

Nutrient transformations between rainfall and stormwater runoff in an urbanized coastal environment: Sarasota Bay, Florida

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Abstract

To determine the relative importance of atmospheric deposition and stormwater runoff as nitrogen sources to Sarasota Bay, Florida, we examined dissolved inorganic nitrogen (DIN) concentrations and $\delta^{15}\text{N}$ compositions of rainwater and stormwater runoff. Rainwater collected in Sarasota, Florida, had ammonium concentrations of 2.1–29.0 $\mu\text{mol L}^{-1}$ in the summers of 1999 and 2000. Corresponding rainwater nitrate concentrations were 3.7–56.0 $\mu\text{mol L}^{-1}$. Rainwater ammonium $\delta^{15}\text{N}$ values were -11.6‰ to -0.3‰ , and nitrate $\delta^{15}\text{N}$ values were -5.1 to $+3.8$ over the 2-yr period. Decreases on the order of 50% in ammonium concentration and $\delta^{15}\text{N}$ enrichments as great as $+24\text{‰}$ relative to rainwater ammonium were typically observed in the evolution of rainwater into stormwater. Stormwater $\delta^{15}\text{NH}_4$ values were $+7$ to $+18$ ‰. Nitrate (NO_3) concentrations were typically elevated in stormwater relative to rainwater, although this trend was not statistically significant, and $\delta^{15}\text{N}$ values were generally slightly enriched in stormwater. Rainfall phosphate (PO_4) concentrations were always low (<2.1 $\mu\text{mol L}^{-1}$), whereas stormwater consistently had elevated PO_4 concentrations (up to 13.8 $\mu\text{mol L}^{-1}$). ^{15}N -enriched N in the environment has generally been interpreted as an anthropogenic signal (wastewater and agricultural runoff). Our results will require the broadening of that interpretation to include stormwater DIN.

Urban sprawl has become an increasingly important global issue. The past century has seen a dramatic urbanization of the landscape. Between 1990 and 2015, the number of cities with a population of >1 million people is expected to increase from 118 to 272, and the number of megacities (population >10 million) is expected to increase from 14 to 27 (Walsh 2000). This increase in major population centers will have a large impact on the Earth's surface, particularly challenging water resource managers and aquatic scientists as they try to identify and mitigate increasing pollutant loads to receiving waters.

Elevated water-column nitrogen concentrations and enriched $\delta^{15}\text{N}$ compositions of dissolved inorganic nitrogen (DIN) and primary producers are often associated with wastewater and agricultural nitrogen loading to an ecosystem (Fry et al. 2003). The elevated $\delta^{15}\text{N}$ signature of wastewater results from coupled nitrification and denitrification processes that are often used in the process of sewage treatment. Both nitrification and denitrification involve a high degree of isotopic fractionation by different bacteria, in which the

lighter nitrogen isotope reacts more rapidly (Mariotti et al. 1981). Nitrification is an aerobic microbial process in which NH_4 is oxidized to NO_3 . The isotopically lighter $^{14}\text{NH}_4$ is preferentially utilized leading to ^{15}N enrichment of the residual NH_4 pool. Similarly, denitrification, a process in which bacteria utilize NO_3 as an electron donor instead of oxygen, preferentially utilizes the lighter $^{14}\text{NO}_3$, leading to ^{15}N enrichment of the remaining NO_3 . Denitrification has traditionally been thought to be an exclusively anaerobic process; however, recent evidence suggests that aerobic denitrification may occur in the natural environment (Patureau et al. 2000). Products of these microbially mediated reactions are by contrast isotopically lighter than the DIN substrate utilized. Cold temperatures can limit both processes by limiting microbial activity (McKenney et al. 1984; Jorden et al. 1997).

Although often closely associated, elevated $\delta^{15}\text{N}$ values are not unique to anthropogenically affected waters. Nitrification and denitrification can elevate the $\delta^{15}\text{N}$ of nitrogenous compounds in ecosystems affected by any nitrogen source, be it natural or anthropogenic (Mariotti et al. 1981; Fry et al. 2003). Generally, excess inputs of N to a system will result in greater N "leakiness" in the form of denitrification and subsequent ^{15}N enrichment (Fry et al. 2003). For example, Fry et al. (2003) observed enriched ^{15}N values at a site with high deposition of seagrass wracks, which they hypothesized subsequently decomposed in a natural microbial analogue of a sewage treatment process, exporting nutrients with enriched ^{15}N values. Similarly, fertilizer application can lead to excess N and subsequent ^{15}N enrichment caused by nitrification/denitrification processes that drive up the $\delta^{15}\text{N}$ composition of residual NH_4 and NO_3 , even though the fertilizer has an initial $\delta^{15}\text{N}$ composition of $\sim 0\text{‰}$. Volatilization of ammonia (NH_3) due to abiotic factors such as elevated temperatures can also lead to isotopic enrichment of the remaining $\text{NH}_4 + \text{NH}_3$ pool—the lighter $^{14}\text{NH}_3$ is preferentially

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volatilized more rapidly than $^{15}\text{NH}_3$ because of its lighter mass (Heaton 1986; McClelland and Valiela 1998).

