NUTRIENTS ON ASPHALT PARKING SURFACES IN AN URBAN ENVIRONMENT

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Abstract. Amounts of readily soluble nutrients on asphalt parking lot surfaces were measured at four locations in metropolitan Phoenix, Arizona, U.S.A. Using a rainfall simulator, short intense rainfall events were generated to simulate 'first flush' runoff. Samples were collected from 0.3 m^2 sections of asphalt at 8 to 10 sites on each of four parking lots, during the pre-monsoon season in June-July 1998 and analyzed for dissolved NO_3^--N, NH_4^+-N, soluble reactive phosphate (SRP), and dissolved organic carbon (DOC). Runoff concentrations varied considerably for NO_3^--N and NH_4^+-N (between 0.1 and 115.8 mg L^{-1}) and DOC (26.1 to 295.7 mg L^{-1}), but less so for SRP (0.1 to 1.0 mg L^{-1}), representing average surface loadings of 191.3, 532.2, and 1.8 mg m^{-2} respectively. Compared with similar data collected from undeveloped desert soil surfaces outside the city, loadings of NO_3^--N and NH_4^+-N on asphalt surfaces were greater by factors of 91 and 13, respectively. In contrast, SRP loads showed little difference between asphalt and desert surfaces. Nutrient fluxes in runoff from a storm that occurred shortly after the experiments were used to estimate input-output budgets for 3 of the lots under study. Measured outputs of DOC and SRP were similar to those predicted using rainfall and experimentally determined surface loadings, but for NH_4^+-N and particularly for NO_3^--N, estimated rainfall inputs and surface runoff were significantly higher than exports in runoff. This suggests that parking lots may be important sites for nutrient accumulation and temporary storage in arid urban catchments.

Keywords: ammonium, arid urban environments, asphalt parking lot surfaces, DOC, nitrate, phosphorus, storm runoff

1. Introduction

A significant proportion of contaminant loads to recipient systems originate from atmospheric deposition (Burian *et al.*, 2001; Grennfeld and Hultberg, 1986; Howarth *et al.*, 1996; Hicks, 1998). Such deposition can be significantly enhanced in and around urban areas, particularly for nutrients (Bytnerowicz and Fenn, 1996; Russell *et al.*, 1993; Lovett *et al.*, 2000; Smith *et al.*, 2000) and may make a measurable contribution to the nutrient cycling of urban ecosystems (Baker *et al.*, 2001).

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However, little has been done to determine direct measurements of nutrient dry deposition to inert urban surfaces, and modeled estimates are hampered by a lack of knowledge of deposition velocities for typical urban surface types such as asphalt (Sehmel, 1980). Urbanization not only enhances pollutant deposition, but also modifies natural drainage patterns and hydrologic pathways. Replacement of natural ground cover by paved surfaces increases the volume and rate of storm runoff (Leopold, 1968), prevents natural infiltration of stormwater to the subsurface and increases soil erosion and pollutant runoff (Burian *et al.*, 2001). This increase in impervious surface area coupled with enhanced pollutant deposition has meant that most cities are net exporters of nutrients and contaminants. Urban drainage from paved areas transports dissolved, colloidal, and solid constituents in a heterogeneous mixture, of which heavy metals are typically the most prevalent pollutant constituents, along with organic and inorganic compounds (Sansalone *et al.*, 1998). Such urban stormwater can degrade the quality of streamflow with oil and grease, pesticides, and trace metals (e.g., Lopes *et al.*, 1995).

Materials accumulating on street surfaces and contributing to pollutant loads in urban storm runoff have been studied by the National Urban Runoff Program or NURP (Sartor and Boyd, 1972; EPA, 1983). The focus of such work has been largely on the contaminant chemistry of runoff, in particular heavy metals (e.g., Pitt and Amy, 1973), petroleum hydrocarbons (e.g., Latimer *et al.*, 1990; Lopes *et al.*, 2000), and particulates (e.g., Sansalone *et al.*, 1998). Furthermore, most studies have concentrated on street surfaces where nutrient concentrations in runoff typically are not very high (Sartor and Boyd, 1972; EPA, 1983; Lopes *et al.*, 1995). However, little attention has been paid to nutrient accumulation and storage on parking lot surfaces, which not only have significant extent in cities, but also potentially accumulate larger surface loads than streets, due to slower vehicle speeds, leakage of petroleum hydrocarbons from stationary vehicles, and less frequent surface cleaning.

In the arid desert ecosystems of the southwestern US, the pools of major nutrients stored in plants and soils is low compared to other terrestrial ecosystems (Peterjohn and Schlesinger, 1990), while dry deposition of nutrients typically comprises a significant fraction of total deposition (Bytnerowicz and Fenn, 1996). Hence parking lot surfaces in urban environments could constitute important nonpoint sources of nutrients, potentially contributing to chronic, low-level degradation of stormwater quality.

The aims of this study were to: i) measure the maximum amounts of readily soluble nutrients likely to have accumulated on asphalt parking lot surfaces in Phoenix after an extended period of dry weather, ii) examine variations in surface loads with respect to site/land use, traffic type and density, surface slope, pavement condition and distance to the nearest curb, iii) compare nutrient loadings on parking lot surfaces with those for an adjacent undeveloped desert soil surface, iv) use a mass balance approach to compare nutrient inputs in rainfall and from asphalt surfaces, with losses in runoff during an actual storm event in the mini-watersheds

TABLE I

Site descriptions

Site name	U.S.G.S. station number	Land use & surface type	Land use (%)	Basin area (ha)	Impervious area (%)	Number of plots
Box Culvert	09512185	Light industrial & asphalt	84	0.159	80	9
Peoria Avenue	09513885	Commercial & asphalt	97	1.4	96	9
Olive Avenue	09513925	Residential & asphalt	100	7.2	60	10
Papago Park	no station	Desert park & soil	99	n. a.	3	10
Sycamore Creek	09510200	Desert & soil	100	n. a.	<2	12

studied, and v) use these findings to clarify the likely role of parking lot surfaces in urban nutrient cycling.

