mu$ m based on total volume applied) layer of Apezion L grease. During 21 sampling, the plate was mounted onto a tripod at a height of 2 m.

Total suspended particulate matter (TSP) were collected over a 24-hour period on a 2.0
 μm pore Teflon filter (Pall Life Science, R2PJ037) with a diameter of 37 mm. A metered flow

rate of 16 l min<sup>-1</sup> was maintained during all sampling intervals. For this configuration particles
with a diameter of 54 µm will be collected with a 50 percent collection efficiency (Hinds, 1999),
which is consistent with image analyses of the NRI Mylar strips. TSP measurements were not
obtained during the summer 2002 and a portion of the fall 2002 sampling events.

5 Meteorological data, including wind speed and direction, temperature, relative humidity 6 and barometric pressure, were also measured during each sampling period using a portable 7 meteorological station (PortLog, Rain Wise, Inc.). All the samples were collected during dry 8 period.

## 9 2.3. Sample preparation and analysis

10 Prior to sampling, Mylar to be mounted on the NRI or deposition plates was cut to the 11 desired size (e.g. strips or sheets), wiped with methanol and soaked in 10% nitric acid followed 12 by methanol for 5 minutes each, then rinsed with distilled water, and allowed to air dry. Mylar 13 strips/sheets were coated with a thin layer of Apeizon L grease and mounted onto collector stages 14 of the NRI and deposition plates, and stored in clean, airtight containers for transport to the field. 15 After sampling, all Mylar strips from the NRI were placed in a clean Petri dish prior to analysis 16 and Mylar sheets from deposition plates were removed, folded (greased side inward), and placed 17 inside a clean glass jar.

For TSP sampling a clean Teflon® filter was loaded into the TSP sample holder, and the sample holder was stored in a clean plastic bag for transport to the field. After sampling, the filter was stored in a clean Petri dish prior to analysis and the entire Petri dish was rinsed to collect any particles lost from the filter during transport.

1	For chemical analysis, the Mylar strips and Teflon filters and rinse water were placed into
2	clean 15 ml plastic centrifuge tubes and 10 ml of 5% Optima Grade nitric acid was added to the
3	tubes and capped tightly. The samples were acid-digested at 65° C under sonication for a
4	minimum of 24 hours.
5	Mylar sheets were cut into 10 smaller pieces and rinsed three successive times with 15 ml
6	of n-hexane. The rinses were combined into a 50 ml centrifuge tube. The Mylar® pieces were
7	then rinsed with 5% Optima Grade nitric acid and the acid and hexane rinses were combined.
8	The hexane was evaporated in a 50° C water bath and the remaining sample was acid digested at
9	65° C under sonication for a minimum of 24 hours.
10	All acid-digested samples were transferred to a centrifuge tube and analyzed for metals
11	per EPA Method 200.8 using inductively coupled plasma-mass spectroscopy (ICP-MS). Method
12	detection limits were 0.5ng for Pb and 1.0 ng for the remaining metals. Crustal elements had
13	higher detection limits (10 ng for Al and 50 ng for Fe).
14	Laboratory blanks were analyzed with each batch of 15 or fewer samples and were all
15	non-detectable. Field blanks were collected during every sampling period for each type of media
16	(Mylar strips, including duplicate blank Mylar strips for each stage of the NRI, Mylar sheets, and
17	Teflon filters) and analyzed with the samples. All samples were corrected for levels measured in
18	their respective field blank.
19	Concentrations of metals were calculated for each NRI stage using the measured metal
20	mass and the known NRI rotation speed (Noll et al., 1985). For most sampling sites, only a 24-
21	hour total concentration was obtained by compositing all of the strips for each stage.
22	Concentrations for each size range between NRI cutoffs were obtained as the difference of the

 $\,$  high and low range NRI concentrations. The metal concentration for particles smaller than 6  $\mu m$ 

1 was calculated by subtracting the NRI stage A (> 6  $\mu$ m) concentrations from the measured TSP 2 concentration. An example of the size dependent concentration values resulting from this 3 analysis is shown in Fig. 2a.