The increase in impervious surface cover caused by rapid urbanization has recently brought attention to stormwater runoff as a source of contaminants to receiving waters. Stormwater can be a source of pathogenic bacterial contamination (Schiff and Kinney 2001) and various pollutants such as organics, metals (Pitt et al. 1995; Foster et al. 2000), suspended solids, phosphorus, and nitrogen (Chui 1997; Graves et al. 1998; Brezonik and Stadelmann 2002). Many studies have characterized DIN concentrations and the nitrogen isotopic composition of rainfall (Paerl and Fogel 1994; Russell et al. 1998). To our knowledge, no studies to date have directly compared the concentrations of nutrients (ammonium, nitrate, and phosphate) and $\delta^{15}\text{N}$ values of DIN in rainwater and stormwater.

This study was a portion of a broader study investigating nitrogen sources and sinks for Sarasota Bay, Florida. Our objectives were to investigate the two N sources that are believed to be the largest: rainfall and subsequent stormwater runoff. The Sarasota Bay National Estuary Program estimates that direct rainfall provides 27% of the nitrogen to the Bay, whereas stormwater runoff delivers 45% of the total nitrogen. The remaining nitrogen sources are thought to be municipal wastewater treatment plants (20%) and groundwater (8%). To investigate the two largest sources, we collected rainfall samples during the summers of 1999 and 2000 and coincident stormwater samples during 2000. These samples were analyzed for nutrient concentrations and DI^{15}N signatures.

With the exception of Whitaker Bayou, which receives advanced treated wastewater from an outfall, stormwater drainage systems in Sarasota are separated from the sewage systems. The drainage systems are designed with an emergency bypass system that allows wastewater to overflow into the stormwater drainage system during intense storm events. Records of these overflows are kept by the city of Sarasota. During our study period, there were no overflows in our study area (D. Taylor pers. commun.). Only one overflow occurred during this entire period, and it was at a lift station on the north end of Siesta Key during Hurricane Gordon (16 September 2000). This lift station is across the Bay from our stormwater sampling locations and therefore would have had no effect on our results.

Methods

Thirty-one storm events were sampled from 18 May to 10 September 1999. Rainwater samples were collected on Lido Key (Fig. 1), a barrier island several kilometers west of the city of Sarasota, Florida, with a mechanical rain collector that opens during rain events, collecting rain in an acid-washed (10% HCl) 25-cm-diameter polyethylene bucket. After each event, acid-washed sample bottles were rinsed with rainwater three times and then filled and frozen. Rapid and/or small rain events were not usually sampled. When small storm events were not sampled, the sample collection bucket was emptied and acid washed before the next sample collection. Comparisons with rain data collected by the Atmo-

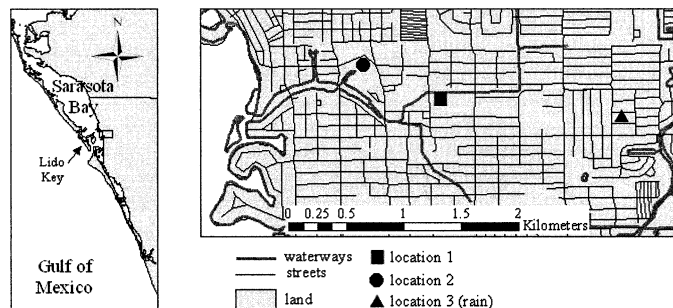


Fig. 1. Map of Sarasota Bay and sampling locations. Rainwater samples from 1999 were collected from south Lido Key. Location 1 is the residential stormwater site, location 2 is the urbanized/commercialized stormwater site, and location 3 is the rain sampling station.

spheric Integrated Research Monitoring Network (AIRMoN) from the same site showed that 29 of 31 samples were collected from rain events that deposited >500 ml (>1 cm rainfall) into an adjacent, identical AIRMoN mechanical rain collector.

Nine storm events were sampled between 15 July and 24 September 2000 in Sarasota, ~ 4 km to the east of central Sarasota Bay (Fig. 1). At this site (referred to as location 3), rainwater samples were again collected with a mechanical rain collector. Acid-washed sample bottles were rinsed with rainwater three times and then filled and frozen. Coincident with each rain event, duplicate stormwater samples were collected in acid-washed Nalgene bottles directly from stormwater drainage pipes at two different locations. Location 1 represents stormwater drainage from a suburban residential area and location 2 was a more commercialized urban area. The samples were filtered through combusted glass-fiber filters within 30 min after collection, poured into clean Nalgene bottles, and then frozen until analysis. Except for the 31 July 2000 rain sample, which had a volume of 0.5 liter (1 cm rainfall), all rain samples for 2000 had volumes >1 liter (>2 cm rainfall). When small storm events were not sampled, the sample collection bucket was emptied and acid washed before the next sample collection.

