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Atmospheric deposition of carbon and nutrients across an arid metropolitan area

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ABSTRACT

Urbanization is increasing rapidly in semi-arid environments and is predicted to alter atmospheric deposition of nutrients and pollutants to cities as well as to ecosystems downwind. We examined patterns of wet and coarse dry deposition chemistry over a five-year period at 7 sites across the Central Arizona-Phoenix (CAP) study area, one of two urban sites within the National Science Foundation's Long-Term Ecological Research (LTER) program. Wet and dry deposition of organic carbon (oC) were significantly elevated in the urban core; in contrast, mean annual wet and dry fluxes of nitrogen (N) were low (<6 kg ha^{-1} yr^{-1}) compared to previous estimates and did not differ significantly among sites. Wet deposition of sulfate (SO_4^{2-}) was high across CAP (mean 1.39 kg ha^{-1} yr^{-1} as S) and represented the dominant anion in rainfall. Dry deposition rates did not show strong seasonal trends with the exception of oC, which was 3-fold higher in winter than in summer; ammonium (NH_4^+) deposition was high but more variable. Dry deposition of NO_3^- and oC was strongly correlated with particulate base cations and dust-derived soluble reactive phosphorus (SRP), suggesting that urban-derived dust is scrubbing the atmosphere of acidic gases and entrained particles and increasing local deposition. Differences between measured and predicted rates of dry N deposition to the urban core may be explained by incomplete collection of gas phase N on surrogate deposition surfaces in this hot and arid environment. The extent of urban enhancement of cations and oC inputs to desert ecosystems appears to be restricted to the urbanized metropolitan area rather than extending far downwind, although a low number of sites make it difficult to resolve this spatial pattern. Nevertheless, wet and dry inputs may be important for biogeochemical cycles in nutrient and carbon-poor desert ecosystems within and near arid cities.

1. Introduction

Atmospheric deposition is recognized as an important source of nutrients to many ecosystems, particularly those in arid environments (West and Skunjins, 1977). Urbanization contributes to an increase in the sources of airborne pollutants such as nitrogen (N), sulfur (S), and organic carbon (oC), and can lead to significant deposition of both nutrients and pollutants in cities as well as to

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ecosystems downwind, with potentially detrimental consequences for human health and ecological functioning (Greenfelt and Hultberg, 1986; Russell et al., 1993; Bytnerowicz and Fenn, 1996; Howarth et al., 1996; Lovett et al., 2000; Smith et al., 2000; Burian et al., 2002; Fenn et al., 2003a; Grimm et al., 2008). In particular, studies have shown urbanization can increase emission and deposition of particulate oC compounds that have a variety of adverse health effects (e.g., Pope et al., 2002; Krewski and Rainham, 2007). Other studies have shown that elevated N deposition can result in changes in plant and microbial community composition and declines in sensitive organisms in both aquatic and terrestrial ecosystems (see Fenn et al., 2003b for review). Despite a global trend towards increased urbanization, with biogeochemical cycles progressively more influenced by human activities (Grimm et al., 2008), there are few spatially explicit deposition data for most urban areas (Lovett et al., 2000).

Cities are not well represented in national monitoring networks (e.g., National Atmospheric Deposition Program (NADP) for wet deposition and the Clean Air Status and Trends Network for dry deposition), since such programs are aimed at monitoring regional and national patterns. Meanwhile, air-quality monitoring networks operated by state agencies are concentrated on cities but they typically focus on health-related pollutants (e.g., ozone, particulate matter (PM), carbon monoxide (CO), and fine-particulate materials) rather than nutrients of ecological interest. This situation is particularly true for rapidly urbanizing, inland, semi-arid to arid regions of the western USA (Fenn et al., 2003a). Given that arid and semi-arid lands represent a third of global terrestrial lands (Graf, 2002) and are expected to experience disproportionate increases in human populations and land transformation worldwide (United Nations, 2005), they are increasingly subject to altered atmospheric deposition, the effects of which have not been fully investigated. Quantifying the spatial and temporal patterns of inputs of oC and nutrients to urban areas and surrounding semi-arid systems is a critical first step in understanding their impact on these ecosystems (Kaye et al., 2006).

Our current understanding of spatial patterns of atmospheric deposition in urban settings is limited mostly to short-term studies concentrated in temperate or coastal cities (Lovett et al., 2000; Sun et al., 2006). For example, Lovett et al. (2000) quantified throughfall and bulk deposition fluxes along an urban to rural gradient, within and to the north of New York City (NYC) over two one-month study periods, and showed that concentrations and fluxes of nutrients decreased significantly with distance from the city. Lovett et al. (2000) suggested that the urban atmosphere acts as a scrubber, removing nitric acid vapor with dust particles containing calcium and magnesium oxides and depositing them near the city as coarse particles. Most other studies have focused on deposition of nitrate, sulfate, and organic carbon compounds such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in particular urban centers (Noll et al., 1990; Holsen et al., 1991; Lovett et al., 2000; Hughes et al., 2002; Lestari et al., 2003). Thus, questions remain about the extent to which total fluxes of nutrients and oC can be predicted by proximity to the urban core and how they vary with intra- and inter-annual climate conditions.

Compared to mesic metropolitan areas, atmospheric deposition of nutrients to inland urban areas of the western USA is likely to vary substantially both in terms of timing and relative importance of dry versus wet inputs. A large extent of the western USA is characterized by an arid to semi-arid climate where dryfall as particulate and gaseous material can be the dominant pathway of atmospheric deposition (Katrinak et al., 1995; Malm et al., 2004). The few studies of cities in this region have focused on the Los Angeles metropolitan area and surrounding coastal mountains in California; these studies documented high N deposition rates (20–45 kg N ha^{-1} yr^{-1}, maximum 90 ha^{-1} yr^{-1}; Fenn et al., 1996; Fenn and Poth, 1999; Hughes et al., 2002). Loads for other locations are primarily derived from atmospheric deposition models (Fenn et al., 2003a) or site-specific measures (Katrinak et al., 1995). For example, Fenn et al. (2003a) reported modeled N deposition loads of 7–18 kg N ha^{-1} yr^{-1} for the rapidly urbanizing region of central Arizona, with the highest predicted deposition rates in downwind desert ecosystems to the east of Phoenix. To date, however, no empirical studies have evaluated these modeled deposition estimates, or the spatial extent of the urban influence in the surrounding regional landscape.

The goal of this study was to characterize atmospheric deposition across the Central Arizona-Phoenix (CAP) region, including the developed urban core and outlying desert. Specifically, we asked, 'To what extent are concentrations and fluxes of materials enhanced at sites within the urban core relative to undeveloped desert sites upwind and downwind of the city'? We expected higher rates of wet and dry deposition within the urban core and at downwind locations compared to an upwind desert site. We also expected patterns of deposition to vary as a function of proximity to the urban core (e.g., Lovett et al., 2000). We present event-based concentrations and annual wet deposition fluxes of carbon and nutrients across the CAP metropolitan area over a 5-year period (2000–2005). We also examine patterns of coarse dry deposition and compare these estimates with published atmospheric fine-particle concentrations for Phoenix and surrounding locations within Arizona collected as part of the Interagency Monitoring of Protected Visual Environments (IMPROVE) network (Malm et al., 1994).