4 2.4. Deposition velocity and flux calculation

8

5 The dry deposition flux (*F*) of a particle associated metal is directly proportional to the 6 airborne metal concentration (*C*) and a size - dependent deposition velocity ( $V_d$ ) at some 7 reference height  $z_r$  above the surface:

 $F = V_d C$ 

9 Size-dependent deposition rates were calculated using established theoretical expressions 10 for the deposition velocity  $V_d$ . For particles with a gravitational settling velocity  $V_g$ , which are 11 assumed to adhere to the surface upon contact without resuspension, the deposition velocity is 12 determined by the transport properties in the atmosphere (Seinfeld and Pandis, 1998):

13 
$$V_{d} = \frac{1}{r_{a} + r_{b} + r_{a}r_{b}V_{g}} + V_{g}$$
(2)

where  $r_a$  is the resistance due to turbulent transport through the overlying atmosphere to the molecular sub-layer and  $r_b$  is the resistance of the molecular scale diffusive transport at the boundary where deposition is occurring. In this study the effects of atmospheric stability were neglected and the aerodynamic resistance given by (McRae et al., 1982):

$$r_a = \frac{0.74}{C_d u_r} \tag{3}$$

19 where  $u_r$  is the velocity at height  $z_r$  and  $C_d$  is a drag coefficient given by:

7

(1)

1 
$$C_d = \left[\frac{k}{\ln(z_r / z_0)}\right]^2$$
(4)

2 in which k is the Von Karman constant (0.41) and  $z_o$  is the aerodynamic surface roughness height.

3 For particles the resistance  $r_b$  is given by (McRae et al., 1982):

4 
$$r_b = \frac{2Sc^{2/3}}{kC_d^{1/2}u_r}$$
(5)

5 In this expression, transport of particles by Brownian diffusion is represented by the Schmidt 6 number, which is defined as  $Sc = v/D_p$ , where v is the kinematic viscosity of air and  $D_p$  is the 7 Brownian diffusion coefficient calculated as a function of the particle diameter  $d_p$  using the 8 Stokes-Einstein relationship:

9 
$$D_p = \frac{k_B T}{6\pi d_p \mu}$$
(6)

10 in which  $k_B$  is the Stefan-Boltzman constant, *T* is the absolute temperature, and  $\mu$  is the dynamic 11 viscosity of air. The gravitational settling velocity ( $V_g$ ) is given by:

12 
$$V_{g} = \frac{(\rho_{p} - \rho_{a})gd_{p}^{2}C_{c}}{18\mu}$$
(7)

13 in which  $\rho_p$  and  $\rho_a$  is density of particle and air, respectively, g is the gravitational acceleration 14 and  $C_c$  is the Cunningham slip correction factor(Finlayson-Pitts and Pitts, 2000).

15 The above equations were used to calculate the deposition velocity for each metal as a 16 function of particle size at each of the sampling sites using site-specific values of air temperature 17 and wind velocity, measured at  $z_r = 2$  m. The estimated aerodynamic roughness height  $z_o$  at all

1 measurements sites was set equal to 1.0 meter on the basis of values obtained from the South 2 Coast Air Quality Management District, which ranged from 0.08 m at the Malibu site to 0.66 to 1.4 meters at the other more urban sites. A size independent particle density  $\rho_p = 1800 \text{ kg m}^{-3}$ 3 4 was assumed. Calculated deposition velocities were then used to obtain a size-dependent 5 deposition mass flux for each metal at each site and season. For each size range the flux was 6 defined as the average of the fluxes computed from Eq. (1) using the deposition velocity 7 associated with the low and high values of particle size and the measured metal concentration 8 associated with that range. For the largest size range (greater than 29  $\mu$ m) a maximum particle 9 size of 60 µm was assumed based on the results of image analysis of the NRI stages (see below). 10 An example of the size dependent deposition flux values resulting from this analysis is shown in 11 Fig. 2b. Total deposition fluxes were computed as the sum of the fluxes from all size ranges.

