The Importance of Dry Deposition : Dry Deposition Fluxes of Heavy Metals In Seoul, Korea During Yellow-Sand Events

Seung-Muk Yi

Seoul National University, College of Public Health, Department of Environmental Health, 28, Yongon-Dong, Chongro-Gu, Seoul 110-799, Korea

Abstract

Mass and elemental dry deposition fluxes and ambient particle size distributions were measured using dry deposition plates and a cascade impactor, from March to November 1998 in Seoul, Korea. During the spring sampling period several yellow sand events characterized by long range transport from China and Mongolia impacted the area. During these events the mass fluxes were statistically the same as during springtime non-yellow-sand events. However, most elemental fluxes were higher. In general, the flux ratios of both crustal (Al, Ca, Mn) and anthropogenic elements (Ni, Pb) to total mass measured during the daytime yellow-sand events were substantially higher than those measured in spring daytime during non-yellow-sand time periods. During all seasons the average measured daytime fluxes were about two times higher than at nighttime. The flux of primarily anthropogenic metals (Cu, Ni, Pb, Zn) and Mn was on average one to two orders of magnitude lower than the flux of the crustal metals Al and Ca.

As is typically found two modes, fine (0.1~1.0 μm) and coarse (1.0~10.0 μm) were present in the measured size distributions (<10 μm). The particles in the coarse mode constitute a major portion of the measured mass size distribution during the yellow-sand events possibly due to the long-range transport of those particles from China.

Introduction

The interest in atmospheric deposition has increased over the past decade due to concerns about the effects of deposited materials on the environment. Atmospheric dry deposition influences the fate of airborne toxics and often controls the transfer of material from the atmosphere to natural surfaces. Dry deposition provides a significant mechanism for the removal of particles from the atmosphere and is an important pathway for the loading of toxic trace metals and heavy metals into the aquatic ecosystem (Caffrey *et al.*, 1998)

The measurement of dry deposition is difficult due to large spatial and temporal variations and because interactions between the surface and the atmosphere can have significant effects on the amount of deposited material. Surrogate surfaces can be used over extended periods at

different locations to provide quantitative information on temporal and spatial variations in dry deposition (Holsen and Noll, 1992; Davidson *et al.*, 1985). Therefore, it is an increasingly important technique in the investigation of dry deposition.

Pollutants emitted into the atmosphere can be transported and deposited to aquatic/terrestrial reservoirs far away from their original sources. For instance, soil particles from deserts and exposed regions are blown into the air and transported 5000 - 10000 km eastwards over the North Pacific Ocean (Zhang *et al.*, 1992). This material is called yellow-sand due to its yellowish, light brown, or red colors and is mostly observed in the spring when large-scale dust storms occur in northern China and Mongolia (Duce, 1980; Nagoya University, 1991). Both Japan and Korea are affected by the long-range transport of dust from the west during yellow-sand events. One study using satellite images and isobaric trajectories estimated that yellow-sand events occurred in April 1993 in Seoul, Korea and lasted for 148 hours over ten days (Lee *et al.*, 1993). Most research studies on yellow-sand events have attempted to identify the source regions and to simulate the transport of yellow-sand (Iwasaka *et al.*, 1983; Kai *et al.*, Yoon, 1990; Ishizaka, 1987; Tanaka *et al.*, 1989; Lee *et al.*, 1993; Kotamarthi *et al.*, 1993). How yellow-sand events impact atmospheric deposition have not been investigated (Lee, 1998).

The objectives of this research were to measure the dry deposition fluxes and particle size distributions of total mass and trace elements in Seoul, Korea and to examine the impact of yellow-sand events on those measurements. The hypothesis of this study was that mass and elemental fluxes are greater during yellow-sand events than they are during other time periods.

Experimental Section

±In this study, dry deposition was collected with a grease-coated smooth plate with a sharp leading edge similar to those used in previous studies (Holsen *et al.*, 1992; Paode *et al.*, 1998; Sofuoglu *et al.*, 1998). In addition, the particle size distribution < 10 μm in diameter was measured with a cascade impactor.

Sampling

Samples were collected on the roof of the Asan Engineering Building at Ewha Women's University, a five-story building located in a mixed institutional, commercial, and residential area in Seoul, Korea. Dry deposition fluxes and ambient particle size distributions were measured simultaneously during the daytime (from 09:00 to 18:00) and nighttime (from 18:00 to 09:00) during dry periods. (One of the daytime samples was collected over two days for a total of 18 hours). Meteorological data were obtained every 5 minutes at the sampling site on a meteorological tower.