2. Materials and methods

2.1. *Study region*

The study was conducted at the Central Arizona-Phoenix (CAP) Long-Term Ecological Research (LTER) site in Phoenix, Arizona, USA, one of two urban ecosystems within the National Science Foundation's LTER program. The CAP LTER study site is located in a large alluvial basin in central Arizona surrounded by eroded mountain remnants that together provide the physical template upon which the city has developed. Since 1990, the population of this region has increased by 47% to over 3.5 million people (U.S. Census Bureau, 2002). The CAP LTER encompasses the rapidly expanding Phoenix metropolitan area (13% of the total LTER site) and includes 23 municipalities, surrounding agricultural lands (10%), and undeveloped or sparsely populated Sonoran desert lots and parks distributed throughout the urban matrix (77%; Fig. 1).

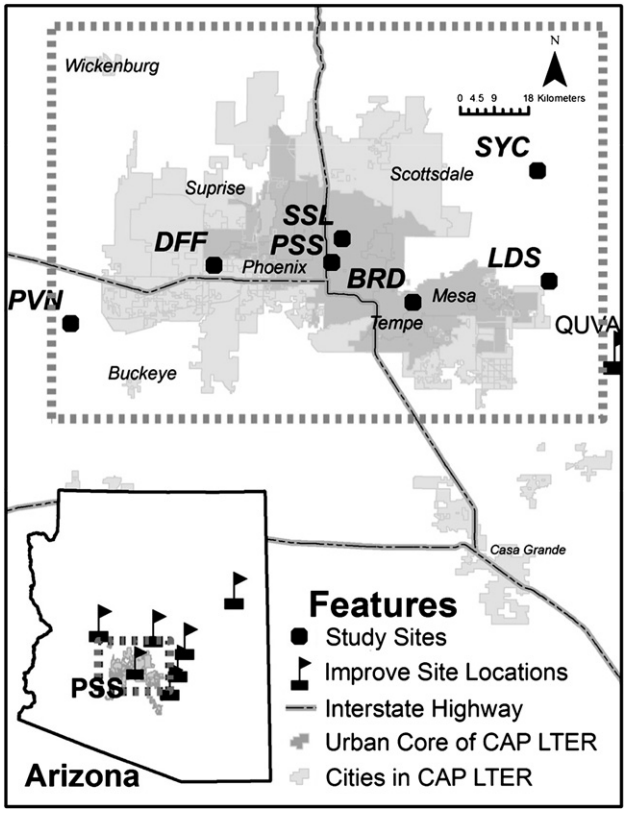

Fig. 1 – Atmospheric deposition sampling locations in the Central Arizona-Phoenix (CAP) area (solid circles) and IMPROVE sites (flagged). Upwind desert and agricultural sites are Palo Verde Power Plant (PVN) and Duncan Family Farm (DFF), respectively. Urban core sites are Phoenix Supersite (PSS) and Sunnyslope (SSL). Downwind urban site is Brooks Road (BRD) and downwind desert sites are Lost Dutchman (LDS) and Sycamore Creek (SYC).

Climate within the CAP study area is hot and arid with a mean annual temperature of 22 °C (maximum of 33 °C in July and minimum 11 °C in January) and a mean annual precipitation of 193 mm, 204.5 mm for the study years 2000–2005. The region experiences two main rainfall periods: (i) a summer monsoon that occurs between June and September with intense, localized convective storms; and (ii) a winter rain season from October to April, with more evenly distributed, gentle rains that are typically associated with Pacific frontal storms. Intense dust storms often occur during the summer and are associated with thunderstorm activity (Nickling and Brazel, 1984).

2.2. *Sample collection and analysis*

To explore the pattern of atmospheric deposition across the CAP LTER study area, we installed seven wet–dry deposition collectors (AeroChem Metrics (ACM), Bushnell, FL) to form a transect running approximately west to east: from outlying desert to the west, upwind of the urban core based on prevailing wind direction (PVN), through agricultural (DFF) and urban sites (PSS and SSL) embedded within the metropolitan matrix, to downwind urban (BRD) and desert sites located east and northeast of Phoenix (SYC and LDS) (Fig. 1). ACM collectors have two side-by-side 3.5-gallon linear polyethylene (LPE) buckets, one for wet and the other for dry deposition. Between precipitation events, a motor-driven lid covers the wet-side bucket. When precipitation occurs, a sensor activates the motor, which moves the lid from the wet-side bucket to the dry-side bucket and protects the dry-side bucket from contamination by splash and dry deposition. When precipitation ends, the motor is activated to cover the wet-side bucket and protect the wet-side bucket sample from evaporation and contamination by dry deposition (National Atmospheric Deposition Program, 2007).

For sample collections, we followed protocols developed by the National Atmospheric Deposition Program (National Atmospheric Deposition Program, 2007) and modified by the CAP LTER. Our main modification was collection of rainfall samples from the 'wet side' of the wet–dry bucket samplers within 24 h of rainfall events to avoid potential problems caused by rainfall samples being exposed to prolonged hot and dry ambient field conditions (Krupa, 2002). In brief, after a rainfall event, a collector was approached from the downwind side and inspected for any damage and/or precipitation on the dry-side. The wet-side bucket was carefully inspected for contamination such as soil, insects, bird droppings, detailed notes of possible contamination were made, and then a clean lid was snapped on the bucket. Once in the lab, rainfall samples were then poured into pre-acid-washed and rinsed polyethylene bottles from the 'wet side' of the wet–dry bucket samplers. Samples were rarely contaminated, but on the very infrequent occasion that they were, we simply did not use the data from the sample point (<3% of samples out of 918 total).

Whereas wet deposition can be measured directly in precipitation, measurement of dry deposition is much more challenging (Wesely and Hicks, 2000). All methods for estimating dry deposition are hampered by uncertainties associated with variability in physical, chemical and biological properties of the surrogate surfaces and the complexity and interactions of substances (Wesely and Hicks, 2000). Dry bucket collectors have been shown to under-represent the fine fraction of depositing airborne particles (<1 μm diameter), particularly biologically reactive ammonium (NH_4), nitrate (NO_3) and phosphate (PO_4) (Feely et al., 1985) and do not capture gaseous materials (Hicks et al., 1980; Wesely and Hicks, 2000). Nonetheless, dry bucket samplers do provide a comparative measure of coarse-particulate deposition across the study area and a minimum estimate of dry fluxes. Dry bucket samples were collected monthly following field protocols described above and processed in the lab by adding 500 ml of 18.2 mΩ deionized water to the bucket, agitating for 15 min on an orbital shaker, and treating the resulting solution as the wet bucket samples.