### 12 2.5. Image analysis of NRI Mylar strips

Particle size distributions were determined from the photographs of Mylar strips from Stage A taken from the NRI sampler. Images were viewed using an optical microscope (LW Scientific) set at a magnification of 100x. Because the particles were observed to be relatively uniformly distributed on the Mylar strip, only one image was analyzed for each strip. For each image the distribution of the equivalent projected area diameter  $d_{PA}$  was determined. Values of  $d_{PA}$  were converted to an aerodynamic particle diameter  $d_p$  using

19 
$$d_p = \frac{1}{\overline{S_v}} \left(\frac{\rho_p}{\rho_o S_D}\right)^{\frac{1}{2}} d_{PA}$$
(8)

20 where  $S_D$  is a dynamic shape factor set equal to 1.41 (Davies, 1979),  $\rho_p$  is the particle density, 21  $\rho_0$  is a unit particle density of 1000 kg m<sup>-3</sup>, and  $\overline{S_v}$  is the volume averaged shape factor. Shape

1 factor values have been reported with a range from 1.61 (Lin et al., 1994; Tai et al., 1999) to 1.89 2 (Noll et al., 1988) for urban area, and 1.16 (Fang, 1989) for a non-urban area. For this study a 3 value of 1.61 for was used for the urban sites and 1.16 for the non-urban sites. Particle 4 atmospheric mass concentrations and deposition fluxes for the four NRI size ranges (6-11µm, 11-5 20µm, 20-29µm, and above 29µm) were determined using the known NRI rotation speed and collection efficiency (Noll et al., 1985),  $d_p$  and  $\rho_p$  to calculate particle mass, and Eq. 7 to 6 7 calculate particle settling velocity. It was not possible to compare these results with measured 8 elemental concentrations on the NRI strips because of the presence of material such as 9 hydrocarbons that were not analyzed chemically.

10

#### **3.** Results and Discussion

Measured and calculated values of concentration and deposition rate for five metals with significant anthropogenic sources (Cr, Cu, Pb, Ni and Zn) are presented in this section. In all cases where averages were calculated, measured values below the detection limit were replaced by half the detection limit.

#### 15 3.1. Particle Metal Concentration

16Averages of metal concentrations based on TSP samples were similar to those measured17in other studies in California (Table 1). These averages were not true annual values, as TSP18measurements were not obtained during the summer 2002 and half of the fall 2002 sampling19events. Seasonal variations in metal concentrations and the size distribution of metal mass as20determined from TSP and NRI samples are shown in Fig. 3. These data indicate the majority of21the metal mass was associated with particles smaller than 6 μm. However, as discussed below,22the mass of larger particles was sufficient to constitute the major portion of the deposition flux.

1 Sabin et al. (2006) analyzed a full year of data from Stage A of the NRI, representing the 2 concentration of metals on particles larger than 6 µm for chromium, copper, lead, nickel and 3 zinc. They found there was little statistical difference between the annual mean concentrations at 4 the six urban sites, but the concentrations were significantly lower at the one non-urban site in 5 comparison with the urban sites. In addition, they found no significant seasonal differences in 6 metal concentrations or significant correlations between metal concentrations and wind speed, 7 temperature and relative humidity, with the exception of nickel, which was correlated with wind 8 speed. However, antecedent rainfall did affect metal concentrations with the lowest values 9 consistently observed within five days after a rain event.

10 3.2. Measured Metal Deposition Flux and Velocity

11 Annual averages of measured dry deposition mass fluxes of metals at all sites were 12 similar to those obtained in studies of other urban locations (Table 2). As was the case for the 13 measured concentrations, the annual dry deposition mass fluxes were similar between urban 14 sites, but significantly lower at the non-urban site. Seasonal values of metal deposition fluxes 15 (Fig. 4) were also similar. The general level of precision for the deposition plate measurements 16 was reflected in relative standard deviation (RSD) for field duplicates; average RSDs for the five metals were 47% (chromium), 42% (copper), 79% (nickel), 41% (lead), and 58% (zinc). These 17 18 values are consistent with other studies of metal deposition in urban areas using the same 19 measurement techniques (e.g. Tasdemir and Kural, 2005), and reflect an acceptable level of 20 precision for field duplicates because differences of less than a factor of two between fluxes 21 measured during different sampling events were not considered significant in this study.

The flux-averaged deposition velocities, calculated as the measured total deposition flux divided by the total concentration, for the full suite of metals analyzed range from 0.34 cm sec<sup>-1</sup>

1 (Sn) to 1.5 cm sec<sup>-1</sup> (Zn, Sr). These values compare well with those obtained in urban
2 environments by Yi et al. (2001).