1.1. STUDY SITES

The Central Arizona-Phoenix Long Term Ecological Research (CAP LTER) study site encompasses an extensive, rapidly expanding metropolitan area of 3 million people, located on a large alluvial floodplain in the Sonoran desert of the southwestern US. The climate is hot (average annual temperature 30 °C) and dry, with a mean annual rainfall of 180 mm, approximately half of which occurs during low-intensity winter rains (Feb-April) that span the entire basin. The remaining rainfall is produced by summer (July-September) convective storms, which are intense and highly-localized (Ricci, 1984). Rapid development of the Phoenix metropolitan area over the past 50 yr has led to an extensive urban area characterized by heterogeneous landscape consisting of residential, commercial, industrial, transportation, and remnant desert land uses, with agriculture on the periphery of the urban development in the west and southeast parts of the valley (Stefanov *et al.*, 2001). The developed urban core of metropolitan Phoenix consists of a mosaic of land use types (residential, transportation corridors, commercial, and institutional) that include significant (around 50%) impervious surface cover.

Parking lots were selected in areas surrounded by four different land uses: desert, commercial, light industrial, and residential (Table I, Figure 1). At three of these sites (considered as urban ‘mini-catchments’) a suite of chemical constituents in storm runoff have been monitored by the United States Geological Survey (USGS) since the early 1990s as part of the National Pollutant Discharge Elimination System permitting requirements of the Environmental Protection Agency (Lopes *et al.*, 1995). The commercial parking lot site is surrounded by businesses including a restaurant and retail stores; about half of the pervious area is undeveloped and half has desert landscaping with some irrigation. At the light in-

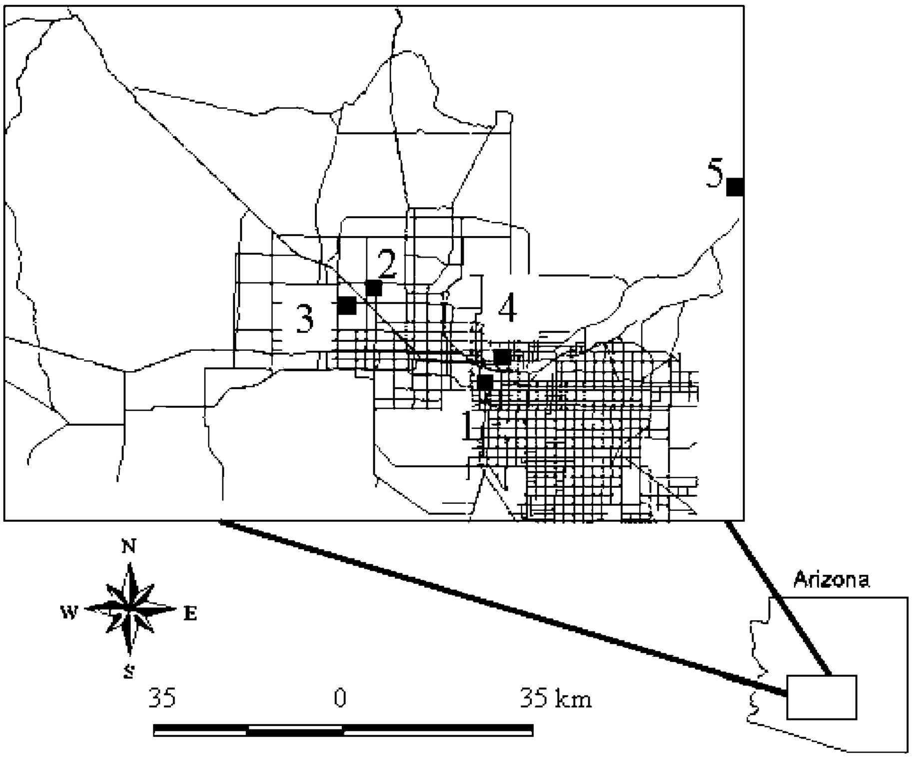

Figure 1. Location of the research sites within the Central Arizona-Phoenix study area. The sites are: 1 – Box Culvert at 48th St., Tempe; 2 – Peoria Avenue and 43rd Ave., Phoenix; 3 – Olive Ave. and 67th Ave., Glendale; 4 – Papago Park, Tempe; 5 – Sycamore Creek.

dustrial site, businesses include offices, warehouses, small manufacturing, heavy equipment rental, a hotel, and a restaurant; pervious areas consist of irrigated landscaping strips with a surface cover of decomposing granite adjacent to parking lots, along with a number of long grassy swales that line several of the channels and route storm runoff to the USGS-gauged outlet draining the site. The residential site consists mostly of homes, of which half have desert landscaping and half irrigated lawns. At the desert site, asphalt parking surfaces were surrounded by an undeveloped desert remnant (Papago Park) within the urban matrix. In addition to the parking lot sites, comparable experiments to determine the nutrient content of runoff from undisturbed desert soil surfaces were carried out in Sycamore Creek (33°45′N, 111°30′W), a 505 km^2 undeveloped Sonoran desert watershed 35 km northeast of the Phoenix metropolitan area. The watershed is underlain by pre-Cambrian granite and some Quaternary or Tertiary basalt. Annual rainfall at Sycamore Creek averages 295 mm divided roughly in half between summer and winter rains (Thomsen and Shumann, 1968). Soils are compact with abundant eroded mineral grains scattered over the surface; plant litter is largely confined to the base of vegetation clumps except where annual grass growth is locally abundant.