Ammonium (NH_4) was measured colorimetrically with a modification of the phenol-hypochlorite method described by Bower and Holm-Hansen (1980). The lower limit of detection for NH_4 was $0.5 \mu\text{mol L}^{-1}$. Nitrate + nitrite ($\text{NO}_3 + \text{NO}_2$) was measured with a chemiluminescence detector (Braman and Hendrix 1989) after being reduced to nitric oxide in an acidic medium that contained vanadium (III) at $80\text{--}90^\circ\text{C}$. Nitrite (NO_2) concentrations were determined colorimetrically as described by Strickland and Parsons (1972). Nitrate (NO_3) concentrations were then determined by the difference. The lower limits of detection for NO_2 and NO_3 were 0.1 and $0.5 \mu\text{mol L}^{-1}$. Soluble reactive phosphate (PO_4) was determined colorimetrically as described by Strickland and Parsons (1972). The lower limit of detection for PO_4 was $0.5 \mu\text{mol L}^{-1}$. The extraction of NH_4 for isotopic analysis was done using the ammonium diffusion method described by Holmes et al. (1998). NO_3 for isotopic analysis was extracted from each sample with a modified diffusion method described by Sigman et al. (1997). Extraction effi-

Table 1. Rainwater NH_4 and NO_3 concentrations and $\delta^{15}\text{N}$ values for samples collected during the summer of 1999 on Lido Key, Sarasota, Florida. Measurements and SDs in ^{15}N results represent six comparisons against a working laboratory standard.

Sample date	NH_4 concentration ($\mu\text{mol L}^{-1}$)	Extraction Eff(%)	$\delta^{15}\text{NH}_4$ (‰)	SD	NO_3 concentration ($\mu\text{mol L}^{-1}$)	Extraction eff(%)	$\delta^{15}\text{NO}_3$ (‰)	SD	AIRMoN* volume (ml)
18 Apr 99	16.2	98	1.19	0.09	47.2	96	3.79	0.17	500
31 May 99	34	95	-2.91	0.02	45.2	92	2.83	0.04	385
03 Jun 99	14.7	99	-6.85	0.05	19.1	112	0.11	0.09	669
06 Jun 99	29	102	-7.89	0.03	56	105	0.88	0.04	730
08 Jun 99	8.8	101	-3.13	0.05	10.3	82	0.31	0.12	560
10 Jun 99	4.8	103	-9.63	0.17	8.6	106	-1.04	0.06	639
14 Jun 99	7	111	-5.2	0.14	19.7	104	1.72	0.04	948
18 Jun 99	2.7	108	-4.41	0.3	4.2	139	-3.52	0.25	1502
20 Jun 99	8.1	108	-4.15	0.07	10	96	-3.56	0.06	1370
21 Jun 99	4.5	105	-10.5	0.08	6.7	94	0.19	0.08	933
22 Jun 99	4.4	109	-7.76	0.14	5.6		NA		210
01 Jul 99	2.9	111	-0.34	0.25	3.7	105	0.16	0.12	3255
02 Jul 99	5.3	105	-5.26	0.05	8.6	192	0.46	0.02	1903
03 Jul 99	6.6	102	-2.7	0.11	6.9	207	-2.21	0.06	1434
04 Jul 99	4.3	96	-7.15	0.09	4.6	128	0.17	0.35	3638
05 Jul 99	4.1	106	-6.43	0.13	13.2	83	0.1	0.06	1019
14 Jul 99	12.2	108	-5.06	0.02	37.9	109	3.27	0.01	3571
15 Jul 99	7.4	102	-5.14	0.1	30	104	2.52	0.01	795
16 Jul 99	9.5	107	-5.6	0.06	13	105	-1.09	0.08	1447
18 Jul 99	6.7	108	-5.41	0.07	6.8	108	-0.66	0.12	1589
31 Jul 99	10.5	103	-4.96	0.02	25	107	0.7	0.01	2002
05 Aug 99	9.5	100	-4.03	0.09	15.7	101	NA		1289
06 Aug 99	10.1	107	-5.08	0.03	10.4	101	-1.54	0.04	813
07 Aug 99	2.3	108	-2.8	0.03	6	101	-0.96	0.03	2772
10 Aug 99	2.2	112	-3.98	0.06	8.2	101	0.84	0.09	3049
12 Aug 99	7.4	104	-3.56	0.02	15.5	111	-0.57	0.02	1619
13 Aug 99	10	105	-2.71	0.06	12.6	111	-1.23	0.03	1741
23 Aug 99	2.1	113	-1.52	0.06	3.9	98	2.25	0.06	6207
01 Sep 99	26.9	114	-7.61	0.02	34.1	100	0.19	0.02	876
08 Sep 99	2.9	100	-7.17	0.05	17.7	84	1.58	0.09	982
10 Sep 99	17	98	-3	0.03	21.9	100	0.11	0.03	1189
Average	9.8		-4.94		17		0.2		1601
SD	7.94		2.38		14		1.78		1262

NA = Sample data not available because of error during analysis.

* Total volume collected in adjacent identical AIRMoN rain collectors.

ciencies were calculated as the amount estimated from the pressure manometer on the final sample trap of the vacuum line divided by the amount expected based on sample concentrations.