3 For each sampling event, the measured deposition fluxes of the complete set of metals 4 analyzed were generally well-predicted by the deposition rates calculated using the equations in 5 section 2.4 for all seasons except spring, for which the calculated fluxes were high at some sites 6 (Figure 5). The differences between the measured and calculated deposition fluxes were likely 7 the result of limitations of the theoretical expressions for deposition and variability in the 8 deposition measurements. Clearly, the plates do not fully represent the larger scale roughness of 9 the land surface implied in the values of  $z_o$  used in the calculations. To reduce the impact of 10 measurement error, annual average deposition fluxes for each method were compared (Table 3). 11 The annual average measured and calculated fluxes were within 20% for chromium, copper, lead 12 and zinc, and within 60% for nickel, indicating reasonable agreement.

13 3.3 Uncertainty in the deposition velocity calculations

14 The equations used to calculate particle deposition velocity in this study reflect the 15 current state of knowledge of these processes and assumptions about important parameters. For 16 the particle size range of interest, the most important factor in determining the deposition rate is 17 the gravitational settling velocity of the particles. The error in the computed deposition rate, 18 which is directly proportional to the difference between the actual particle density and the assumed value of 1800 kg m<sup>-3</sup>, is likely to be no more than 10-20%. The effect of atmospheric 19 20 stability on the deposition rate was neglected in computing the aerodynamic resistance (Eq. 3). 21 This factor, which can be relatively significant for dry deposition of vapor constituents (McRae 22 et al., 1982), has no significant effect on the computed deposition for particles larger than about 1 23  $\mu$ m. The use of a constant value of  $z_0$  is justified because of the relative insensitivity of the result 1 to this parameter value.

2 There are a number of issues related to the computation of the drag coefficient given by 3 Eq. (4). First, Eq. (4) is based on the logarithmic velocity profile, which for rough surfaces is 4 known to be valid only for  $z > 50z_0$  (Brutsaert, 1982), a criteria that was not met by the 5 measurement height (2 meters) and estimated roughness height (~1 meter) used in this study. For  $z < z_0$ , the actual velocity will be greater than that predicted by the logarithmic law, so the 6 7 use of the logarithmic law will tend to overestimate the value of the drag coefficient. Second, this 8 expression does not include a displacement height  $z_d$ , which would modify the argument of the logarithm to be  $(z_r - z_d)/z_o$ . The displacement height is commonly used for surfaces with canopy 9 10 type roughness and is thought to be on the order of 2/3 of the canopy height (Brutsaert, 1982). 11 Addition of this factor would increase the computed drag coefficient and deposition rate. These 12 two factors have opposite effects on the computed deposition rates, but only affect the 13 aerodynamic and surface resistances, which are far less important than the settling rate for 14 particles larger than 1  $\mu$ m.

The expression used to calculate the boundary resistance (Eq. 5) is relatively wellestablished for vapor transport, and is similar, but not identical to, other formulations applied to diffusive particle deposition (e.g. Giorgi, 1986). However, for the particle size range considered in this study, deposition by diffusion is much smaller than deposition by gravitational settling.

The boundary resistance formulation (Eq. 5) also neglects the effect of inertial particle deposition. This process, which is thought to be potentially most important for particles in the size range 1-10 μm, has proven to be one of the most difficult to predict theoretically. Expressions developed for inertial transport through a viscous sublayer on surfaces with relatively uniform roughness (Slinn, 1977) are not likely to be valid for the highly irregular and

1 canopy-like surface of a watershed. These expressions have the additional drawback that the 2 associated transport resistance is proportional to the square of the measured velocity, thus 3 amplifying the velocity profile uncertainties discussed above. Expressions for particle deposition 4 by impaction in canopies more typical of natural surfaces indicate that this process is only 5 significant compared to gravitational settling if the presence of very fine  $(1-10 \ \mu m)$  vegetative 6 "hairs" is postulated (Davidson and Friedlander, 1978; Giorgi, 1986). While this assumption may 7 be valid for relatively densely vegetated surfaces, it is less likely to be so for a typical urbanized 8 surface where many of the collecting surfaces are sufficiently large that significant inertial 9 deposition does not occur. Finally, experimental studies have documented a high fraction of loss 10 to "bounce off" of particles contacting a surface by inertial deposition (Wu et al., 1992). For 11 these reasons, we believe it was justified to omit explicit inclusion of deposition by inertial deposition. To the extent that inertial deposition is important, the estimates presented here should 12 13 be considered lower bounds on actual deposition rates.