Wet samples and dry bucket solutions were filtered through pre-combusted 0.7-μm Whatman glass fiber filters (GF-F), and analyzed for nitrate (NO_3^-; values reported as N), ammonium (NH_4^+, values reported as N), soluble reactive P (SRP, values reported as P), sulfate (SO_4^{2-}; values reported as S) and chloride (Cl^-) on a Lachat QC80000 auto analyzer, dissolved organic carbon (oC) on a Shimadzu TOC analyzer,

and calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and potassium (K^{+}) on a Varian flame atomic-absorption spectrometer. Samples were screened for contamination using high SRP values (>0.2 mg L^{-1}) as an indicator. Minimum detection limits (in mg elemental mass/L) were 0.07 for Cl^{-}, 0.0001 ug/L for SRP, 0.0009 for NO_3^-, 0.003 for NH_4^+, 0.33 for SO_4^{2-}, 0.4 for oC, 0.02 for Ca^{2+}, 0.01 for K^{+}, 0.004 for Mg^{2+}, and 0.01 for Na^{+}.

2.3. Data analysis

Wet deposition fluxes were calculated as the product of concentration and precipitation volume for each collection period and sampler. Mean annual ion concentrations (volume-weighted) in wet deposition were calculated at each site as event concentration times precipitation volume, summed over the annual period and divided by total annual precipitation. Monthly and annual loads (kg $ha^{-1}yr^{-1}$) were estimated as the total mass deposited per month or year divided by the area of the deposition collector (0.0629 m^2). Dry bucket deposition rates were determined by dividing mass of soluble material in each sample by time sampled and sampler area; daily estimates were then summed to obtain monthly and annual rates. Monthly wet and dry estimates were annualized by multiplying the monthly load by 365 days divided by the number of days of the month. If event or dry monthly data were missing due to contamination or loss of data, then we extrapolated from the wet event or monthly dry sample on either side of the missing value, respectively.

Nonparametric Kruskall–Wallis (K–W) Rank Sum tests were used to test for differences in mean annual wet and dry bucket nutrient loads among sites. Differences in annual deposition rate among sites might arise from variation in total rainfall, and we wanted to account for this potential relationship before asking whether or not rates vary as a function of landscape position. To do this, we first regressed annual wet and dry deposition for each analyte, from all sites and years, against annual precipitation. In cases where this bivariate relationship was statistically significant, we used the K–W test to compare the average residual values among sites. Here, higher residual values would indicate that deposition rates are high even after accounting for variable precipitation amount. In cases where there was no significant bivariate relationship between annual deposition and rainfall, we used the K–W on raw data to make comparisons among sites. Nonparametric Tukey tests were performed on the ranked values for comparison of all means (Zar, 1999). A significance level of $\alpha = 0.05$ was used for all statistical tests, which were carried out with JMP software (SAS 2005).

Relationships among event-based concentrations in wet deposition, site attributes, and seasonal and event-based rainfall characteristics were evaluated using multiple regression analysis. Rainfall characteristics considered were storm size (total event precipitation in mm), time since last storm, and season (summer: May–September; winter: October–April). Site attributes considered were land-use category (urban, agricultural, or desert) and distance from urban core. Stepwise regression was used to identify variables that contributed significantly to the explanatory power of each model. Continuous variables were log-transformed to meet the assumption of normality and constant variance.

2.4. Measurements of fine-particle concentration

Independent measurements of atmospheric particle concentrations across Arizona were obtained from the IMPROVE database (http://vista.cira.colostate.edu/IMPROVE/), which includes monthly air-quality data from sites distributed throughout the US (Malm et al., 2004). The IMPROVE data are used here to (1) validate the spatial patterns observed across the CAP region and (2) evaluate the potential contribution of aerosol-phase N constituents to the CAP LTER study area. The basic IMPROVE sampler consists of four independent modules that collect fine (PM2.5; 0–2.5 μm) and coarse (PM10; 0–10 μm) particles onto Teflon, nylon, and quartz filters; collected materials are then analyzed for elemental content using X-ray florescence (XRF), ion chromatography (IC), and thermal optical reflectance (TOR). Of the sites used, one was co-located in Phoenix with a CAP LTER deposition monitoring station (PSS). Other sites were distributed along an east–west transect in Arizona and include the Hillside (HILL1), Ike's Backbone (IKBA), Petrified Forest (NP) (PEFO), Queen Valley (QUVA), Sierra Ancha (SIAN), and Tonto National Park (TNP) IMPROVE monitoring stations. We compare fine-particle concentrations (μg/m^3) across these sites as reported elsewhere (Malm et al., 2004) given that we do not know depositional velocities, which depend on the wind, surface, chemical species (for gas) and size (for particles). In the absence of surface characterization, meteorological data, and particle size data, flux estimates from the IMPROVE data would be highly uncertain.

3. Results and discussion

3.1. Wet deposition

Wet deposition of carbon and inorganic nutrients was highly variable over the central Arizona study area during 2000–2005 (Fig. 2). Rain water nutrient concentrations, especially oC, NO_3^-, and NH_4^+, were inversely correlated with storm size (Table 1, Fig. 3). An exception was SO_4^{2-}, for which there were no relationships between concentration and rainfall characteristics (Table 1). A significant interaction between storm size and season was observed for NH_4^+, NO_3^-, oC, Ca^{2+}, Mg^{2+}, and Na^{+} (Table 1), such that the difference between seasons (i.e., summer>winter concentrations) were most pronounced for large storms but minimal for smaller events (Fig. 3). oC and to a lesser extent Ca^{2+} and K^{+} concentrations increased with time since last rainfall (Table 1). Negative charge was in close balance with positive charge (slope=0.94; data not shown) during wet deposition events in summer, but there was much scatter around the 1:1 line ($r^2 = 0.49$). Conversely, negative charge greatly exceeded positive charge during winter events (slope=0.62), suggesting acidic precipitation.