Results and Discussion

The 31 rainwater samples from 1999 had NH_4 concentrations that were 2.1–34.0 $\mu\text{mol L}^{-1}$ (Table 1), with an average concentration of $9.5 \pm 7.9 \mu\text{mol L}^{-1}$ (all variances given as +SD). Independently measured NH_4 samples from an AIRMoN rain collector located next to the rain collector used in this study yielded identical results (slope = 1.00; $r^2 = 0.97$). The $\delta^{15}\text{N}$ value of these NH_4 samples was -10.5‰ to -0.3‰ , with an average value of $-4.9\text{‰} \pm 2.4\text{‰}$ (Table 1). Rainwater NO_3 concentrations from these same rain events (Table 1) were 2.7–66.4 $\mu\text{mol L}^{-1}$ (average = $17.0 \pm 14.0 \mu\text{mol L}^{-1}$), with $\delta^{15}\text{N}$ values ranging from -3.6‰ to $+3.8\text{‰}$ (average = $+0.2\text{‰} \pm 1.8\text{‰}$). Nitrate concentrations were very similar to those measured from the adjacent

AIRMoN rain collector (slope = 0.95; $r^2 = 0.97$). Rainwater collected the same summer at the Gandy Bridge in Tampa, Florida, ~ 100 km north of our site, and analyzed at S. Maccko's lab at the University of Virginia had very similar average $\delta^{15}\text{NH}_4$ and $\delta^{15}\text{NO}_3$ values— -5.7‰ and -0.6‰ , respectively (Earls 2001).

The nine rainwater DIN samples from the summer of 2000 (Table 2) had similar concentrations and $\delta^{15}\text{N}$ signatures as those measured in 1999. Rainwater NH_4 concentrations were 3.1–26.1 $\mu\text{mol L}^{-1}$ (average $[\text{NH}_4] = 11.0 \pm 9.6 \mu\text{mol L}^{-1}$), and the $\delta^{15}\text{NH}_4$ values were $-11.6\text{‰} \pm 0.3\text{‰}$ to $-1.9\text{‰} \pm 0.1\text{‰}$ (average $\delta^{15}\text{NH}_4 = -7.2\text{‰} \pm 2.0\text{‰}$). Stormwater ammonium concentrations were generally lower than those in rainwater (Table 2, Fig. 2a), but the differences were not statistically significant at the 95% confidence level. The three exceptions to this trend (24 Jul, 12 Aug, and 17 Sep) had relatively low rainwater NH_4 concentrations ($< 4.2 \mu\text{mol L}^{-1}$). Rainwater NH_4 concentrations were statistically greater ($p < 0.05$) than the stormwater samples if these three rain events are removed from the data set. These three storms

Table 2. Rainwater (location 3) and stormwater (locations 1 and 2) NH_4 and NO_3 concentrations and $\delta^{15}\text{N}$ values for samples during the summer of 2000. Measurements and SDs in ^{15}N results represent six comparisons against a working laboratory standard.

Date	Storm direction	Location	NH_4 concentration ($\mu\text{mol L}^{-1}$)	$\delta^{15}\text{NH}_4$ ‰	SD	NO_3 concentration ($\mu\text{mol L}^{-1}$)	$\delta^{15}\text{NO}_3$ ‰	SD
15 Jul 00	NW	3	7.81	-4.63	0.10	12.67	-5.08	0.08
		1	4.74	7.52	0.06	30.84	-5.02	0.02
		1	4.53	7.35	0.13	30.13	-5.12	0.02
		2	7.51	6.76	0.03	19.73	-2.35	0.04
		2	6.39	7.25	0.16	16.93	-2.20	0.11
24 Jul 00	SW	3	4.21	-7.05	0.04	13.49	-1.13	0.07
		1	3.16	10.64	0.12	18.33	2.16	0.01
		1	2.38	10.04	0.12	15.94	0.55	0.04
		2	5.17	12.07	0.04	32.11	2.47	0.03
		2	5.19	11.47	0.09	32.51	2.12	0.02
31 Jul 00	SE	3	8.87	-8.40	0.16	35.43	-4.12	0.04
		1	1.83	8.58	0.65	14.43	4.15	0.04
		1	1.49	8.43	0.07	14.53	4.03	0.09
		2	2.69	17.82	0.10	33.68	2.24	0.02
		2	2.60	18.13	0.19	33.50	1.07	0.04
02 Aug 00	SE	3	3.08	-9.45	0.12	12.63	-3.88	0.08
		1	0.85	5.32	0.11	10.59	3.57	0.05
		1	1.08	6.41	0.09	9.54	0.25	0.12
		2	2.67	8.83	0.01	13.93	-2.16	0.07
		2	2.63	7.85	0.12	13.80	NA	
09 Aug 00	SE	3	17.90	-11.56	0.03	30.81	-0.96	0.03
		1	10.67	11.53	0.05	47.68	0.26	0.01
		1	10.61	11.53	0.09	47.75	NA	
		2	8.58	11.03	0.06	47.52	0.32	0.05
		2	9.05	10.68	0.18	47.32	-1.85	0.02
12 Aug 00	NW	3	2.16	-6.01	0.10	5.29	-2.15	0.18
		1	4.33	10.71	0.03	6.90	-0.32	0.14
		1	4.28	10.60	0.08	7.03	-2.86	0.10
		2	2.92	8.33	0.09	7.75	1.79	0.12
		2	2.93	8.11	0.16	7.85	2.55	0.05
24 Aug 00	E	3	25.31	-6.83	0.02	44.67	-1.26	0.02
		1	8.79	11.67	0.07	49.40	-0.40	0.03
		1	8.19	11.87	0.08	48.91	-1.27	0.03
		2	14.12	12.65	0.02	53.83	-1.93	0.02
		2	13.80	12.72	0.03	52.17	-2.85	0.02
17 Sep 00	SW	3	3.43	-1.89	0.13	3.44	-3.69	0.22
		1	5.80	11.84	0.04	8.96	-0.40	0.07
		1	5.79	11.33	0.09	8.88	0.33	0.02
		2	4.99	9.80	0.13	7.09	1.46	0.12
		2	4.50	9.60	0.13	7.23	0.55	0.21
24 Sep 00	NE	3	26.10	-9.22	0.01	64.77	-2.62	0.03
		1	7.52	14.54	0.10	40.44	0.54	0.01
		1	7.14	15.38	0.07	40.78	1.21	0.04
		2	5.05	13.91	0.15	55.50	-1.18	0.02
		2	4.69	15.30	0.09	52.89	-1.15	0.03

