

## The chemistry of wet deposition for a tallgrass prairie ecosystem: inputs and interactions with plant canopies

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**Abstract.** The chemistry and nutrient inputs of wet deposition, and the N chemistry of throughfall, were characterized for a tallgrass prairie in north-central Kansas. Dominant ions in wetfall were  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{H}^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ ; weighted mean pH was 4.79. Principal sources of ions appeared to be natural emissions and wind-blown soils. Concentrations of  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N, and organic N in wet deposition were 0.31, 0.30, and 0.17 mg/L, respectively, resulting in N inputs of 2.5, 2.5, and 1.4  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ . Comparisons with bulk precipitation suggested that at least 50% of atmospheric N inputs were from dry deposition. Concentrations of  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N, and organic N in unburned prairie throughfall were 0.27, 0.28, and 1.28 mg/L, and in burned prairie throughfall were 0.33, 0.37, and 0.91 mg/L, respectively. The prairie canopy intercepted up to 48% of incident precipitation. Lower inorganic N and higher organic N concentrations in throughfall relative to wet deposition probably resulted from leaf uptake of N and immobilization by microbes associated with the standing dead plant materials of the prairie canopy. The removal of these materials by fire is important in maintaining N availability for tallgrass prairie. Much of the N immobilization appeared to have been of N that was supplied to the prairie canopy by dry deposition.

### Introduction

Water and nutrients interact to control productivity of prairies (Dodd & Lauenroth 1979). This close interaction indicates the importance of understanding both the amount and the chemical composition of precipitation that enters the prairie ecosystem. Furthermore, some nutrients are deposited atmospherically through both wet and dry processes (Whitehead & Feth 1964; Schlesinger et al. 1982) and the predominant phase of deposition of a nutrient can affect nutrient availability (Lindberg & Harriss 1982). Although atmospheric deposition has been well-studied for much of North America, more information is needed for the central plains region (Munger & Eisenreich 1983). The purpose of this paper is to characterize the chemistry and nutrient inputs of wet deposition for a tallgrass prairie ecosystem.

Fire is an integral abiotic component of the tallgrass prairie ecosystem, having direct and indirect influences on availability of water, N, and energy through alteration of the mass and live/dead composition of the prairie grass

canopy (Gilliam et al. 1987; Knapp & Seastedt 1986). Nitrogen, usually growth-limiting in tallgrass prairie (Risser & Parton 1982), is of particular importance because it is affected by fire. Volatilization and particulate up-draft during prairie fires can result in substantial losses of N (Raison 1979), ranging up to 30 kg/ha for a single fire (Elwell et al. 1941). Total annual atmospheric inputs of N for tallgrass prairie systems have been estimated to be between 10 and 17 kg/ha (Woodmansee 1979; Seastedt 1985); thus, atmospheric deposition can supply a significant portion of the N lost from a single prairie fire.

The importance of dry deposition varies among nutrients and, for a particular nutrient, between sites. Nutrients that tend to have a substantial dryfall phase are either soil-derived, such as  $\text{Ca}^{2+}$ , or occupy relatively large aerosol fractions, such as  $\text{NO}_3^-$ -N. Furthermore, differences in quantities of dry deposition between sites are influenced by the source and amount of atmospheric chemical constituents (Swank 1984). The relative contribution of dry deposition of N for tallgrass prairies has been estimated as 25 to 50% of total atmospheric inputs through comparisons of studies at different prairie sites (Woodmansee 1979).

Plant canopies alter the chemical composition of precipitation. Nutrient flux in throughfall is relatively well-understood in a variety of forest ecosystems, but has not been investigated adequately for prairies (Parker 1983). Gilliam et al. (1987) found that throughfall amounts were 62 and 81% of incident precipitation in unburned and burned tallgrass prairie, respectively. At the same site, Seastedt (1985) determined that unburned and burned canopies retained 77 and 58% of the inorganic N in bulk precipitation and concluded that retention occurred as a result of microbial immobilization. Chemical changes in precipitation passing through plant canopies are influenced by inputs of wet and dry deposition, evaporation, foliar uptake and leaching, and epiphyllic microbial activity (Parker 1983).

The primary objective of this study was to describe the chemistry and nutrient input of wet deposition for a tallgrass prairie. Although other nutrients are important, N is usually the most limiting nutrient in prairies (Dodd & Lauenroth 1979). Therefore, estimates were derived for canopy processing of deposited N.

### **Study area**

This study was conducted on the Konza Prairie Research Natural Area, located 15 km south of Manhattan, Kansas, USA, in the northeast Kansas Flint Hills. The Konza Prairie is approximately 3490 ha of ungrazed tallgrass, or true, prairie (Küchler 1964), with the predominance of warm

season (C-4) grasses: big bluestem (*Andropogon gerardii* Vitman.), indian-grass (*Sorghastrum nutans* L. Nash), little bluestem (*A. scoparius* Michx.), and switch grass (*Panicum virgatum* L.).