In contrast to our expectations, there were no significant regressions between concentrations in wet fall and distance from the urban core or land use. These results contrast with previous urban studies, which have suggested spatial variation in wet deposition can be explained as a function of rainfall and proximity to the urban center (Lovett et al., 2000). Our inability to detect spatial relationships among our sites may in part be explained by low statistical power related to the

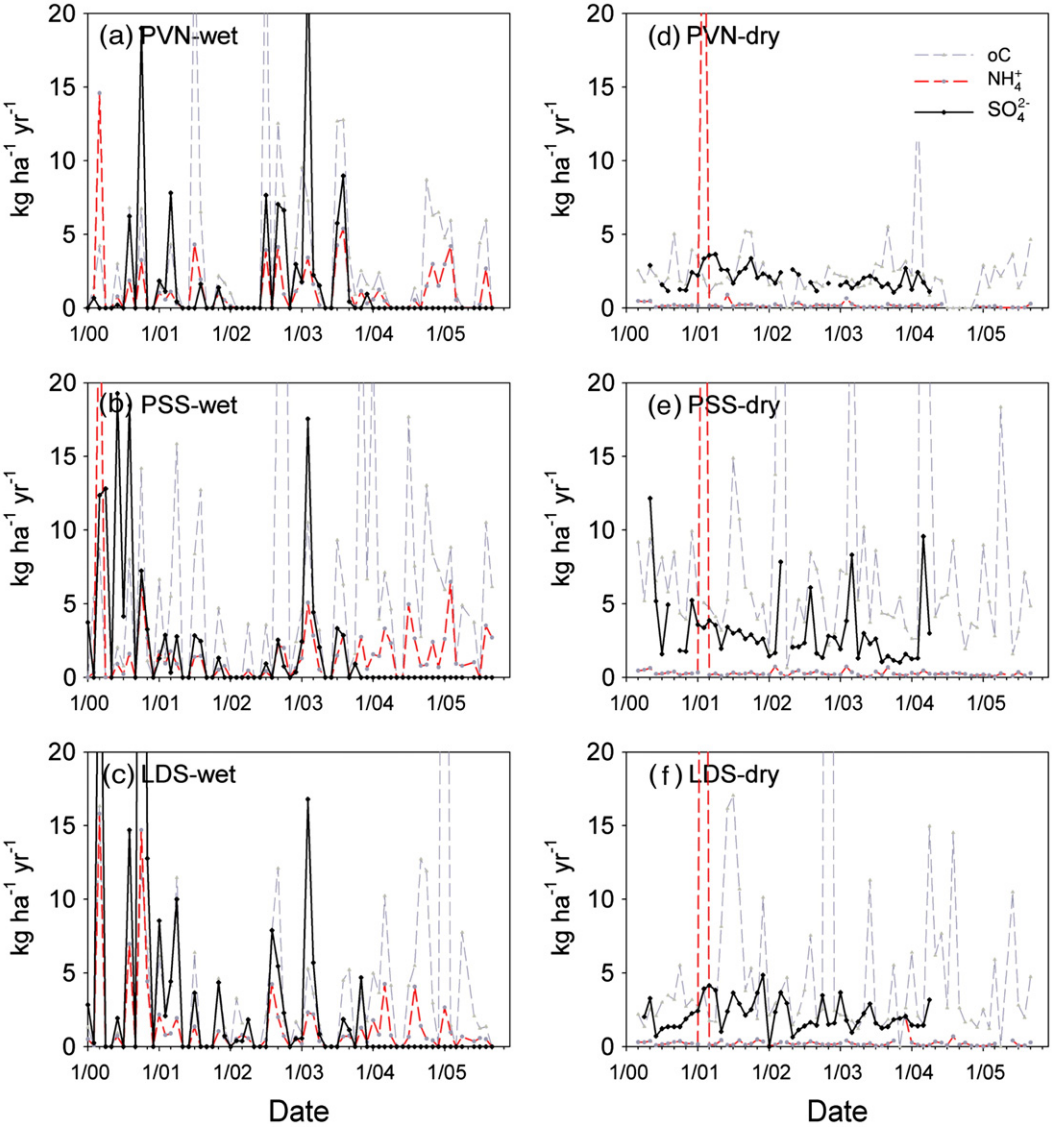

Fig. 2 – Annualized monthly wet and dry deposition of oC (grey), NH_4^+ (red) and SO_4^{2-} (black) (kg ha^{-1} yr^{-1}) for the upwind desert site (PVN) (a, b), urban core site (PSS) (c, d), and downwind desert site (LDS) (e, f). Note SO_4^{-2} is missing for 2004–2005.

current experimental design (7 sites), although Lovett et al. (2000) had a similar number of sites in their design and much lower temporal resolution. Alternatively, our assumption that pollutants are transported coherently from west to east may not have been valid; the relatively high mixing heights and low prevailing wind speeds characteristic of the Phoenix metropolitan area may have increased atmospheric mixing compared to coastal urban centers so that deposition was localized to the urban core in the CAP area. In the present study, spatial variation in wet deposition appeared to be more related to storm characteristics and season, variables which have been used to explain deposition patterns in other areas of the desert Southwest (Welter et al., 2005; Baez et al., 2007). Our findings suggest these patterns and controls on wet deposition fluxes can be generalized to the region.

Similarly, no differences in mean annual wet deposition were found among sites, with the exception of oC ($\chi^2=15.06$, df 6, $P<0.05$) Mean annual wet deposition of oC did not show a positive relationship with annual rainfall and was high across the CAP ranging from 3.6 to 8.0 kg oC ha^{-1} yr^{-1} (Fig. 4). Post-hoc nonparametric tests showed wet oC was significantly higher at a downwind site (SYC) compared to an upwind agriculture site (DFF). Annual wet deposition for 3 of the 9 analytes was significantly and positively related to annual rainfall (NH_4^+: $r^2=0.33$, $P=0.001$; NO_3^-: $r^2=0.27$, $P=0.004$; SO_4^{2-}: $r^2=0.32$, $P=0.002$; $n=27$). In each of these cases, however, the average value of the residuals from the regression line was not significantly different among sites. Wet deposition rates of NO_3^- and NH_4^+ were low (1.0 to 3.0 kg N ha^{-1} yr^{-1}) and highly correlated ($r=0.85$). Compared to other available data sets (National Atmospheric Deposition Program, 2007), wet SO_4^{2-} deposition was high across the CAP (mean 1.39 kg SO_4^{2-} ha^{-1} yr^{-1} as S) and highly correlated to NH_4^+ ($r=0.71$) and NO_3^- ($r=0.74$) (Table 2), suggesting scavenging of aerosol components (e.g., $(NH_4)_2SO_4$ and NH_4NO_3) during rainfall events. Elevated inputs of Ca^{2+} in wet fall (2.0–6.0 kg ha^{-1} yr^{-1}) balanced these anion loads in the core sites; Na^+, Mg^{2+}, and K^+ inputs were similar among sites.

Table 1 – Coefficient estimates from multiple linear regression analyses that relate log event-based concentrations in wet deposition to rainfall characteristics including season (SN), and mm storm size (SS), and time since last rainfall (TSLR) and their interactions for 2000–2005

log (Solute)	log (TSLR) [a]	Season (SN)	log (SS)	log SS × SN	n	R^2
DOC	0.151***	0.253***	−0.409***	0.05*	400	0.60
NH_4^+		0.116**	−0.297***	0.114***	436	0.29
NO_3^-		0.424***	−0.402***	0.100**	439	0.50
SRP		0.225***	−0.252***	0.068 NS	355	0.15
Ca^{2+}	0.118*	0.415***	−0.325***	0.101 NS	419	0.35
Mg^{2+}		0.372***	−0.313***	0.185**	340	0.23
K^+	0.118*	0.350***	−0.272***	0.176**	358	0.23
Na^+		0.219**	−0.167**	0.195**	339	0.12
Cl^-		−0.079 NS	−0.336***	−0.007 NS	415	0.13
SO_4^{2-}		−0.01 NS	−0.064 NS	−0.01NS	243 [a]	0.008

Statistical significance indicated as follows: *P<0.05, **P<0.01, and ***P<0.0001.
[a] 2000–2003.