NA = sample data not available because of error during analysis.

originated to the west of Sarasota in the Gulf of Mexico and were likely increasing in NH_4 content as they moved near and over land; large atmospheric NH_4 sources are usually associated with agriculture and livestock farming (Aherne and Farrell 2002). There were no statistical differences in stormwater NH_4 concentrations between the two types of drainage areas (urban commercialized vs. residential).

Stormwater $\delta^{15}\text{NH}_4$ values were significantly enriched ($p < 0.001$) relative to the rainwater $\delta^{15}\text{NH}_4$ values (Table 2, Fig. 2b), ranging from $+7.0\text{‰} \pm 0.4\text{‰}$ to as high as

$+18.0\text{‰} \pm 0.2\text{‰}$. This is within the isotopic range often associated with wastewater nitrogen ($\delta^{15}\text{N} = +10\text{--}25\text{‰}$; Cifuentes et al. 1988; Desimone and Howes 1996; McClelland and Valiela 1998). Enrichment of ^{15}N between rainfall NH_4 and corresponding stormwater NH_4 was between $+12\text{‰}$ and $+24\text{‰}$ in all cases, even when stormwater NH_4 concentrations were greater than that of the rainwater. No statistical differences were observed in the $\delta^{15}\text{NH}_4$ values between the residential and commercial stormwater sampling locations.