2. Methods

The runoff experiments were performed in early June 1998 shortly before the onset of summer 'monsoon' storms. This is typically the driest season in the northern Sonoran Desert; experiments were preceded by several weeks of dry weather during which dry-deposited material could accumulate.

2.1. SAMPLE PLOT LOCATION AND CHARACTERIZATION

Rainfall-runoff experiments were conducted on between 8 and 10 asphalt plots at each of the four sites, for a total of 38 plots overall (Table I). Plots for runoff simulations were stratified within each site by positioning a similar number in each of two categories: 'byways' (areas where vehicles move) and 'stationary' (areas where vehicles park). Within these general areas sites were chosen by walking a random number of paces from an arbitrary point. The following characteristics of each plot were recorded: pavement condition, plot type (either byway or stationary), parking density, slope of the asphalt surface, and distance from the nearest curb. Pavement condition was described according to the method used by the NURP study (Sartor and Boyd, 1972), which involved assigning a score between 1 and 4 corresponding to excellent (score = 1: smooth surface, no cracks, essentially new condition), good (2: few cracks, near new condition), fair (2: cracks, some pavement deterioration), and poor (4: many cracks, moderate to extensive deterioration). Parking density was also described and scored following Sartor and Boyd (1972) as light (1: very few vehicles parked), moderate (2: around half available spaces filled), or heavy (3: parking mostly continuous). Simulated rainfall experiments also were carried out on 12 plots at the undisturbed desert site in the lower portion of the Sycamore Creek watershed.

2.2. SIMULATED RAINFALL-RUNOFF EXPERIMENTS ON ASPHALT

The rainfall simulator consisted of a water-filled 0.6 × 0.6 m tank punctured by metal needles arranged in a regular grid (spacing 25 mm). This was designed specifically for rainfall-runoff of studies, with the needles sized to deliver a continuous stream of discrete droplets from a tank containing deionized water, suspended on an aluminum frame at a height 1.64 m above the ground surface. This arrangement produced droplets of realistic hydrometeor size and velocity, while flow rate was controlled by a regulator valve. Water was applied at a rate of 0.82 L min^{-1} for 5 min, corresponding to a rainfall intensity of 170 mm hr^{-1}. This rate was chosen to simulate the upper end of the range seen in rainfall events in Phoenix; rain of this intensity typically falls once or twice every 6 yr (Miller *et al.*, 1973). Due to the large volumes of water required, along with the variable chemistry of monsoon rainfall, it was not considered practical to attempt to simulate natural rainfall chemistry.

All the runoff was captured using a 0.3 m^2 circle of 15 cm wide aluminum soldered to form a circular hoop. This size of 'capture area' was the largest that could be rained on effectively by the simulator; it was also such that a 5 min simulated rain storm could be generated with a practical, portable amount of applied water (5 L). Leakage from beneath the mini-watershed was minimized using a foam lining that formed a temporary seal when pressed lightly onto the asphalt surface. All the surface runoff was collected via aspiration using rubber tubing and a peristaltic pump into a 3 L pre-washed Nalgene bottle. Samples of rainfall from the simulator also were collected for analysis during each experiment and blanks of deionised water stored in sample bottles for a similar length of time also were collected and analyzed. All samples were stored on ice during transport back to the laboratory.

2.3. DESERT SOIL SURFACE RAINFALL-RUNOFF EXPERIMENTS

Similar artificial runoff experiments were performed on 12 plots in the lower part of the Sycamore Creek watershed. Both sites were on open desert slopes with minimal annual plant growth and litter accumulation. As in the parking lots, the experiments used the same mini-watersheds constructed of aluminum flashing, in this case compressed at one end to form a tear-drop-shape to funnel the runoff. A hole was drilled at the compressed ends, covered with nylon mesh and a polyethylene tube was fitted to the outside opening from which to collect the runoff, which flowed via gravity into the sample bottle. Leakage from beneath the mini-watershed was minimized using a foam lining that sealed it temporarily to the soil surface. Water was added using a garden watering can with sprinkler head, since the rainfall simulator was insufficiently portable to use at the desert sites. Runoff volumes (on average 47% of the amount applied) were recorded and subsamples collected in 60 mL acid-washed bottles, which were refrigerated prior to analysis.

2.4. SAMPLE HANDLING (SPLITTING, FILTRATION) AND LAB ANALYSES

For the parking lot samples, the total volume of each sample was measured on return to the laboratory and then split into 5 to 10 subsamples using a Teflon cone splitter to produce identical subsamples in terms of both volume and particle size distribution. Subsamples were filtered through ashed Whatman GF/F (0.7 μm pore size) filters to ensure no organic carbon contamination (Likens and Wetzel, 1991) and analyzed within 48 hr for nitrate (NO_3^--N) and soluble reactive phosphorous (SRP) on a Bran Lubbe TRAACS 800 flow injection analyzer. NH_4^+-N was analyzed colorimetrically (Solorzano, 1969) using the phenol-hypochlorite method on a Shimadzu-UV160U spectrometer. Dissolved organic carbon (DOC)