Particulate dry deposition flux was measured with Mylar strips (5.7 cm × 1.8 cm exposed surface area) coated with Apezion L grease (~5 μmm thick, 4 mg mass) attached to smooth acrylic plates. These plates had sharp leading edges (< 10° angle) pointed into the wind by a wind vane. The sharp leading edge provides laminar flow over the strips thereby minimizing turbulent deposition. The greased surface eliminates particle bounce while collecting particles of all sizes. The strips were weighed before and after exposure to determine the total mass of particles collected (Paode *et al.*, 1998; Sofuoglu *et al.*, 1998). The dry deposition mass flux was calculated by dividing the measured difference in the greased strip mass before and after sampling by the greased area and sampling time.

Atmospheric particle concentrations were measured with a 1 ACFM nonviable ambient particle sizing sampler (AAPSS) with a preseparator. It is a multistage, multi-orifice cascade impactor which collects particles < 10 μm in diameter and separates particles into the following size ranges: >9, 9-5.8, 5.8-3.3, 3.3-2.1, 2.1-0.65, 0.65-0.43 and <0.43 μm.

Sample collection started on March 1998 and concluded in October 1998. Yellow-sand events occurred for a total of 13 days in 1998, 5 days and 2 nights of which were sampled.

Analysis

Analytical methods followed the procedures outlined by Paode *et al.*, (1998) and Sofuoglu *et al.*, (1998). Briefly, the grease and associated particles from the deposition strips and cascade impactor were washed into Teflon containers and digested with an ultra-pure nitric acid solution in a microwave oven at 70 psi (CEM MDS-2000). Samples were subsequently analyzed for Al, Ca, Cu, Mn, Ni, Pb, and Zn with a Varian Ultramass 700 Inductively Coupled Plasma - Mass Spectrometer (ICP-MS) in the Research Center of Natural Science located in Wonju, Korea.

Quality Assurance/Quality Control

Method detection limits (MDLs) were calculated by injecting a low concentration sample seven times into the ICP-MS. MDL is defined as three times the standard deviation of the concentrations obtained in the seven runs. MDLs for the seven metals ranged from 0.009 ppb (Pb) to 1.615 ppb (Ca). Metal concentrations in the process blanks were either below or of the same magnitude as the MDLs. Typical sample concentrations were 10 times MDLs.

Background contamination was routinely monitored by using operational blanks (unexposed Mylar strips), which were processed simultaneously with field samples. At least 10% of the samples were analyzed in duplicate and spiked with a known amount of metal to calculate recovery efficiencies. No significant contamination was found (<5% of the levels found in the samples) and recovery efficiencies averaged 95% and varied between 83% and 107%.

Statistical Comparisons

To compare total mass fluxes, elemental fluxes, and the dry deposition flux ratio of elements to total mass during each season of the year a t-test was performed by assuming equal variance in two populations at a 95% confidence level.

Results and Discussion

Total Mass Flux

There was no statistical difference between the daytime fluxes measured during each season of the year (Figure 1). However, the highest average flux was in summer daytime (210 ± 97 mg/m^2/day) followed by spring daytime (210 ± 81 mg/m^2/day), fall daytime (150 ± 58 mg/m^2/day) and spring yellow-sand daytime (148 ± 58 mg/m^2/day). The average mass fluxes during the nighttime of spring yellow-sand events, in spring non-yellow-sand events, summer and fall were not statistically different (82 ± 73, 93 ± 23, 120 ± 55, and 76 ± 44 mg/m^2/day, respectively,). However, they were substantially lower than those during daytime due to the lower wind speeds (1.3 m/sec vs. 2.3 m/sec) and a more stable atmosphere. The average dry deposition mass flux measured in Seoul, Korea (137 mg/m^2/day) was similar to those measured in an urban area in Chicago, IL U.S.A. (130 mg/m^2/day) (Holsen *et al.*, 1993).

The finding of no statistical difference between mass fluxes during yellow-sand events and other spring periods suggests that the yellow-sand event is characterized by an increase in the concentration of particles <10 μm in size (see size distribution section). These particles are able to be transported long distances but do not contribute significantly to mass deposition which is primarily controlled by particles >10 μm (Holsen *et al.*, 1993; Paode *et al.*, 1998; Sofuoglu *et al.*, 1998).