Extraction efficiencies for the nine rainwater $^{15}\text{NH}_4$ sam-

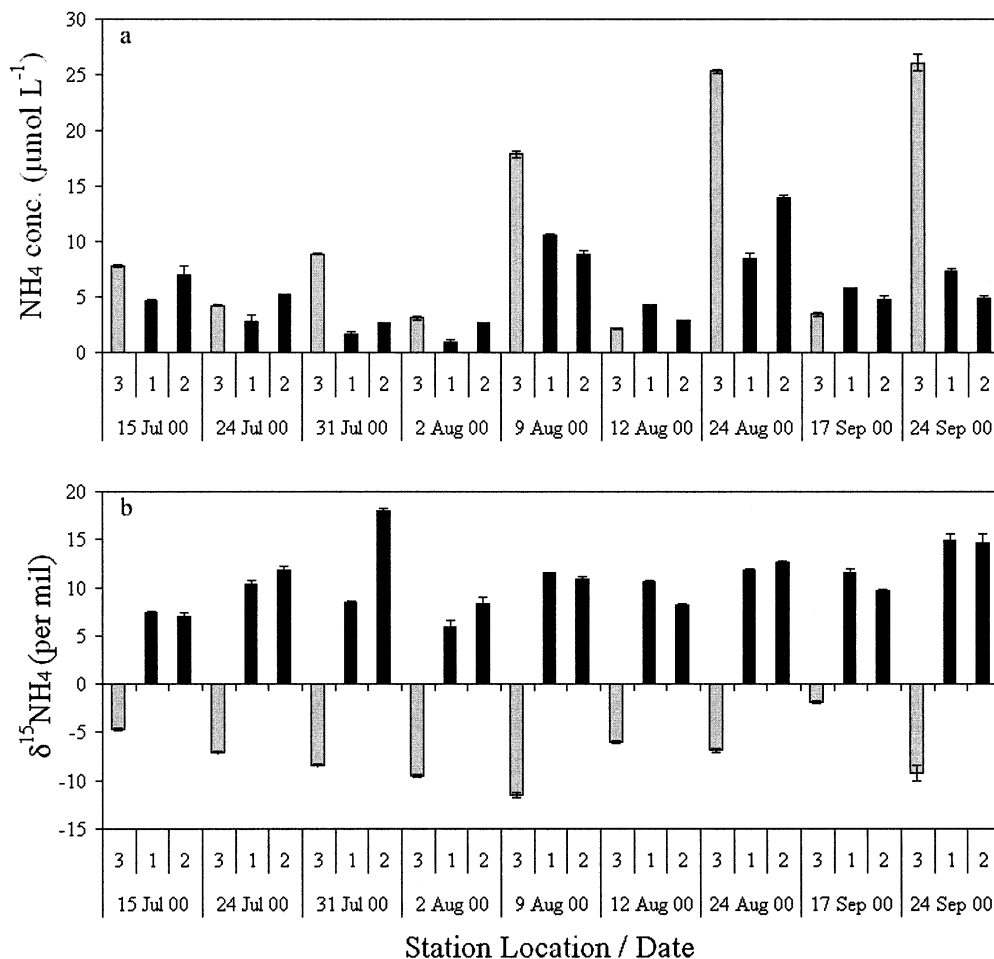


Fig. 2. (a) NH_4 concentrations and (b) $\delta^{15}\text{NH}_4$ values for rainwater and stormwater collected during the summer of 2000. The gray bar in each set is the rainwater (location 3), and the two black bars are stormwater samples (locations 1 and 2). Error bars for the rain samples are either half the range for duplicate analysis of a single NH_4 sample or the SD of six comparisons on the mass spectrometer. For stormwater samples, error bars are half the range for duplicate samples collected at each stormwater sampling location.

ples collected in 2000 were 84–119% (Table 2). In 1999, rainwater ammonium-sample extraction efficiency was 96–114%. $^{15}\text{NH}_4$ standards had similar extraction efficiencies (84–107%). However, $^{15}\text{NH}_4$ extraction efficiencies for some stormwater samples were $\gg 100\%$ (Dillon 2003). The high extraction efficiencies may be due to some negative interference with the colorimetric method used to detect NH_4 in stormwater samples or to labile dissolved organic nitrogen (DON), which may have been converted to NH_4 at the high pHs required for the isotopic extraction procedure. Such labile DON would likely serve as a bioavailable N source in addition to any NH_4 present. Additionally, some DON may have been entrained into the stormwater as it flowed over impervious surfaces. More work should be conducted to investigate this additional DON and the N transformations that occur in the evolution of rainwater into stormwater.

Rainwater NO_3 concentrations were 3.4–64.8 $\mu\text{mol L}^{-1}$ (average $[\text{NO}_3] = 24.8 \pm 20.6 \mu\text{mol L}^{-1}$). Stormwater NO_3 concentrations were higher than those of the rainwater from

the same storm event for six of the nine rain events sampled (Fig. 3a), although the differences were not statistically significant. There were no significant differences in stormwater nitrate concentrations between the two types of drainage areas (residential vs. commercialized urban). The NO_3 stable isotope ratios for rainwater were between $-5.1\text{‰} \pm 0.1\text{‰}$ and $-0.8\text{‰} \pm 0.1\text{‰}$ (average $\delta^{15}\text{NO}_3 = -2.7\text{‰} \pm 1.5\text{‰}$). Stable nitrogen isotope ratios for stormwater NO_3 were significantly enriched ($p < 0.001$) in ^{15}N relative to the rainwater nitrate from the same storm event (Fig. 3b) and showed a broader range of values ($-5.1\text{‰} \pm 0.1\text{‰}$ to $+4.1\text{‰} \pm 0.1\text{‰}$) than the rainwater samples. The average $\delta^{15}\text{NO}_3$ value for stormwater was $0.0\text{‰} \pm 2.2\text{‰}$. No significant differences were observed in the $\delta^{15}\text{NO}_3$ values between the two stormwater sampling locations.

Extraction efficiencies for $^{15}\text{NO}_3$ samples were 82–117%, with the exception of two samples. One stormwater sample from location 2 on 8 August 2000 had a low recovery (51%) and showed a depletion of 2.2‰ compared with the dupli-

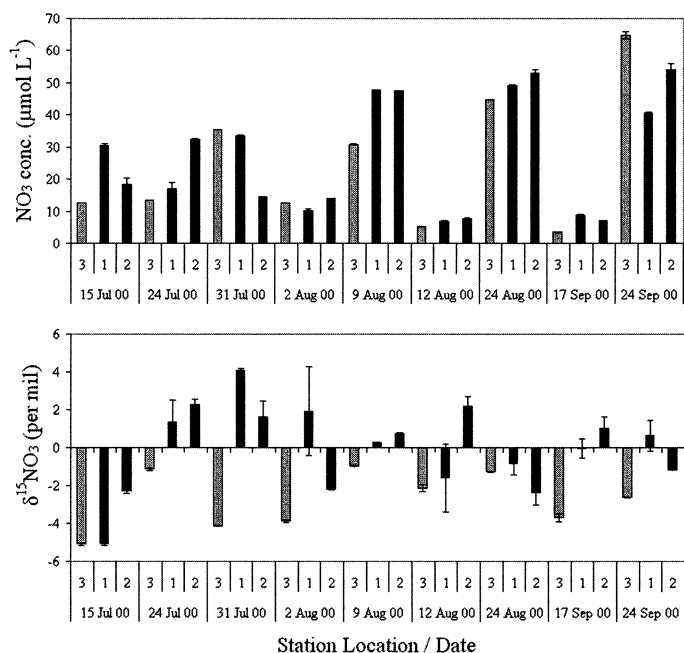


Fig. 3. (a) NO₃ concentrations and (b) δ¹⁵NO₃ values for rainwater and stormwater collected during the summer of 2000. The gray bar in each set is the rainwater (location 3), and the two black bars are stormwater samples (locations 1 and 2). Error bars for the rain samples are either half the range for duplicate analysis of a single NO₃ sample or the SD of six comparisons on the mass spectrometer. For stormwater samples, error bars are half the range for duplicate samples collected at each stormwater sampling location.