TABLE II

Storm event duration, intensity, total precipitation and estimated nutrient inputs in rainfall to the mini-urban watersheds during the storm on July 6th 1998

Site	Duration	Intensity	Total precip	Average precipitation composition[a]			
				NO_3^--N	NH_4^+-N	SRP	DOC
	mins	mm min^{-1}	mm	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
Storm event duration, intensity, total precipitation amount and composition[a]							
Light industrial	45	0.66	7.6	1.0	1.2	0.022	4.2
Commercial	52	3.96	17.0	1.1	1.3	0.047	3.7
Residential	72	6.40	6.6	1.1	1.3	0.047	3.7
Estimated contribution of nutrients input in rainfall to exports measured in storm runoff at the watershed outlets (%)							
Light industrial				119	117	8	6
Commercial				66	28	14	3
Residential				34	38	6	3

[a] Taken from average concentrations in June & July rain events from 1999 and 2000 at CAP monitoring sites (light industrial from Brooks Rd, Mesa; commercial & residential both from Central Phoenix).

was analyzed on Shimadzu TOC-5000 analyzer. Duplicate analyses were run in all cases.

2.5. WHOLE WATERSHED STORM RUNOFF SAMPLING AND ANALYSIS

Shortly after the simulation experiments, on July 6th 1998, a monsoon rain storm produced significant surface runoff from all 3 of the USGS gauged watersheds. Rainfall lasted for 45, 52 and 72 min, with total precipitation amounts of 7.6, 17.0 and 6.6 mm, at the light industrial, commercial and residential sites respectively (Table II). Samples of the resulting runoff were collected by the USGS with automatic-pumping samplers (ISCO, Inc., Model 3700) set to trigger when storm runoff began. Samples were collected in 1 L teflon-lined polyethylene bottles and combined to form a flow-weighted composite sample, then split into subsamples using a Teflon-lined churn splitter, filtered and analyzed for nitrate (NO_3^--N), ammonium (NH_4^+-N), ortho-phosphorus (corresponds closely to SRP), and DOC by the USGS National Water-Quality Laboratory.

2.6. CALCULATION OF SURFACE LOADS AND MASS BALANCES

Data from the simulated rainfall experiments were used to calculate parking lot surface nutrient loadings (*i.e.*, the amount of accumulated material available to be exported in storm runoff) during the first 5 min of an intense summer monsoon rainfall event. Because the experiments were done after the prolonged dry season, which typically occurs prior to the monsoon, these surface loadings are likely to represent maximum figures, rather than typify accumulations throughout the entire year. For each plot, the total mass of each nutrient was determined from sample volume and concentration, then divided by the area washed (0.3 m^2) to convert the concentration into a nutrient amount (loading) per m^2 of asphalt. Similarly, the mass of each nutrient in surface runoff from the desert plots was normalized to the surface area of desert surface from which the sample was taken. To calculate the available nutrient input from the entire parking lot surface ($N_{surface}$) the area covered by asphalt in the whole watershed was determined from aerial photographs and multiplied by the mean surface loadings for each nutrient. Since there were also areas of roof and pervious surfaces potentially contributing some water to the overall storm runoff at the catchment outlets, these estimates are likely to represent minimum values for inputs from surfaces in the contributing drainages.

Precipitation chemistry of the rainfall at the three monitored urban catchments was not available, so rainfall inputs (N_{precip}) were estimated using average concentrations of NO_3^--N, NH_4^+-N, SRP, and DOC for the monsoon rainfall period, collected in adjacent wet deposition collectors as part of CAP LTER routine sampling. Catchment outflows were sampled during the first natural storm runoff after the simulated rainfall-runoff experiments were carried out. Nutrient exports (N_{export}) were calculated by multiplying the total volume of storm runoff by the concentration of each constituent in the flow-weighted composite samples (Lopes *et al.*, 1995). Inputs were then compared with exports and the inferred change in nutrient storage determined as follows:

$$\Delta N_{storage} = N_{precip} + N_{surface} - N_{export} \ .$$

2.7. STATISTICAL ANALYSES

To look for differences between sites, pavement conditions, and plot types, one and two-way ANOVAs were performed on the entire data set (which was log transformed to adjust for a slight positive skew). Pairwise differences between individual sites and pavement condition categories were examined using Bonferroni multiple comparison tests.

3. Results

Asphalt runoff samples generated by the rainfall experiments were highly colored, varying from yellow-brown at the desert site to dark brown-black at the commercial, residential, and light industrial sites. Of the 4–5 L of water rained onto the plots, on average a sample volume of 2.7 L (66%) was recovered, with the remaining water having been lost via evaporation (air temperatures were typically in excess of 35 °C when the experiments were conducted) and infiltration into the asphalt. On the desert soil plots, slightly more (just over half) water was lost to infiltration and evaporation, with 47% of the added rainfall collected in runoff. Concentrations of nutrients in blank samples collected directly from the rainfall simulator were usually very low (below detection limit); where they were above this level, the average concentration in the blank were used to correct sample data collected for the particular nutrient and site concerned.