Annual wet nutrient and oC inputs across the CAP study area varied with local- to regional-scale climate patterns, depending on the analyte. Deposition of oC was elevated in the urban core (PSS) throughout the study period (2000–2005) (Fig. 5). Loads of SO_4^{2-} in wet fall were elevated in 2000 at all sites; inputs were as high as 4.7 kg S ha^{-1} yr^{-1} (or 14.2 ha^{-1} yr^{-1} as SO_4^{2-}) with Ca^{2+} and NH_4^+ balancing loads of SO_4^{2-} (Fig. 5). Elevated inputs of NH_4^+ and wet fall SO_4^{2-} in 2000 corresponded to one regional-scale Pacific tropical storm and preceding dust storm (Fig. 2). One possible mechanism explaining these high wet fluxes of sulfate is that insoluble mineral dust particles are incorporated in droplets within convective clouds; geophysical studies have documented that dust particles may be effective as 'cloud condensation nuclei' (CCN), particularly when layers of SO_4^{2-} and NO_3^- form on their surface (Levin et al., 1996; Yin et al., 2002). Alternatively, urban activities and/or dust storms may stir up material containing sulfate-bearing minerals (e.g. $CaSO_4$), and then this sulfate is deposited as wet fall. Regardless, the high SO_4^{2-} fluxes measured in this study exceed those reported by the NADP for the desert Southwest (0.33–0.66 kg ha^{-1} as SO_4^{2-} as S) and are comparable in magnitude to those found in rural portions of the Northeast USA (National Atmospheric Deposition Program, 2007).

3.2. *Coarse dry deposition*

Compared to wet fluxes, measured dry bucket nutrient deposition did not show strong seasonal trends with the exception that deposition of oC was three times higher in the urban core (PSS) during fall/winter compared to spring/summer months ($Z=2.165$, $P<0.05$); this seasonal pattern was not observed for other sites (Fig. 6). oC deposition peaked in the urban areas in the winter months, likely because of lower vertical mixing heights during this season, compared to the warmer summer months (Holzworth, 1972; Brazel et al., 1988). Measured dry bucket deposition of NH_4^+ was high in the fall/winter months but variable (CV=36–216%) and thus not significantly different than summer months, whereas NO_3^- deposition was low and relatively uniform across seasons at the CAP sites. Consistent with our dry bucket deposition data, the IMPROVE data showed that fine-particulate oC concentrations were substantially higher in the urban core (PSS) (5.72–7.52 μg m^{-3}) than the rural sites (0.85–1.25 μg m^{-3}) during the fall/winter months. Similar to our data, fine-particulate $(NH_4)_2SO_4$ concentrations from the IMPROVE data did not differ substantially between the urban core site (PSS) (1.05–2.11 μg m^{-3}) and rural sites (0.5–1.6 μg m^{-3}). In contrast, concentrations of fine-particle NH_4NO_3 were elevated in the urban core (PSS) in fall (2.21 μg m^{-3}) and winter (2.39 μg m^{-3}) relative to rural sites (0.2–0.49 μg m^{-3}). These IMPROVE observations contrast with measured dry N deposition in our study, suggesting that we did not detect the deposition of fine-particulate or gaseous forms of N with the dry bucket collectors. While the IMPROVE estimates of fine-particle N concentrations are elevated in the urban core relative to the desert sites, it should be noted that these values are 5–30 times

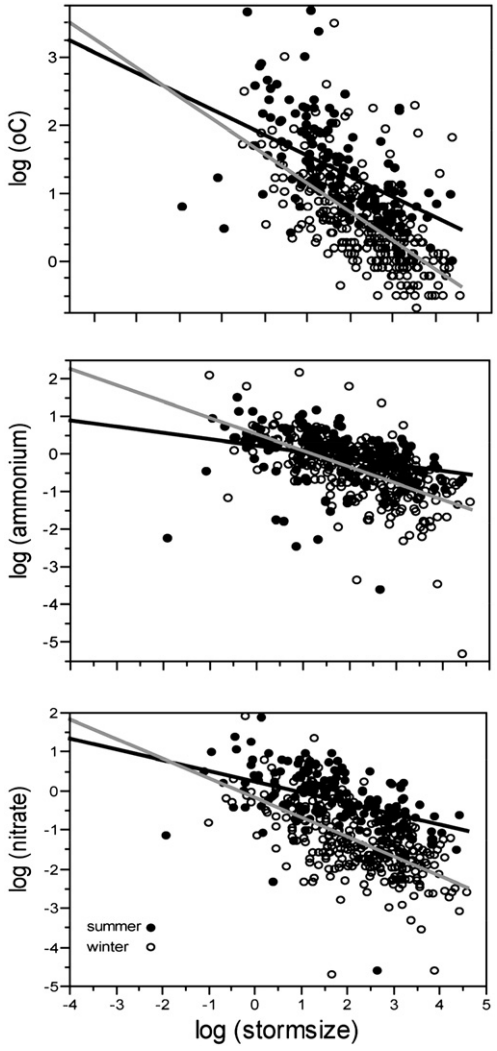

Fig. 3 – Log–log relationships between storm size (mm) and event-based concentrations of (a) oC, (b) NH_4^+, and (c) NO_3^- (mg/L) plotted both for summer (black circles) and winter (open circles) events.