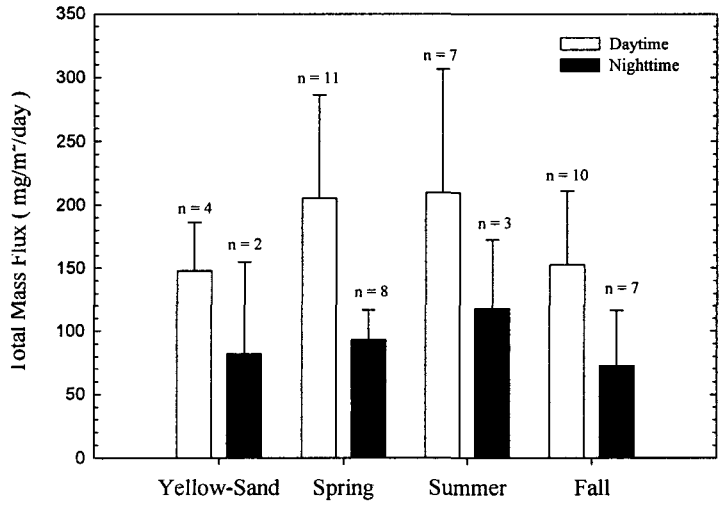

Figure 1. Measured total mass fluxes for different sampling periods

Elemental Flux

Fifty three deposition samples were collected and analyzed for seven elements (Ca, Al, Zn, Cu, Pb, Mn, Ni). The average fluxes of each of these elements as well as the calculated standard deviations are shown in Figures 2 and 3. The standard deviation of all metal fluxes was of the same magnitude as the average flux indicating large variations in the elemental flux during each sampling period. The larger variations in average elemental fluxes during the daytime were due to the more unstable atmosphere and a larger variation in wind speeds than during the nighttime.