3.1. SIMULATED 'FIRST FLUSH' RUNOFF CONCENTRATIONS

Concentrations of dissolved NO_3^--N, NH_4^+-N, and DOC in runoff samples ranged widely both between plots within individual sites and across all plots, while SRP concentrations showed much less variation (Table III). Despite a slight positive skew, means were mostly very similar to medians. Inorganic N in runoff from the asphalt plots was dominated by NO_3^--N (Table III) with a NO_3^--N:NH_4^+-N ratio of 14 overall, although this varied widely between sites. Nitrate-N concentrations varied by two orders of magnitude from 1.1 to 115.9 mg L^{-1} (Table III) and were highest at the light industrial and desert parking lot sites and lowest at the residential site. Ammonium-N was a significant component of the inorganic N in runoff from the commercial and residential plots (approximately one third and two-thirds, respectively); the highest NH_4^+-N concentrations were found at the residential and commercial sites (both in the NW valley) and the lowest concentrations were obtained at the light industrial and desert sites (both in the east-central part of the valley). Inorganic N concentrations in runoff from the undeveloped desert site were much lower than from any of the urban sites, averaging 0.7 mg L^{-1} and 0.4 mg L^{-1} for NH_4^+-N and NO_3^--N, respectively.

DOC in simulated runoff showed the highest concentrations of all nutrients, ranging from 26.1 to 295.9 mg L^{-1}, with more variation within sites than between them (Table III). Mean DOC concentrations were highest at the commercial site, this being largely due to one exceptionally high value. In contrast to the other nutrients, SRP concentrations were consistently low with a maximum concentration of 1.02 mg L^{-1} and differed by a factor of only 15 across the entire data set. The variance in SRP concentrations at individual sites was much lower than for the other nutrients (Table III). SRP concentrations in desert runoff (mean of 0.19 mg L^{-1}) were similar to those from asphalt.

3.2. ESTIMATED SURFACE LOADINGS

Concentrations in the 'first flush' runoff samples from asphalt represented mean surface loadings of 151.1 mg m^{-2} for NO_3^--N, 40.2 mg m^{-2} for NH_4^+-N, 532.2 mg m^{-2} for DOC, and 1.8 mg m^{-2} for SRP (Table IV). The mean surface load for SRP in the artificially-generated runoff from desert soil surfaces at Sycamore Creek was 2.2 mg m^{-2}, with surface loads of 1.6 mg m^{-2} for NO_3^--N and 3.1 mg

TABLE III

Concentrations of dissolved nutrients in simulated storm runoff from asphalt parking lot surfaces

Site	NO_3^--N	NH_4^+-N	SRP	DOC
Mean, range and variance (in mg L^{-1})				
Box Culvert (light industrial)				
Mean	26.6	0.8	0.18	47.6
Variance	1009.9	0.2	> 0.01	146.4
Range	6.2–115.8	0.2-1.7	0.13–0.26	32.3–73.1
Peoria & 43rd Ave (commercial)				
Mean	14.2	9.6	0.30	81.2
Variance	21.9	10.2	0.08	6876.2
Range	6.3–21.0	6.5–17.0	0.14–1.02	32.8–295.9
Olive & 67th Ave (residential)				
Mean	3.4	6.7	0.13	59.1
Variance	1.1	2.7	0.00	133.3
Range	1.9–5.7	4.4–9.1	0.07–0.23	41.1–81.5
Papago Park (remnant desert)				
Mean	16.0	1.2	0.15	42.2
Variance	8.0	0.1	0.01	107.2
Range	11.6–19.8	0.6–1.8	0.09–0.39	26.1–57.4
All parking lot sites				
Mean	15.4	4.6	0.19	57.7
Variance	339.8	17.4	> 0.1	1888.3
Range	1.9–115.8	0.1–17.0	0.07–1.02	26.1–295.9
Sycamore Creek (undeveloped desert)				
Mean	0.4	0.7	0.19	n.a.

m^{-2} for NH_4^+-N. These latter two values were lower those for the asphalt parking lot surfaces by factors of 13 and 91 respectively (Table IV).

An ANOVA on asphalt surface loads (Table V) showed significant differences between the different parking lot sites for all nutrients except DOC, which was uniformly high, irrespective of site. NH_4^+-N loads differed for most pairwise site comparisons; differences in NO_3^--N loads were between the residential site and the

TABLE IV

Nutrients on surfaces calculated from simulated storm runoff

Site	NO_3^--N	NH_4^+-N	SRP	DOC
Surface loadings (in mg m^{-2})				
Box Culvert (light industrial)				
Mean	156.3	11.5	1.5	408.9
Std. error	10.9	1.2	0.4	36.2
Peoria & 43rd Ave (commercial)				
Mean	127.1	84.3	2.7	724.2
Std. error	17.3	10.2	0.9	255.7
Olive & 67th Ave (residential)				
Mean	28.7	57.1	1.1	504.1
Std. error	3.3	5.7	0.2	50.5
All parking lot sites				
Mean	151.1	40.2	1.8	532.2
Std. error	33.7	6.1	0.3	66.6
Desert sites				
Mean	1.6	3.1	2.2	n.a.

TABLE V

Differences in asphalt plot surface loadings due to site, pavement condition and plot type from one and two-way ANOVA

Dependent variable	Site	Pavement condition	Plot type	Site* pavement condition	Site* plot type	Pavement condition *plot type
Significance levels (log-transformed data, $n = 36$ samples)[§]						
$L_n NH_4^+$	$0.000^{a,b,c,d,e}$	$0.003^{C,E}$	0.806	0.041	0.153	0.380
$L_n DOC$	0.557	0.108	0.241	0.866	0.008	0.004
$L_n SRP$	0.015^{f}	0.069	0.041	0.167	0.323	0.055
$L_n NO_3^-$	$0.000^{c,e,f}$	0.057^{F}	0.998	0.332	0.229	0.182

[§] Superscripts denotes where Bonferroni multiple comparison test showed significant differences between individual pavement condition categories (^{A} poor:fair; ^{B} poor:good; ^{C} poor:excellent; ^{D} fair:good; ^{E} fair:excellent; ^{F} good:excellent) and between different sites (^{a} desert:industrial; ^{b} desert:commercial; ^{c} desert:residential; ^{d} industrial:commercial; ^{e} industrial:residential; ^{f} commercial:residential).* Denotes test for interaction.