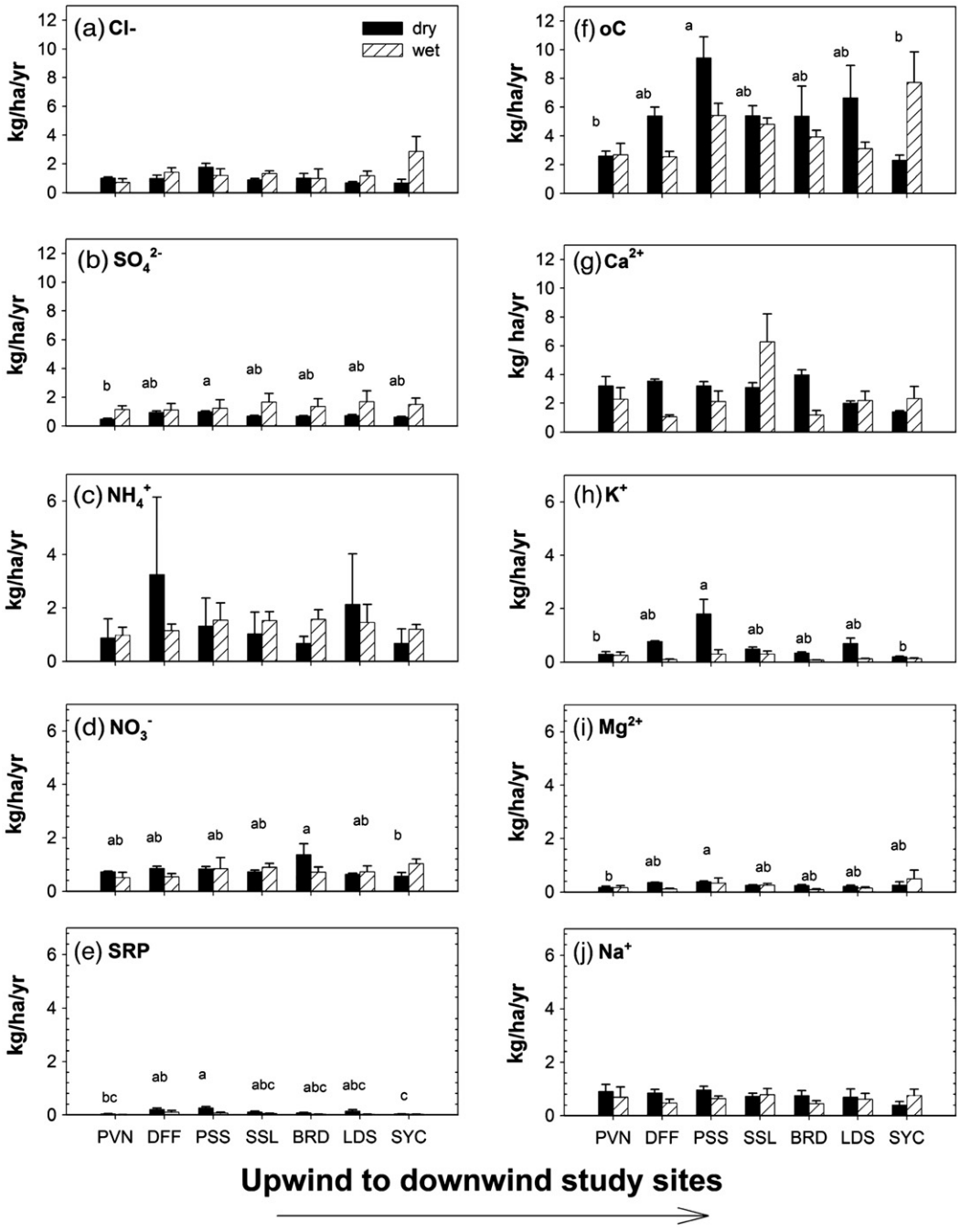

Fig. 4 – Mean annual nutrient loads as wet (white hatched) and dry (black) deposition ± standard error. Different lower case letter indicate significant differences in mean residual values for dry bucket loads among sites (nonparametric Tukey HSD, $P<0.05$). Only wet deposition of oC were significantly different among sites (see text for details). Note differences in scales.

lower than concentrations reported in the Los Angeles area (11–75 μg m^{-3}) (Hughes et al., 2002).

Mean annual loads from dry deposition were equivalent or higher than wet deposition inputs for most nutrients across the CAP with the exception of SO_4^{2-} (Fig. 4). Of all analytes considered here, only dry deposition of Na^+ was significantly (and inversely) related to annual precipitation ($r^2=0.52$, $P<0.001$; $n=28$); in this case, the average residual values from the regression line were not significantly different among sampling locations. Mean annual dry deposition of oC ranged from 2 to approximately 10 kg ha^{-1} yr^{-1}, and loads were significantly enhanced in the urban core (PSS) compared to an upwind desert site (PVN) and downwind desert site (SYC) ($\chi^2=17.03$, df 6, $P<0.01$). Mean annual dry bucket NH_4^+ fluxes were more variable than those of other nutrients, particularly at the agricultural site (DFF) where inputs were as much as two-fold higher than desert and urban sites. More variable NH_4^+ fluxes were likely associated with dust particles generated from nearby agriculture. Dry deposition of NO_3^- was relatively low (<1 kg ha^{-1} yr^{-1}) but differed significantly among sites

Table 2 – Correlation matrix of annual wet and dry deposition loads (kg ha^{-1} yr^{-1}) for CAP region (n=34)

Wet	Cl^-	DOC	NH_4^+	NO_3^-	SRP	SO_4^{2-}	Ca^{2+}	K^+	Mg^{2+}	Na^+
Cl^-		0.352	0.374	**0.474**	0.073	**0.644**	0.332	0.175	**0.536**	−0.130
DOC			−0.085	0.194	−0.073	0.005	0.063	0.083	**0.488**	0.021
NH_4^+				**0.852**	−0.032	**0.711**	**0.405**	−0.002	−0.178	−0.341
NO_3^-					−0.033	**0.743**	**0.499**	0.008	0.057	−0.203
SRP^-						−0.123	−0.062	0.248	−0.053	0.074
SO_4^{2-}							**0.589**	−0.112	0.143	−0.324
Ca^{2+}								0.259	0.299	0.051
K^+									0.151	**0.491**
Mg^{2+}										0.179
Na^+										

Dry	Cl^-	DOC	NH_4^+	NO_3^-	SRP	SO_4^{2-}	Ca^{2+}	K^+	Mg^{2+}	Na^{2+}
Cl^-		**0.520**	0.323	**0.579**	0.321	**0.556**	0.361	**0.399**	**0.532**	0.286
DOC			−0.100	0.161	**0.708**	**0.434**	0.109	**0.631**	0.246	0.106
NH_4^+				0.335	−0.127	**0.404**	0.139	−0.093	0.115	−0.196
NO_3^-					0.015	**0.446**	**0.694**	−0.005	**0.474**	0.138
SRP						**0.493**	0.064	**0.789**	0.352	0.163
SO_4^{2-}							0.347	**0.463**	**0.530**	0.185
Ca^{2+}								0.097	0.337	**0.631**
K^+									**0.435**	0.303
Mg^{2+}										**0.414**
Na^+										

Bold numbers show significant pairwise correlations (P<0.05).

with loads higher in the urban core (BRD) than a downwind desert site (SYC) (NO_3: χ^2=13.11, df 6, P<0.05, Fig. 4). SRP and SO_4^{2-} deposition rates were significantly elevated in the urban core (PSS) relative to the upwind desert site (PVN) and downwind site (SYC, for SRP) (SRP: χ^2=19.47, df 6, P<0.005, SO_4^{2-}: χ^2=17.95, df 6, P<0.01), where they reached 0.3 and 1.0 kg ha^{-1} yr^{-1}, respectively. Dry deposition of Na^+ occurred at similar rates among sites, while Ca^{2+} K^+ and Mg^{2+} deposition were significantly different among sites (Ca^{2+}: χ^2=19.20, df 6, P<0.005, K^+: χ^2=21.30, df 6, P<0.001, Mg^{2+}: χ^2=13.74, df 6, P<0.05) (Fig. 4). It should be noted that the proportion of total dry deposition (including fine particles and gases) captured by these measurements is unknown, particularly for N.