## 14 3.4 Diurnal Variations in Concentration and Flux

15 With the exception of the NRI samples obtained during the summer at LA1, for which the 16 strips were not composited before chemical analysis, the image analysis of NRI strips provides 17 the only estimates of variability in particle mass concentrations on an hourly time scales as well 18 as the only estimates of total particle mass concentration and total particle deposition flux. Metal 19 concentrations measured at LA1 varied an order of magnitude between day and night (Fig. 6). 20 The diurnal variation of total particle mass concentration at the urban sites and flux at an urban 21 site and the non-urban site are contrasted in Fig. 7 and the results of analysis of all of the urban 22 sites in Table 4. Although the total particulate concentration at the urban sites does not vary 23 greatly from day to night, both deposition and the number of large particles was greater during

1 the day, suggesting an anthropogenic source, although increased wind velocities during the day 2 could also be a contributing factor. In contrast, at the non-urban site both particle concentration 3 and deposition were greatest at night. The pattern of variation at the non-urban site indicates that 4 larger particles were largely absent during the day but present at night, probably associated with 5 advection of urban air during the early evening when a seaward wind flow typically occurs 6 associated with cooling of the air over the land. The occurrence of such an event was clearly 7 indicated in the wind and temperature data collected at the site. The average seaward wind speed during the night was  $2.7 \text{ mi hr}^{-1}$  for duration of 9.8 hrs.8

9 3.4 Comparison with Crustal and Dust Composition

10 The anthropogenic contribution to the mass concentration or flux of a given metal can be 11 assessed by examining the ratio of a concentration or flux of a potentially anthropogenic metal to 12 the concentration or flux of a non-anthropogenic (crustal) element measured in the same sample. In this context "anthropogenic" refers to the source of the metal and not the mode of 13 14 resuspension, which may be affected by human activities for all metals. The enrichment factor 15 for a given metal is defined as this ratio divided by the same ratio in crustal material (Wdedpohl, 16 1995). In this study, iron was used as reference element for determining metal enrichment, 17 because of its higher correlation to other metals compared to aluminum (Schiff and Weisberg, 18 1999). Enrichment factors (Table 5) were high in our measurements and in the ARB and MATES 19 II samples. Pearson correlation analysis found high correlation between pairs of crustal elements (r > 0.95 for Al, Fe, Si, and Mg) and the anthropogenic metals (0.5 < r < 0.83 for Cr, Ni, Pb, and Pc)20 21 Zn). These high correlations suggest an efficient process resulting in the mixing of crustal and 22 anthropogenic material originating from different sources. It is well-known that dust resuspended 23 from road surfaces by moving vehicles and from other surfaces by wind is a major source of contaminants to the atmosphere (Watson and Chow, 2000). Data on paved road dust samples in
 the Los Angeles area (SCAQMD, 2003) indicate road dust is also enriched in non-anthropogenic
 metals, but the relative enrichment factors for different metals are not definitive in terms of
 identifying road dust as the source of the metals.

5 4. Conclusions

6 The results of this study indicate metals in the atmosphere above Los Angeles are 7 associated with a wide range of particle sizes, but that atmospheric deposition is dominated by 8 particles larger than 10 µm. With the exception of a non-urban site located directly on the 9 coastline, the spatial uniformity of measured concentration and deposition at six sites within the 10 inland urban area is consistent with earlier modeling results (Lu et al., 2003) and evokes a picture 11 of particles being relatively well-mixed in the atmosphere over the air basin. This picture is not 12 consistent with the dominance of larger sizes, which should deposit close to sources, unless there 13 is substantial resuspension from both road and non-road surfaces. The likelihood of significant 14 resuspension is suggested by the elemental profile in measured particle concentrations and 15 deposition fluxes.