TABLE VI

Nutrient mass balances for three urban parking lots in metropolitan Phoenix during a monsoon storm on July 6th 1998

NH_4^+- N and NO_3^-- N (mg m^{-2})

Site	NO_3-N				NH_4^+-N			
	Inputs		Export	Δ Storage	Inputs		Export	Δ Storage
	Surface runoff	Precipitation			Surface runoff	Precipitation		
Light industrial	75.3	3.0	2.6	75.8	3.3	3.7	3.2	3.8
Commercial	6.7	11.8	17.9	60.9	43.4	13.5	47.9	9.1
Residential	3.9	1.2	3.4	1.7	8.9	1.3	3.5	6.7

SRP (mg m^{-2}) and DOC (g m^{-2})

Site	SRP				DOC			
	Inputs		Export	Δ Storage	Inputs		Export	Δ Storage
	Surface runoff	Precipitation			Surface runoff	Precipitation		
Light industrial	0.7	0.1	0.9	– 0.1	182.4	12.6	226.4	– 31.4
Commercial	1.0	0.5	3.6	– 2.1	214.3	35.7	1285.7	–1000.0
Residential	0.1	0.04	0.7	– 0.5	69.4	4.2	111.1	– 27.8

Inputs from rainfall and nutrients washed off the asphalt surfaces (calculated using the data from the simulated rainfall experiments) were compared with nutrient exports in storm runoff measured at the parking lot outlets. Total storm input and export estimates are expressed per square meter of parking lot, to allow comparison between the different sites.

others; for SRP there was only a significant difference between the commercial and residential sites (Table V). These differences in asphalt surface loads of NH_4^+-N and NO_3^--N were related to pavement condition. This relationship was an inverse one; loads were highest on the poorest pavement conditions. The commercial site had the highest frequency of asphalt plots rated to be in ‘poor’ condition and these plots had particularly high NH_4^+-N loads. There also was a significant interaction between site and pavement condition for NH_4^+-N loads (Table V). SRP and DOC asphalt surface loads showed no differences according to pavement condition, although pavement condition and site together did produce a significant difference in DOC load (Table V). SRP load also differed according to whether the plot was in classified as ‘stationary’ or ‘byway’, with higher loads measured on stationary plots at all but the residential site. Other measured variables (traffic type, distance from curb and slope) did not appear to influence nutrient surface loads and these variables are not discussed further.

3.3. PARKING LOT NUTRIENT MASS BALANCES

The natural rainfall event on July 6th 1998 at the three USGS-monitored watersheds lasted from between 45 to 72 min and deposited from 6.6 to 17.0 mm of rain (Table II). Total runoff exports for the entire storm, calculated from measured flow and analyses of composite runoff samples at the parking lot outlets, were divided by the total surface area of each site to allow comparison between sites (Table VI). These exports ranged from 2.6 to 17.9 mg m^{-2} for NO_3^--N and from 3.2 to 47.9 mg m^{-2} for NH_4^+-N; measured SRP losses in storm runoff almost an order of magnitude lower at 0.7 to 3.6 mg m^{-2}, while DOC exports were over an order of magnitude higher at between 111.1 and 1285.7 mg m^{-2}.

The degree to which storm exports at the parking lot outlets corresponded with predicted inputs from the readily soluble nutrient loads on the asphalt surfaces (as determined by the simulation experiments) varied with constituent and site. When the contribution from the asphalt surfaces was estimated for the entire parking lot surface, it generally was sufficient to account for export at catchment outlets. Indeed for NO_3^--N and NH_4^+-N, rainfall inputs alone were sufficient to account for between 30 to 120% of inorganic N exiting the catchments in storm runoff (Table II) and more inorganic N appeared to be entering than was exiting. In the case of NO_3^--N at the light industrial site, predicted inputs from the asphalt surface were 43.5 times greater than exports at the outlet. Conversely for SRP and DOC the amounts predicted to be contributed by asphalt washoff and estimated rainfall inputs were similar to, or very slightly lower than, total losses from the parking lots in storm runoff. For these two nutrients, rainfall inputs accounted for only a small proportion of storm exports from the basins (6–14% in the case of SRP and 3–6% for DOC).

4. Discussion

A major aim of the study was to quantify the maximum likely amount of accumulated nutrients that could be readily dissolved and transported in the first flush conditions produced by an intense monsoon rainfall following an extended dry period. Advantages of using the rainfall simulator were that the conditions generated would correspond closely to natural rainfall:runoff conditions, while at the same time standardizing conditions for all the plots, rather than sampling natural storms where the amount of surface material solubilized and transported is partly influenced by the size (precipitation and runoff volume) of the event. In addition, natural runoff integrates sources from the whole catchment surface area, giving no information on the contribution from individual surface types and locations within the drainage area, whereas a rainfall simulator permits the investigator to determine the degree of spatial variability across the contributing area.