Dry bucket deposition fluxes of oC, NO_3^- and NH_4^+ were correlated with other nutrient inputs in particulate form (Table 2). Correlation of dry oC deposition with dust-derived SRP (r=0.71) and to a lesser extent K^+ (r=0.63) and Mg^{2+} (r=0.25) suggested either association of oC with dust in the atmosphere or oC derived from dust. Dry fall of NO_3^- was significantly correlated with dry fall of bivalent cations, Ca^{2+} (r=0.63) and Mg^{2+} (r=0.25), indicating reaction of nitric acid vapor with dust particles containing calcium and magnesium oxides, consistent with other studies (Lovett et al., 2000; Malm et al., 2004). Finally, NH_4^+ and NO_3^- deposition were correlated (r=0.33) as were NH_4^+ and SO_4^{2-} (r=0.40), probably owing to particle deposition as NH_4NO_3 and $(NH_4)_2SO_4$, but NH_4^+ also showed weak associations with other base cations. Taken together, these relationships suggest that dust particles bearing calcium and magnesium oxides and rock phosphate that are generated within the urban area are reacting in the atmosphere with nitric acid or other N oxides to produce calcium and magnesium nitrates in particulate form. As described by Lovett et al. (2000), urban-derived dust particles may "scrub" the atmosphere of N oxide gases and be deposited locally rather than dispersed downwind because of their relatively large size (>2 μm diameter). Our coarse-particulate deposition data suggest that this same process is occurring in the CAP study region.

Similar to wet deposition, inter-annual variation of dry bucket nutrient and carbon inputs across the CAP sites also appeared to reflect differences in local- to regional-scale climate patterns (Fig. 5). Dry oC inputs to downwind sites (LDS and BRD) increased substantially during a dry year (2002), when rainfall averaged 106 mm across the CAP (range 70–150 mm), whereas inputs to the upwind desert site (PVN) remained low regardless of rainfall. The long-term data also revealed that all sites received elevated inputs of dry NH_4^+ in 2000 with the downwind desert site (LDS) receiving 3–4 times as much N (8 kg N ha^{-1} yr^{-1}) as the upwind site (PVN) (3 kg N ha^{-1} yr^{-1}); dry loads of NH_4^+ were lower thereafter at all sites (0.1–0.4 kg N ha^{-1} yr^{-1}). Dry deposition of NO_3 did not vary substantially among sites, whereas SO_4^{2-} was consistently elevated at the urban core and downwind site.

3.3. *Urban enhancement of carbon and nutrients across the CAP*

This study is one of the first to report spatial and temporal patterns of atmospheric deposition across a desert city. Mean annual loads of atmospheric nutrients to the CAP LTER sites were dominated by dry deposition with the notable exception of SO_4^{2-}. Dust emissions derived from human activities appeared to play a key role in scrubbing urban emissions of oC and N and depositing them locally (Katrinak et al., 1995; Lovett et al., 2000). Across the CAP region, we observed higher deposition rates of oC and associated bivalent base cations and mineral particles in and downwind of the urban core during fall and winter months compared to the upwind desert site. Our findings and patterns of fine-particle concentration

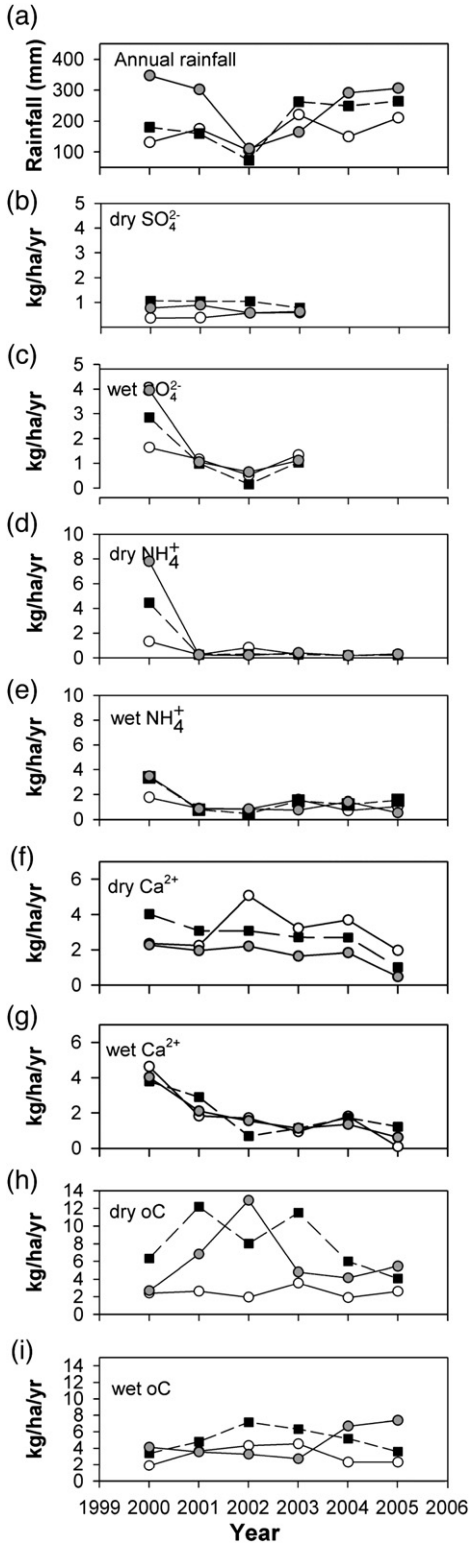

Fig. 5 – Variation in rainfall in mm (a), dry and wet bucket deposition (kg ha^{-1} yr^{-1}) of SO_4^{2-} (b, c), NH_4^+ (d, e), Ca^{2+} (f, g) and oC (h, i) at upwind desert (PVN) (○), urban core (PSS) (■) and downwind desert (LDS) (●).