cate sample, which had a recovery of 97%. The second low recovery was from one of the stormwater samples from location 1, which had a much lower NO₃ recovery (19%) than its duplicate sample (extraction efficiency = 101%), but the δ¹⁵NO₃ value measured from these two samples only differed by 0.6‰. These data suggest that little isotope fractionation occurs with these low NO₃ recoveries; the unrecovered NO₃ may precipitate as nitrate salts during the evaporation step, and these do not redissolve during the extraction process. The precipitation of salts does not lead to a great degree of isotopic fractionation (Claypool et al. 1980). Had the poor recovery been due to loss of ammonium during the diffusion process (after NO₃ is converted to NH₄ with DeVarda's alloy), then sample fractionation would have been much greater (Sigman et al. 1997).

We hypothesize that ¹⁵N enrichment of stormwater NH₄ is caused by one or both of two mechanisms: the volatilization of ammonia (NH₃) or nitrification after rain strikes the ground and flows over heated impervious surfaces. During volatilization, the lighter nitrogen isotope of ammonia, ¹⁴NH₃, is preferentially volatilized because of its lighter mass, leaving the heavier ¹⁵NH₄ in solution (Hübner 1986). Similar enrichments due to volatilization have been observed in farmlands after the addition of urea or manure (Heaton 1986) and in sewage treatment plants and septic systems (McClelland and Valiela 1998). The rate of volatilization or flux of NH₃ depends on temperature, the concentration gradient between the stormwater and ambient air, pH, the degree of water movement over various surfaces (aeration), and

wind speed (Loder et al. 1996). All of these mechanisms can alter the solubility of ammonium, although temperature is likely the greatest factor during the hot rainy summers of southwest Florida. Because of the temperature effect, the volatilization of NH₃ from stormwater is likely to vary seasonally and regionally.

Alternatively, the NH₄ removal and concurrent isotopic enrichment may be due to the oxidation of NH₄ to NO₃ (nitrification). However, in six of the nine rain events that did show increases in NO₃ concentrations, typical nitrate increases in stormwater were usually too high to be attributed to the nitrification of rainwater NH₄ alone, which suggests an additional source of nitrate. For example, on 15 July 2000, the decrease in stormwater NH₄ relative to rainwater NH₄ at location 1 was 3.2 µmol L⁻¹, whereas the increase in stormwater NO₃ at the same location was >17 µmol L⁻¹. The nitrification of rainwater NH₄ would result in ¹⁵N depleted NO₃ for stormwater relative to rainwater, which is contrary to the observed enrichments in δ¹⁵NO₃. The ¹⁵N composition of the NO₃ in stormwater was usually enriched compared with rainwater. However, an additional nitrate source could mask the addition of ¹⁵N-depleted N from nitrification to the stormwater NO₃ pool. Entrained nitrate from dry deposition on impervious surfaces may contribute to the overall isotopic enrichment in stormwater NO₃ that was observed (see below). Denitrification coupled to nitrification could also lead to the isotopic enrichment of stormwater NO₃. Future studies should determine whether ammonium volatilization, coupled nitrification/denitrification, or a combination of both is responsible for the observed changes in DIN between rainwater and stormwater.

Stormwater NO₃ concentrations were elevated compared with the rainwater from the same storm event for six of the nine rain events sampled (Fig. 3a). As was mentioned previously, NO₃ may be entrained into the stormwater as it flows over impervious surfaces. This additional NO₃ could be due to the dry deposition of nitrous oxides from various sources, including automotive exhaust, industrial emissions, and other anthropogenic activities. These nitrous oxides can react with water to form nitric acid, HNO₃, which dissociates in solution, leading to an increase in NO₃ concentrations in stormwater. Because isotopic fractionation is low at high temperatures, the δ¹⁵N signature of these nitrous oxide sources should be similar to the nitrogen oxidized during combustion (δ¹⁵N = -1 to +5 per mil; Earls 2001). Annual estimates for the dry deposition of NO₃ and nitric acid (HNO₃) for Tampa Bay are 0.06 and 0.61 kg N ha⁻¹yr⁻¹ (Poor et al. 2001). Not accounting for seasonal differences, these rates are equivalent to daily dry deposition rates of 1.17 and 11.9 µmol N m⁻² d⁻¹ for NO₃ and HNO₃, respectively. These deposition rates are sufficient to support the increased NO₃ concentrations observed in stormwater. There is likely a first flush effect associated with nitrate entrained into stormwater that would result in the highest stormwater NO₃ concentrations occurring at the beginning of a rain event and decreasing as the rain event continues to cleanse impervious surfaces (Bertrand-Krajewski et al. 1998).