This study supports the use of surrogate surfaces of relatively simple design based on the assumption that gravitational settling is the main mode of deposition for the particles of interest in this study. Annual average deposition mass fluxes measured by these plates were in substantial agreement with values estimated using theoretical expressions for deposition velocity as a function of particle size. The plates are an attractive method for measuring the long-term deposition fluxes of contaminants given the relative difficulty of obtaining size-dependent particle concentrations.

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## 1 Figure Captions

Figure 1 Location of sampling sites and boundaries of associated watershed (BC – Ballona
Creek; DC – Dominguez Channel; LA – Los Angeles River; MA – Malibu Creek; SA – Santa
Ana River).

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6 Figure 2 (a) Size-dependent concentration (ng m<sup>-3</sup>) of zinc measured in air at DC during summer, 7 and (b) resulting calculated deposition flux ( $\mu$ g m<sup>-2</sup> day<sup>-1</sup>) of zinc.

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Figure 3 Size-dependent concentration of metals measured by NRI and TSP samplers: left -- bar height indicates TSP total concentration and light shading is fraction with particle size greater than 6  $\mu$ m based on NRI stage A; right -- bar height indicates NRI stage A concentration and shading indicates breakdown by particle sized based on other NRI stages (solid 6-11  $\mu$ m; grey 11-20  $\mu$ m; striped 20-29  $\mu$ m; white > 29  $\mu$ m). For each season the order of sites is LA1, LA3, SA, LA2, BC, DC, MA except for Fall in the left figures in which there are no data for the first three sites.

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17 Figure 4 Seasonal metal fluxes measured using deposition plates. For each season the order of

sites is LA1, LA3, SA, LA2, BC, DC, and MA. Note that not all sites are representedin each season.

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Figure 5 Comparison between measured and calculated deposition fluxes at different seasons for the complete set of metals for which an analysis was performed: a) summer; b) fall; c) winter; d)

23 spring, and different sampling sites: – LA1, ■ LA2, ▲ LA3, × BC,  $\times$  DC,  $\odot$  SA, + MA.

24 The data points shown are not differentiated by which metal is represented.

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Figure 6 Diurnal variation of metal concentration measured on NRI stage A at LA1 between
12:30 pm on 8/1/2002 and 12:30 pm on 8/2/2002.

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Figure 7 Diurnal pattern of particle mass concentration with particle size analyzed by image analysis; a) urban site (SA), b) non-urban site (MA) between 13:00 pm on 6/23/2003 and 13:00 pm on 6/24/2003.

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Table 1 Summary of average metal concentrations  $\pm$  standard deviation (ng m<sup>-3</sup>) on TSP samples 

measured in the Los Angeles region.

	Chromium	Copper	Lead	Nickel	Zinc
LA1	5.1 ± 2	$71 \pm 20$	$15 \pm 3$	$15 \pm 2$	84 ± 20
LA2	$3.6 \pm 0.2$	$30 \pm 30$	$14 \pm 2$	$4.4 \hspace{0.2cm} \pm \hspace{0.2cm} 0.8$	$54 \pm 20$
LA3	$1.5 \pm 0.7$	$24 \pm 20$	$5.6 \pm 6$	$11 \pm 8$	$31 \pm 6$
BC	$5.7 \pm 3$	$90 \pm 50$	$17 \pm 10$	$5.5 \pm 1.2$	$97 \pm 40$
DC	$6.5 \pm 3$	$43 \ \pm \ 20$	$15 \pm 5$	$10 \pm 6$	$69  \pm  20$
SA	$6.0 \pm 4$	$52 \pm 30$	$14 \pm 10$	$12 \pm 8$	$150 \pm 110$
All Urban Sites	4.9 ± 3	$52 \pm 40$	$14 \pm 7$	$9.2 \pm 6$	84 ± 60
Non-urban MA	$1.3 \pm 1.8$	$6.8 \pm 6$	$2.2 \pm 1.7$	3.3 ± 2	12 ± 8
ARB <sup>a</sup> (2002)	$5.5 \pm 7$	$34 \pm 30$	$11 \pm 9$	$4.5 \pm 4$	$58 \pm 7$
Mates II <sup>b</sup> (1998~1999)	4.9 ± 5	39 ± 30	$25 \pm 30$	8.7 ± 9	110 ± 110