from the IMPROVE sites concur with other studies in Phoenix that oC is the major contributor to atmospheric haze and deposition (Katrinak et al., 1995; Malm et al., 2004). Meat cooking, road dust, and automobile sources (Rogge et al., 1996) as well as fire-related activities (Hawthorne et al., 1992; Smith et al., 2000) are likely to be primary sources of oC emissions, whereas secondary emissions may come from multiple biogenic and anthropogenic sources (e.g. Holsen et al., 1991; Kanakidou et al., 2005; Sun et al., 2006). The composition of the organic compounds deposited, their interaction with vegetation, and their health consequences remain poorly characterized and merit further investigation. One study by Simonich and Hites (1994), for example, showed that PAHs, which are lipolithic and accumulate in animal/human tissues, can be removed from the atmosphere by vegetation. The effect of these organic compounds on biotic communities and the role of Sonoran desert vegetation in removing semi-volatile organic compounds remain unknown. Finally, these seasonally elevated inputs of oC may also have important consequences for microbial community structure and pulsed responses to rainfall in desert ecosystems that are often limited by C substrate supply when water limitation is relieved (Sponseller, 2007). This may be particularly important during dry years when productivity is low and elevated loads of dry fall oC are high such that atmospheric inputs may represent a significant fraction of net primary productivity. In a recent modeling study, Shen et al. (2005) estimated an average aboveground net primary productivity of 72.3 g m^{-2} y^{-1} in

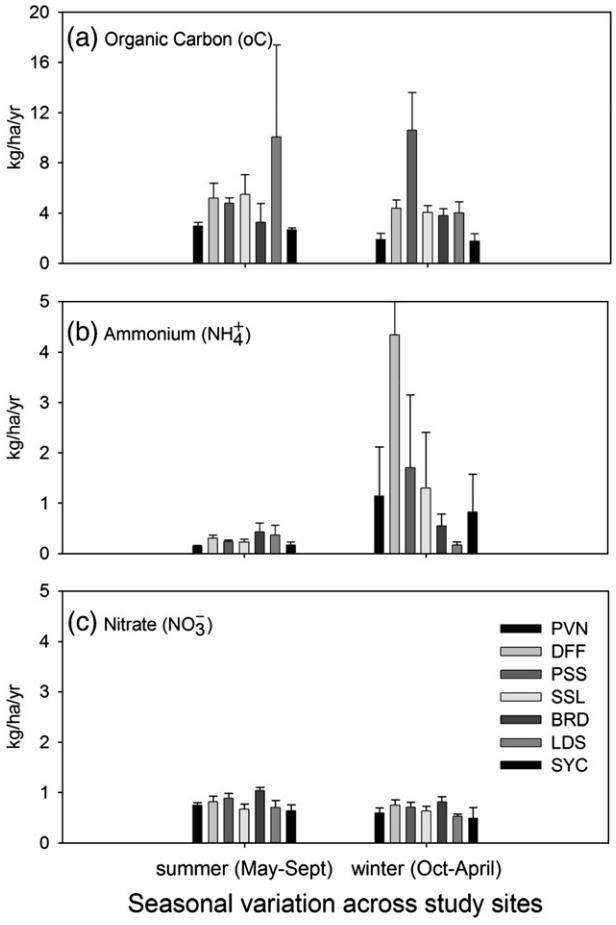

Fig. 6 – Seasonal dry deposition fluxes of a) oC, b) NH_4^+, c) NO_3^- across the CAP LTER study area.

the CAP, ranging from 11.3 to 229.6 g dry matter m^{-2} y^{-1} depending on rainfall (or approximately 5.0 to 103 g C m^{-2} y^{-1} assuming a 45% conversion rate. These estimates suggest that dry deposition inputs may represent as much as 20% of net primary productivity during dry years.

Previous studies have estimated or modeled dry deposition N inputs to the CAP. Baker et al. (2001) estimated that 18.5 kg ha^{-1} yr^{-1} was deposited on the CAP as dry deposition (Baker et al., 2001). More recently, Grossman-Clarke et al. (reported in Fenn et al., 2003a) improved this estimate by scaling a single-day simulation from Models-3/CMAQ to the whole study area, yielding dry deposition estimates of 13.5 kg N ha^{-1} yr^{-1} for the urban core, 15.0 kg N ha^{-1} $yr^{-1}$for the downwind desert and 7.5 kg N ha^{-1} yr^{-1} for the upwind desert, with the most exposed agricultural and desert areas receiving 28.0–29.0 kg N ha^{-1} yr^{-1}. In the present study, measured inputs of N (dry and wet) in 2000 were comparable to the modeled estimates with the upwind desert, urban core, and downwind desert site receiving 7, 11, 12 kg N ha^{-1} yr^{-1}, respectively. Thereafter, annual inputs were considerably lower than previous modeled estimates from Fenn et al. (2003a) and also Baker et al. (2000). Measured deposition rates may be lower than model estimates because of failure to measure inputs of organic N (Neff et al., 2002), aerosol and gas phase N and the volatilization of particulate N from surrogate surfaces to the atmosphere in this hot arid environment, especially for gas phase and fine-particulate N. In addition, the Models-3/CMAQ simulation was based on a high-ozone day, which may have overestimated NO_x deposition rates (Grossman-Clarke, pers comm.). Finally, differences in deposition velocities to real urban surfaces (a complex mixture of built materials, vegetation and bare soil) may also help to explain the disparity between modeled and observed rates of deposition in our collectors (Russell et al., 1993). Studies of gaseous and aerosol atmospheric N chemistry and deposition across the CAP study region are underway and will help to improve fine-particulate and gaseous N deposition estimates.

A somewhat surprising finding from this study was that anions loads were dominated by SO_4^{2-} in wet fall. Dissolution of SO_4^{2-} aerosols in rainwater resulted in high anion fluxes during these events, with loads that were 2–5 times higher than those to the surrounding desert reported by the NADP program. These results are consistent with urban activities or dust storms stirring up sulfate-bearing minerals or possibly sulfate coating desert particles during rain formation (Levin et al., 1996; Yin et al., 2002). Because of high summer temperatures in this environment, N species may remain in gas phase rather than being deposited as dry fall (Watson et al., 1994; Makar et al., 1998). Instead, sulfate may be the dominant anion in this arid environment.

In conclusion, we found that the spatial extent of urban-enhanced deposition in this arid region appears to be mostly limited to the developed urban core (Fig. 1). We do acknowledge that our ability to detect differences among sites and land uses was limited by a low number of sites overall, and a lack of replicate land-use categories. Nonetheless, we observed strong seasonal patterns associated with wet deposition and significant differences in loads as dry deposition among our sites. In particular, we found that increased deposition associated with the urban center of metro Phoenix was dominated by dry deposition of oC and to a lesser extent N in the fall and winter months, when temperatures favored particle formation. We remain cautious about our conclusions from N deposition loads in dry buckets, as more sophisticated studies of gaseous and aerosol atmospheric N chemistry are underway and may reveal a significant missing N fraction that we have not measured. Finally, we were surprised to find that wet fall anions loads were dominated by SO_4^{2} across the CAP and 2–5 times higher than loads to the surrounding desert reported by the NADP program. The consequences of increased deposition of carbon, SO_4^{2-} and other cations and to a lesser extent N for ecological functioning are not clear and merit further investigation. Together, findings from our study suggest that this arid city is similar to other cities in more temperate regions that scrub nutrients from the atmosphere, yet unique attributes result from hot temperatures, complex atmospheric-water interactions and the distribution of NH_3 between gas and water phases.

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