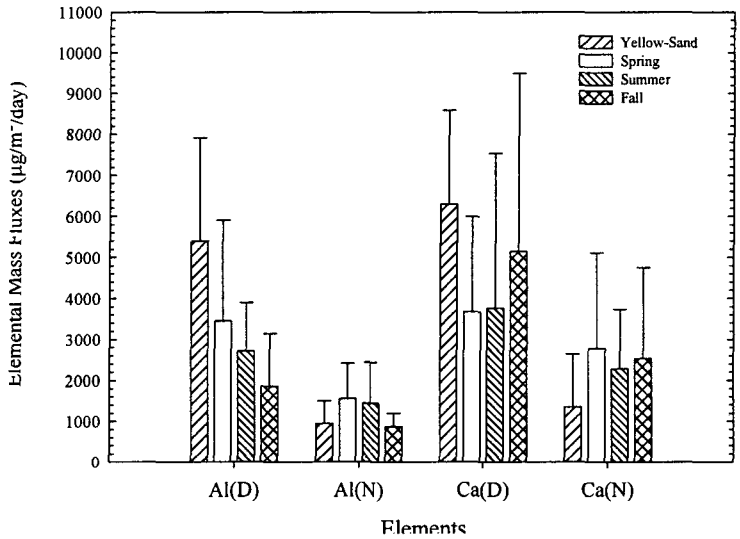

Figure 2. Measured elemental fluxes for different sampling periods

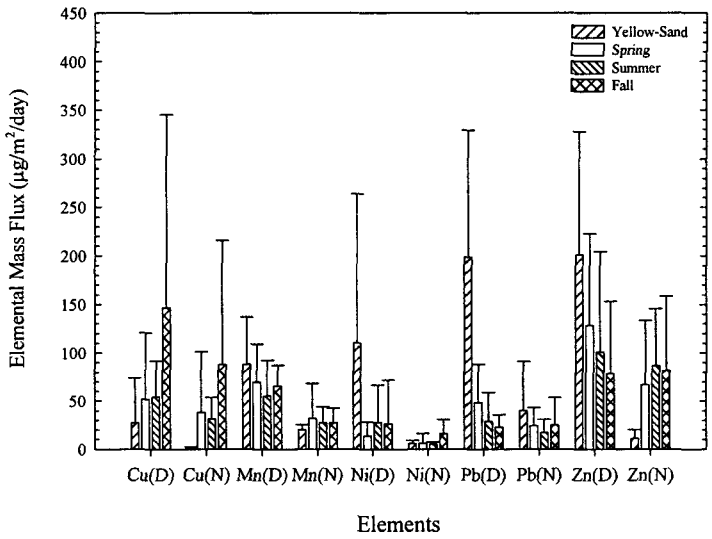

Figure 3. Measured elemental fluxes for different sampling periods

The primarily crustal elements, calcium and aluminum, had similar fluxes. They varied from 89 to 14000 $\mu g/m^2/day$. For Al, the average elemental flux during the yellow-sand daytime was 5400 ± 2500 $\mu g/m^2/day$, which was 2-3 times higher than the average spring non yellow-sand daytime flux and the other daytime sampling periods (although these differences were not statistically significant). This finding indicates that 1) the deposited soil derived particles probably contained some carbonate since typical soil has an Al/Ca ratio of 2-3 (Sposito, 1989), and 2) crustal elements other than SiO_2 (the primary component of sand) are transported from China during yellow-sand events. The average dry deposition flux of Ca was the highest during the yellow-sand daytime (6300 ± 2300 $\mu g/m^2/day$) and was similar to the one measured during the fall daytime (5100 ± 4300 $\mu g/m^2/day$) and statistically higher than spring non-yellow-sand daytime (3700 ± 2300 $\mu g/m^2/day$) and summer daytime (3800 ± 380 $\mu g/m^2/day$) fluxes. Daytime fluxes were also higher than nighttime fluxes.

The flux of the crustal elements Al and Ca was on average 1-2 orders of magnitude higher than the flux of Mn and the primarily anthropogenic elements (Cu, Ni, Pb, Zn). This finding is in good agreement with previous studies (Paode *et al.*, 1998; Sofuoglu *et al.*, 1998; Holsen *et al.*, 1993). The measured average Pb, Cu, and Zn fluxes in Seoul were 50, 60, and 110 $\mu g/m^2/day$, respectively. These anthropogenic metal fluxes compare well with fluxes obtained in other studies. Paode *et al.* (1998) measured Pb, Cu, and Zn fluxes of 70, 60, and 20 $\mu g/m^2/day$, respectively, in Chicago. In another study (Holsen *et al.*, 1993), the Chicago fluxes of Pb, Cu, and Zn were 120, 160, and 700 $\mu g/m^2/day$, respectively. For elements Ni, Pb and Mn, the fluxes varied between 440 and 330 $\mu g/m^2/day$, while the fluxes of Cu and Zn varied between 1.5 and 559 $\mu g/m^2/day$.

Average dry deposition fluxes of Ni, Pb, and Zn during the yellow-sand daytime were 110 ± 150, 200 ± 130, and 200 ± 130 $\mu g/m^2/day$, respectively, which were the highest average fluxes measured during all of the sampling periods. A t-test (95% confidence level) indicated that the dry deposition fluxes of Ni and Pb during the yellow-sand daytime were significantly different from spring non-yellow-sand daytime. These higher anthropogenic fluxes correspond to increased concentration of these elements in the coarse particle size range (See size distribution section).

Zn fluxes were fairly constant except for a significantly higher flux in spring than in fall due to the road painting near the sampling site which is a known source of Zn (Chow *et al.*, 1992). Holsen *et al.* (1993) also measured high zinc fluxes (120 $\mu g/m^2/day$) in Chicago which is comparable to the mean zinc flux in spring daytime (140 $\mu g/m^2/day$) found in this study. For copper, most of the samples in spring and during the yellow-sand events were below the detection limit (the fluxes shown in Figure 3 were calculated by assuming the samples below the detection limit were 2/3 of the detection limit). The dry deposition flux of copper in fall was about 3 to 10 times higher than the other measured anthropogenic elements in that period. Receptor modeling has shown that zinc bearing aerosol originates from coal-fired power plant emissions, incinerator off-gases, vehicle exhaust, and urban road

dust, while atmospheric copper is from coke dust, steel industries, blast furnace emissions, vehicle exhaust and urban dust (Sweet and Vermette, 1993; Paode *et al.*, 1999).

Dry Deposition Flux Ratio of Elements to Total Mass

The deposition flux ratio was calculated by dividing each elemental dry deposition flux by the total mass flux for each sampling period (Figures 4 and 5). In general, the flux ratios of crustal elements (2300 mg/kg~90000 mg/kg) were 30 to 40 times higher than anthropogenic elements (<3300 mg/kg) indicating that these crustal elements constitute a major part of the total mass flux.

The average elemental deposition flux ratios during the yellow-sand daytime was substantially higher than during the daytime of the other seasons (spring, summer, and fall) except for copper. Tthe ratios of Al, Ca, Mn, Ni and Pb during the yellow-sand daytime were statistically different from the non-yellow-sand spring daytime at the 95% confidence level. This result suggests that not only soil-originated elements (Al, Ca, and Mn) but anthropogenic elements (Ni and Pb) were transported into Korea during yellow-sand events.