Our findings differ from the findings of the NURP (Sartor and Boyd, 1972; EPA, 1983) in that the amount of exportable nutrients measured on asphalt parking lot surfaces – particularly for NO_3^--N, are a good deal higher than the mean value of 4.6 mg N m^{-2} reported for street surfaces in the NURP study. One explanation of this difference is that traffic turbulence on street surfaces limits the accumulation of nutrients (specifically those in particulate form) compared to parking lots, where turbulence is likely to be a lot lower due to much slower vehicle speeds. However, our measurements do correspond closely with more recently published findings – for example the estimated loads of 120 mg m^{-2} NO_3^--N and 2 mg m^{-2} NH_4^+-N for urban surfaces in Los Angeles (Burian *et al.*, 2001) and also of 239 mg m^{-2} NO_3^--N and 41 mg m^{-2} NH_4^+-N for French highway surfaces (Pagotto *et al.*, 2000). Conversely for phosphorus, our mean parking lot loading of 1.8 mg m^{-2} is an order of magnitude lower than the mean for city streets nationwide of 19.1 mg P m^{-2} reported by NURP (Sartor and Boyd, 1972). Moreover we found SRP surface loads to be consistently low, showing little within-site variation. DOC concentrations and loadings (not measured during NURP) were high, with an average concentration of 57.7 mg L^{-1} in experiment runoff across all the asphalt sites, compared to typical concentrations in treated wastewater in the region (e.g., 17 mg L^{-1} found by Westerhoff and Pinney, 2000).

4.1. SITE FACTORS RELATED TO NUTRIENT LOADS ON ASPHALT SURFACES

Previous work has shown that the quantity of contaminant material on city street surfaces varies widely and depends principally on surrounding land use, duration since last rainfall or street-cleaning, and street surface type and condition (Sartor and Boyd, 1972). In our study, we only found a direct relationship between nutrient loads on asphalt surfaces and pavement condition in the case of NH_4^+-N. There was no clear relationship between asphalt surface loadings of NO_3^--N, SRP, DOC and pavement condition, although there was sometimes an interactive effect of site and pavement condition combined. Because we had only one site for each dominant surrounding land use type, it was not possible to discern a clear land use effect, but our data do at least indicate that location is a factor.

4.2. SOURCES OF ENHANCED NUTRIENT LOADS ON PARKING LOT SURFACES

Runoff from asphalt at urban sites contained considerably higher soluble inorganic N loads than from natural desert soil surfaces – by a factor of 91 for NO_3^--N and 13 for NH_4^+-N. There are a number of potential sources for elevated levels of leachable inorganic N species in the urban environment, of which the primary one is atmospheric. Deposition rates of oxidized N species to soil and artificial urban surfaces when dry are similar (Grossman-Clarke *et al.*, submitted) and are likely to be low after an extended dry period (Steinberger and Sarig, 1993; Vishnevetsky and Steinberger, 1997), so the low values in soil are unlikely to reflect recent depletion due to plant or microbial uptake in the desert soils. It is more likely that our findings result from enhanced atmospheric N deposition and accumulation rates on the urban asphalt surfaces.

Atmospheric N deposition (particularly dryfall) is significantly enhanced in and around urban areas such as Phoenix (Russell *et al.*, 1993; Bytnerowitz and Fenn, 1996; Lovett *et al.*, 2000; Baker *et al.*, 2001; Grossman-Clarke *et al.*, submitted) due to elevated ambient air concentrations of fine particulate and gaseous nitrogen oxides from fossil fuel combustion (especially vehicle exhausts), as well as emissions from irrigated croplands and landscapes, manure, and wastewater treatment operations (Dignon and Hameed, 1989; Goulding *et al.*, 1998; Baker *et al.*, 2001). While inert urban surfaces have low deposition velocities for many N species relative to vegetation surfaces and open water (Sehmel, 1980), during prolonged periods between rainfall events, significant accumulation may occur on these surfaces. Additional sources of inorganic N to the parking lot surface are from people spilling liquids, animals urinating, and drift of fertilizer applied to landscape areas adjacent to the asphalt surfaces.

The predominance of inorganic N as NO_3^- rather than NH_4^+ on parking lot surfaces (ratio 14:1 overall, but varied significantly between sites) is likely to reflect the relative stability of those compounds and the proximity of the individual parking lot study sites to sources of NH_3 versus NO_x derivatives. Nitric acid and other nitrates are terminal compounds that are relatively long-lived, so deposition can occur over large areas, some distance from source (Singh, 1987). In this study NO_3^--N was dominant at the light industrial and desert sites, located in the central part of the urban area known to be under the plume of pollutants that develops each day (Fernando *et al.*, 2001). In the case of NH_4^+-N, the highest loadings and worst pavement condition were both at the industrial and commercial parking lots, located in the same general (NW) part of the metropolitan area. Ammonia is very reactive with a much shorter atmospheric lifetime and would therefore be expected to show high concentrations near sources, decreasing rapidly with distance from those sources (Asman *et al.*, 1998). We found NH_4^+-N to be highest at the commercial and residential sites, both located in the NW of Phoenix-Glendale (Figure 1) closer to agricultural areas which are likely to emit NH_3 (Baker *et al.*, 2001).

In contrast to inorganic N, phosphate loads did not differ much between the parking lot and desert soil plots. Mean SRP loads were 2.2 mg m^{-2} in the desert compared to 1.8 mg m^{-2} urban plots. Phosphate concentrations in desert soils of the region are typically not limiting to plant growth, as phosphate is readily derived from weathering of P-containing minerals in bedrock. In urban environments, many urban building materials, including asphalt, have moderately high SRP contents; another major source of dry deposition in urban areas such as Phoenix is soil-derived dust (Kleeman and Cass, 1998; ADEQ, 1999; Artaxo *et al.*, 1999). The finding that SRP loads tended to be higher on asphalt plots classified as ‘stationary’ rather than ‘byways’ supports the importance of soil-derived dust that is likely to accumulate more on less disturbed surfaces. Overall we conclude that urbanization appears to have little effect on SRP accumulations to terrestrial surfaces in arid systems such as this.