Rainwater PO₄ concentrations ranged from below detection (<0.5 µmol L⁻¹) to 2.1 µmol L⁻¹ (Fig. 4). Stormwater PO₄ concentrations were significantly higher than concentra-

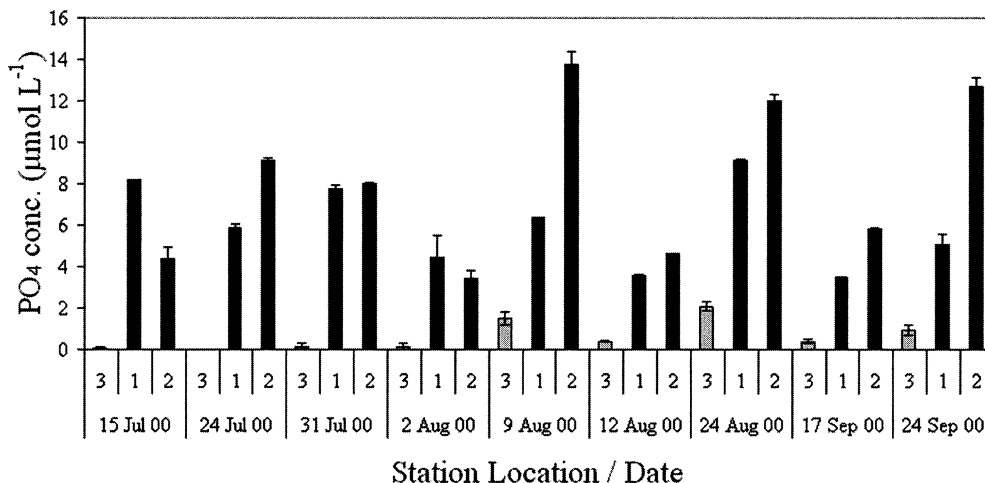


Fig. 4. Phosphate concentrations in rainwater (location 3) and stormwater (locations 1 and 2) collected during nine rain events during summer 2000. The gray bar in each set is the rainwater (location 3), and the two black bars are stormwater samples (locations 1 and 2). Error bars for the rain samples are half the range for duplicate analysis of a single PO₄ sample. For stormwater samples, error bars are half the range for duplicate samples collected at each stormwater sampling location.

tions in rainfall ($p < 0.001$) and were 3.5–13.8 $\mu\text{mol L}^{-1}$, which indicates that PO₄ is also entrained into stormwater (Fig. 4). In six of the nine rain events sampled, PO₄ concentrations were higher in samples from location 2 (commercialized urban area) than from location 1 (suburban residential area), although the differences were not significant. Estimated rates of phosphorus dry deposition to south Florida are $3.62 \pm 2.92 \mu\text{mol m}^{-2} \text{d}^{-1}$ (Ahn and James 2001), which could supply the observed increases of phosphate concentrations in stormwater. As was suggested for the nitrate entrainment, there is likely a first flush phenomenon that would result in higher PO₄ entrainment rates at the beginning of a rain event and lower entrainment rates after impervious surfaces are flushed by stormwater.

The NH₄ and NO₃ wet deposition data (concentrations and ¹⁵N signatures) presented in this study were similar to results obtained from other investigations that examined nitrogen in rainfall (Paerl and Fogel 1994; Russell et al. 1998). NH₄ concentrations of stormwater were usually lower than those of rainwater from the same storm event. We hypothesize that the loss of NH₄ is due to either volatilization or nitrification or to a combination of both. Ammonia is likely lost from stormwater because of increased temperatures, which may explain the large isotopic enrichment, yielding ammonium isotopic values of +7–18 ‰. Coupled nitrification and denitrification, along with entrainment of NO₃ from dry deposition, could also explain the results obtained in this study. Future work should investigate these possibilities, to determine which of these processes are dominant in the evolution of rainwater to stormwater. Our data also show that stormwater is an additional source of NO₃ and PO₄, compared with rainfall. Better characterization of the nitrogen and phosphate in stormwater runoff will assist in developing nutrient budgets for aquatic systems affected by stormwater from urbanized areas.

Fry et al. (2003) noted that municipal sources include urban runoff as well as wastewater, but, to our knowledge, this study is the first to document stormwater DI¹⁵N values, and we have shown that stormwater can be a source of ¹⁵N-enriched DIN. The implications of these findings are relevant for aquatic systems that are in proximity to human population centers. In the past, elevated $\delta^{15}\text{N}$ values of DIN have typically been attributed to anthropogenic loading from agricultural fertilizers and wastewater. Our results will require the broadening of the interpretation of an “anthropogenic signal” to urban stormwater.

Because the volatilization of ammonia, as well as nitrification and denitrification, are strongly influenced by temperature, there could be large seasonal and geographical variations in the ¹⁵N composition of stormwater compared with rainwater. Obviously, more volatilization and/or nitrification/denitrification would be expected during the summer than winter, because all of these processes are highly dependent on temperature. Additionally, the magnitude of seasonality at different geographic areas could result in seasonal shifts in the isotopic composition of ammonium in stormwater. The time interval between rain events may influence the nitrate and phosphate concentrations in stormwater if increases in these nutrient concentrations are due to the entrainment of dry deposition. Long time intervals allow more NO₃ and PO₄ to be deposited on impervious surfaces before stormwater entrainment. The relatively small size of stormwater samples in this study ($n = 9$), differences in the timing of stormwater sampling during a rain event, and the lack of dry deposition data for Sarasota Bay make it difficult to describe the effects of rainfall intervals on stormwater composition. Future studies should examine not only the effects of timing between rain events on stormwater isotopic composition but also the evolution of stormwater during single rain events.

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