Enrichment factors (EFs)(mg/kg in a sample/mg/kg in typical soil) were calculated for these samples and compared to EFs for samples collected in Chicago, IL (Table 1). Both samples in Seoul and Chicago had EFs <1 for Al and >1 for Ca. This finding suggests that sample from both locations contain more $CaCO_3$ than do typical soils. The large EF of Mn during non-yellow sand events suggests that there may be an anthropogenic source of this element in Seoul. Cu is significantly enriched in Chicago but not Seoul, Ni is more enriched in Seoul than Chicago, Pb and Zn are enriched in both locations. The largest enrichment is for Pb during yellow sand events indicating that these events may be a significant source of Pb to Seoul.

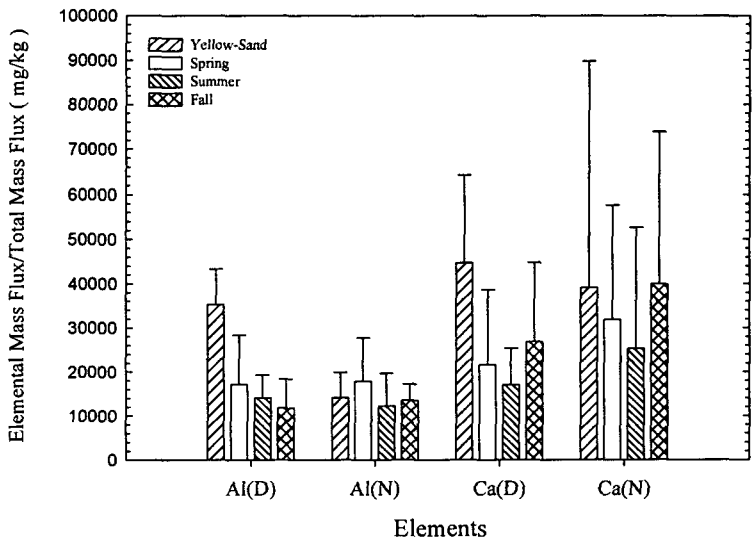

Figure 4. Dry deposition flux ratio of elements to total mass

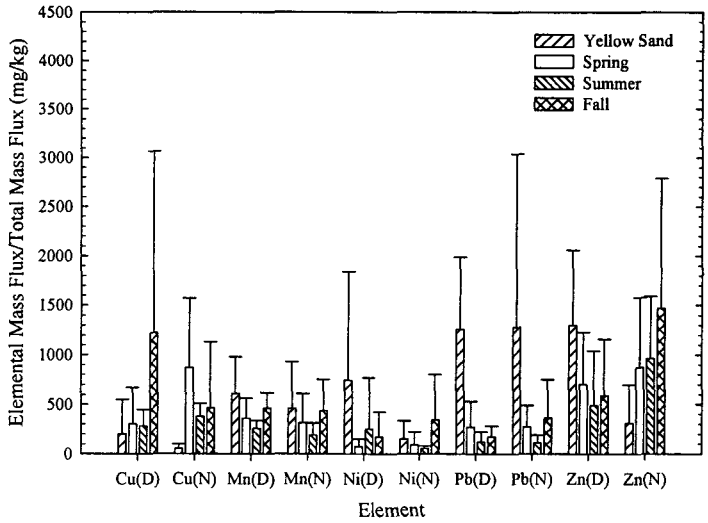

Figure 5. Dry deposition flux ratio of elements to total mass

Table 1. Enrichment factors in Seoul, Korea during yellow sand and non-yellow sand events and those measured in Chicago, IL.

		Enrichment Factors			
		Seoul, Korea		Chicago, IL	
Element	Typical	Y.S.	non Y.S.	deposition[2]	dicot[3]
	Soil (mg/kg)[1]				
Al	72000	0.34	0.20	0.10	0.24
Ca	24000	1.75	1.13	N.A	2.92
Mn	550	5.00	23.41	N.A	1.58
Cu	25	0.97	0.61	17.68	12.37
Ni	19	23.42	8.53	N.A	2.38
Pb	19	66.84	11.43	23.36	28.89
Zn	60	13.42	14.13	22.45	30.28

1. Sposito, 1989
2. From dry deposition measured in Chicago (Paode et al., 1998; Sofuoglu *et al.*, 1998)
3. From dichotomous coarse particle samples measured in Chicago (Yi *et al.*, 2000)

In summary these results indicate that during yellow sand events typical soil constituents and anthropogenic elements are being transported and deposited in Seoul, Korea. For the elements analyzed the Pb flux had the most significant increase. Its flux was approximately 4 times higher than during non-yellow sand events.

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