<sup>a</sup>Air Resource Board annual toxic summary-statewide data 

(http://www.arb.ca.gov/adam/toxics/sitesubstance.html) 

<sup>b</sup>Multiple Air Toxics Exposure Study in the South Coast Air Basin (MATES II):

http://www.aqmd.gov/matesiidf/matestoc.htm 

Table 2 Summary of average measured metal deposition fluxes  $\pm$  standard deviation (µg m<sup>-2</sup> day<sup>-1</sup>) in the Los Angeles region 2

	Chromium	Copper	Lead	Nickel	Zinc
LA1	$6.0 \pm 5$	$21 \pm 20$	$15 \pm 10$	$14 \pm 13$	$130 \pm 110$
LA2	$2.3 \pm 3$	$30 \pm 22$	$31 \pm 32$	$5.0 \pm 5$	$160 \pm 180$
LA3	$9.0 \pm 7$	$16 \pm 20$	$32 \pm 50$	$6.0 \pm 10$	$110 \pm 150$
BC	$2.7 \pm 1.5$	$18 \pm 3$	$20 \pm 20$	$1.7 \pm 2$	$77 \pm 30$
DC	$3.3 \pm 1.3$	$12 \pm 5$	$11 \pm 7$	$2.3 \pm 3$	$74 \pm 40$
SA	$4.3 \ \pm \ 0.6$	$30 \pm 20$	$10 \pm 4$	$0.01 \pm 0$	$180 \pm 90$
All Urban Sites	$4.6 \pm 4$	$21 \pm 20$	$19 \pm 20$	$5.2 \pm 8$	$120 \pm 100$
Non-urban MA	$0.01 \hspace{0.2cm} \pm \hspace{0.2cm} 0.0$	$0.5 \pm 0.7$	$0.3 \pm 0.4$	$3.5 \pm 5$	$8.0 \pm 10$
Chicago	$5.7 \pm 6$	$63 \pm 50$	$38 \pm 30$		$120 \pm 110$
Yi et South al Haven	$0.7 \pm 0.8$	$31 \pm 40$	$23 \pm 60$		51 ± 50
2001 Sleeping Bear Dunes	1.6 ± 4	79 ± 20	$35 \pm 80$		$68 \pm 80$

1 Table 3 Comparison of annual average of calculated and measured deposition fluxes

 $(\mu g m^{-2} da y^{-1})$ 

	Metal	Calculated Flux	Measured Flux	
	Chromium	5.4	4.8	
	Copper	26	21	
	Lead	16	19	
	Nickel	6.3	9.4	
	Zinc	130	120	
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11 12	Table 4 Total particle mass concentration and deposition flux $\pm$ standard deviation determined by microscopic image analysis			
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	Day *	Night *
Concentration( $\mu g m^{-3}$ )		
Urban	$4.2 \pm 2$	$3.5 \pm 1$
Non-urban	$1.4 \pm 0.3$	$4.9 \pm 0.5$
Deposition Flux (mg m <sup>-2</sup> day <sup>-1</sup> )		
Urban	$26 \pm 17$	$18 \pm 5$
Non-urban	$9.2 \pm 7$	$31 \pm 2$
* Day time period: 7am to 5pm; nig	ght time period: 5pm to 7 am	1

Metal	This Study <sup>a</sup>	ARB <sup>b</sup>	MATES II <sup>c</sup>	Paved Road Dust <sup>d</sup>	Unpaved Road Dust <sup>d</sup>
Chromium	1.0	1.2	1.0	0.1	0.1
Copper	52	38	39	4.7	5.2
Lead	22	20	43	6.7	7.3
Nickel	4.0	2.2	3.9	0.2	0.5
Zinc	31	25	41	12	4.8

1 Table 5 Comparison of enrichment factors in air and dust samples

3 <sup>a</sup> Mean values of both urban and non-urban TSP measurements

4 <sup>b</sup> Air Resource Board annual toxic summary-2002 statewide data

<sup>c</sup> Multiple Air Toxics Exposure Study in the South Coast Air Basin (MATES-II, 1998 ~1999)

<sup>d</sup> Data source: Emission Inventory compiled by SCAQMD, 1998

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