The soil at the study sites is a Tully silty clay loam. Tully soils are fine, mixed, mesic Pachic Argiustolls (Jantz et al. 1971), derived from Permian limestone.

The climate of the region is classified as humid continental (Brown & Bark 1971), with temperatures ranging from a mean January low of  $-3^{\circ}\text{C}$  to a mean July high of  $27^{\circ}\text{C}$ . Precipitation averages 835 mm annually, with snowfall common in January and February. Precipitation is distributed bimodally throughout the year, with peaks in June and September and dry winters. Seasonal patterns of precipitation vary greatly from year to year (Gilliam et al. 1987).

### **Sample collection**

Wet and dry deposition collection was initiated in August 1982 using an Aerochem Metrics Automatic Wet/Dry Collector (Model 301) located on a ridge within the Konza Prairie weather station. Wet samples were taken weekly as part of the National Atmospheric Deposition Program (NADP).

Bulk precipitation and throughfall sampling for this study was initiated in December 1983. Bulk precipitation was sampled using three continuously-open polyethylene funnel collectors located throughout the prairie; a fourth sampler was added in March 1985. Throughfall was sampled at two sites: one unburned and one annually burned watershed. During this study, the latter watershed was burned 19 April 1984 and 24 April 1985. Throughfall samples were collected using six metal troughs (5 cm  $\times$  100 cm) per site. Plastic collector jugs were attached to troughs by Tygon tubing and troughs were placed approximately 3 cm above the soil/litter surface. Troughs were removed from the burned watershed just prior to the fire and were replaced within 3 to 4 weeks. Collections of bulk precipitation and throughfall were made simultaneously after each event greater than 4 mm. After each collection, clean (acid-washed) collectors were placed in the field. Phenylmercuric acetate was used (1 ml/collector) to inhibit microbial activity.

### **Chemical analyses**

Wetfall samples were analyzed for pH and specific conductance in the laboratory at Kansas State University (KSU) following standard NADP

procedures as outlined in Bigelow (1982). These determinations were repeated after sample buckets were sent to the NADP Central Analytical Laboratory (CAL). At the CAL  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  were determined using flame spectrophotometry, with La added for divalent cation measurements. In addition,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{PO}_4^{3-}$  were analyzed using Technicon Auto Analyzer II System procedures described by Stensland et al. (1980). A 20-ml subsample of each weekly wetfall collection greater than 100 ml was retained at the KSU laboratory before the bucket was sent to the CAL. This sample was analyzed for  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and total persulfate N as described below. These data provided a check between analytical procedures of the KSU laboratory and the CAL, as well as an estimate of organic N in wetfall.

At the KSU laboratory bulk precipitation, throughfall, and wetfall subsamples were analyzed for  $\text{NO}_3^-$ -N using azo dye colorimetry following cadmium reduction; for  $\text{NH}_4^+$ -N using an automated phenate procedure; for total N using a modified persulfate digestion (Seastedt 1985). Digested samples were analyzed for  $\text{NO}_3^-$ -N. Efficiency of N recovery during digestion was checked against urea and glycine standards. All analyses were carried out on a Technicon Auto Analyzer II System. Organic N concentrations were assumed to be the difference between total persulfate N and the sum of  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N concentrations.

## Results and discussion

### *Wetfall*

The dominant cations in wetfall at Konza Prairie were  $\text{NH}_4^+$ -N,  $\text{Ca}^{2+}$ , and  $\text{H}^+$ , comprising 33, 31, and 23%, respectively, of all cations analyzed. Dominant anions were  $\text{SO}_4^{2-}$ -S and  $\text{NO}_3^-$ -N, representing 55 and 39% of analyzed anions (Table 1). Organic N in wetfall was 0.17 mg/L. The sum of cation concentrations in wetfall was about 9% higher than the sum of anion concentrations. Much of this discrepancy likely can be explained by anions that were not determined in these samples, particularly  $\text{HCO}_3^-$ , but also weak organic acids. Wetfall at Konza Prairie was moderately acidic, ranging from pH 4.14, to 6.36, with a volume-weighted pH of 4.79 (Table 1), calculated from weighted  $\text{H}^+$  concentrations. It should be noted that pH data for this paper were based on "field" analyses (made at the KSU laboratory) rather than those made at the CAL (see Verry 1983).

The concentrations of virtually all ions were correlated significantly ( $p < 0.001$ ) in wetfall. While most correlations resulted from the influence

Table 1. Wetfall nutrient concentrations for Konza Prairie Research Natural Area, 1982–1984.