The DOC loadings on the parking lot surfaces could represent a significant impact to recipient systems from storm runoff. This DOC has three likely major sources – leakage from vehicles (e.g., dripping oil, gasoline, and other hydrocarbon fluids; Lopes *et al.*, 2000), leaching of surface particulates derived from the breakdown of the asphalt surface itself (Sartor and Boyd, 1972; EPA, 1983), and atmospheric deposition (Lovett *et al.*, 2000).

4.3. NUTRIENT MASS BALANCES FOR PARKING LOT WATERSHEDS

From the urban mini-watershed mass balance calculations for the July 6th storm event we found that measured NO_3^--N and NH_4^+-N exports in storm runoff at the parking lot 'catchment' outlets tended to exceed estimated inputs in rainfall and soluble surface nutrient accumulations combined. Indeed at the commercial and light industrial sites, only 27 and 3%, respectively, of the potential surface-accumulated NO_3^--N appeared to be exported, while only 40% of the estimated surface NH_4^+-N loading was exported from the residential site. There are a number of possible explanations for this. We may have overestimated the total amount of NO_3^--N on the asphalt surface due to the high spatial variation from plot to plot at the light industrial site. However, in the case of DOC at the commercial site, where the variance of the DOC data from plot to plot is also very high, measured exports were far greater than estimated inputs to the whole parking lot. Because the difference is in the opposite direction to that observed for NO_3^--N, we suggest that the data are representative of a real difference and not solely a result of errors involved in estimating the total surface nutrient amounts on the study sites. Another possible explanation is that we only simulated the first flush of runoff, which may represent a relatively small proportion of the total storm runoff load (e.g., Deletic, 1998). However, limited data from an ancilliary experiment where the same asphalt plot was rewashed repeatedly five times indicate that the majority of soluble material (on average 70%) is lost in the first 5 min of washing. A recent modeling study by Burian *et al.* (2001) suggested that only a small percentage of the NO_3^--N (1.5%) and NH_4^+-N (1.3%) dry deposited onto an urban catchment in Los Angeles, California was actually discharged in runoff, indicating that there may be other processes that act to remove or store atmospherically deposited inorganic N before it can be transported from the catchment.

Given the above evidence, along with the fact that the contribution of nutrients in runoff from other impervious surfaces (e.g., roofs) was not measured, we conclude it likely that N is accumulated on these parking lot catchments converted to another form or was lost from the catchment by another route (volatilization, denitrification, or microbial uptake). We suggest that significant retention and/or transformation of NO_3^--N and NH_4^+-N must occur either on the parking lot surface or at sites along the flowpath to the catchment outlet. The latter explanation seems to be supported by the fact that the difference in input:output was largest at the light industrial site, the only watershed which included a number of grassy swales through which much of the urban runoff is channeled prior to reaching the outlet.

For SRP differences in the estimated input:output balances for the study catchments are small. Hence, while there may be additional sources of this nutrient in the watersheds (e.g., from other impervious surfaces not measured, such as roofs), they are probably not that significant. For DOC, the mismatches may be due, at least in part, to the extremely patchy distribution of oil and grease deposits on the parking lots, causing the amount of DOC available for export to have been significantly underestimated by the simulation experiments.

Finally, we very much consider the work reported here to form a useful precursor study to further work. Future expansion of the approach outlined here could usefully include: i) simulations of natural rainfall chemistry from the simulator, to test the effect of this on surface wash off chemistry; ii) repeatedly washing off the same section of parking lot until the surface load is exhausted, to enable a 'wash off' function to be computed for the various ions; iii) measure a wider suite of nutrients and other urban contaminants, e.g. total N and organic N, heavy metals, and polyaromatic hydrocarbons; iv) repeat the study on a more widespread basis with more replicate plots, in order to investigate the effect of variables such as different land use types, distance from strong sources of NO_x emissions, e.g. major roadways and from the urban center, as well as studying the variation in N and DOC across individual parking lots and other impervious urban surfaces in more detail.

5. Conclusions

Nitrogen continues to be ubiquitous and poorly controlled, largely due to numerous non-point sources (Smith *et al.*, 1994; Howarth *et al.*, 1996; Vitousek *et al.*, 1997). Atmospheric deposition may constitute a significant input of macronutrients in urban environments (Russell *et al.*, 1993; Lovett *et al.*, 2000; Smith *et al.*, 2000). A recently completed mass balance of N for Phoenix found that NO_x emissions from fossil fuel combustion may contribute around 30% of the total annual N inputs to the ecosystem (Baker *et al.*, 2001). Russell *et al.* (1993) estimated that in the Los Angeles basin, 52% of NO_x emissions and 53% of NH_3 emissions were deposited within the modeled airshed. The methodology used in this study allowed examination of point-to-point variability of the type of area, which in previous work has been treated as a uniform non-point source. The results show that impervious urban surfaces can constitute important sources of nutrients in urban storm runoff, but that the amount of such material exported can vary significantly for different nutrients and with the characteristics of the urban catchment area. Input-output budgets for an actual rain event show that much of the available load on a parking lot surface does not appear to reach surface waters during floods. In contrast, for SRP and especially DOC, parking lot surfaces would appear to be significant source areas, the readily leachable loadings on asphalt accounting for the majority of the runoff export measured during a storm event.

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