Cation	Concentration			Anion	Concentration		
	mg/L*	mg/L†	μeq/L‡		mg/L*	mg/L†	μeq/L‡
Ca <sup>2+</sup>	0.82 (0.13)	0.39	19.5	NO <sub>3</sub> <sup>-</sup> -N	0.49 (0.04)	0.31	22.8
Mg <sup>2+</sup>	0.11 (0.02)	0.04	3.3	Cl <sup>-</sup>	0.26 (0.03)	0.13	3.7
K <sup>+</sup>	0.07 (0.01)	0.04	1.0	SO <sub>4</sub> <sup>2-</sup> -S	0.74 (0.07)	0.52	32.4
Na <sup>+</sup>	0.25 (0.04)	0.10	3.9				Σ = 58.9
NH <sub>4</sub> <sup>+</sup> -N	0.41 (0.03)	0.30	22.1				
H <sup>+</sup>	0.02 (0.00)	0.01	14.6				Σ anions/Σ cations <sup>§</sup> = 0.91
pH = 4.79			Σ = 64.4				

\* Arithmetic mean with 1 standard error in parentheses

† Volume-weighted concentration

‡ Microequivalents based on volume-weighted concentrations

§ Ratio based on μeq/L

of precipitation volume on ionic concentrations in wetfall, some probably resulted from chemical associations in the atmosphere, e.g. NH<sub>4</sub>NO<sub>3</sub> and ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>HSO<sub>4</sub>) aerosols, and to a lesser extent NH<sub>4</sub>Cl aerosols (Lau & Charlson 1977; Levine 1984). Correlation coefficients (*r*) for NH<sub>4</sub>/NO<sub>3</sub>, NH<sub>4</sub>/SO<sub>4</sub>, and NH<sub>4</sub>/Cl were 0.81, 0.84 and 0.50, respectively. All ions except H<sup>+</sup> correlated negatively (*p* < 0.001) with log-transformed wetfall volumes, a relationship describing washout and rainout processes for these ions (Wolaver & Lieth 1972; Gilliam 1983).

Precipitation chemistry reflects aerosol and cloud chemistry that is under local and regional control (Harrison & Pio 1983; Derrick et al. 1984; Pratt & Krupa 1985). Ionic concentrations at Konza Prairie are compared in Table 2 to those in wetfall of a north central Minnesota site (Verry 1983), a southern California coastal site (Schlesinger et al. 1982), and to data summarized for the eastern United States (Gorham et al. 1984). These data support the conclusions of Munger and Eisenreich (1983) and Gorham et al. (1984) that ions in precipitation are derived from three principal sources: natural and anthropogenic emissions, wind-blown soil, and sea spray. Wetfall in the eastern US is dominated by acidic species, ie H<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> (Table 2), a result of high emissions of NO<sub>x</sub> and SO<sub>2</sub> in this region (Stensland 1979). Ions in wetfall for the coastal California site are predominantly of marine origin, eg. Na<sup>+</sup>, Cl<sup>-</sup>, and Mg<sup>2+</sup>. Not surprisingly, wetfall chemistry is similar between north central Minnesota and Konza Prairie. The high Ca<sup>2+</sup> concentrations are probably derived from exposed high-Ca soils that are carried by the wind.

High NH<sub>4</sub><sup>+</sup> concentrations at both sites are attributable to relatively high soil pH. As initially established by Junge (1958), it is now accepted widely

Table 2. Volume-weighted wetfall nutrient concentrations from different sites of the US. Values in parentheses are relative percentage of ions to total cations or anions.

Site	Reference	Cations											
		Ca <sup>2+</sup> mg/l	μeq/l	Mg <sup>2+</sup> mg/l	μeq/l	K <sup>+</sup> mg/l	μeq/l	Na <sup>+</sup> mg/l	μeq/l	NH <sub>4</sub> <sup>+</sup> -N mg/l	μeq/l	H <sup>+</sup> mg/l	μeq/l
Eastern US	Gorham et al. (1984)	0.20	10.0	0.05	4.2	0.04	1.0	0.18	7.9	0.22	16.0	0.05	46.0
		(11.8)		(4.9)		(1.2)		(9.3)		(18.8)		(54.1)	
Southern coastal California	Schlesinger et al. (1982)	0.03	1.5	0.06	4.9	0.01	0.3	0.47	20.4	0.02	1.4	0.02*	20.0
		(3.1)		(10.1)		(0.6)		(42.1)		(2.9)		(41.2)	
North central Minnesota	Verry (1983)	0.30	15.0	0.05	4.1	0.07	1.8	0.35	15.2	0.39	27.8	0.05	50.1
		(13.1)		(3.6)		(1.6)		(13.3)		(24.3)		(43.9)	
Tallgrass prairie	Present study	0.39	19.5	0.04	3.3	0.04	1.0	0.09	3.9	0.31	22.1	0.01	14.6
		(30.5)		(5.2)		(1.6)		(6.7)		(33.4)		(22.7)	
*Estimated from isopleth (Munger & Eisenreich 1983)													
Site	Reference	Anions											
		NO <sub>3</sub> <sup>-</sup> -N mg/l	μeq/l	Cl <sup>-</sup> mg/l	μeq/l	SO <sub>4</sub> <sup>2-</sup> -S mg/l	μeq/l	SO <sub>4</sub> <sup>2-</sup> -S mg/l	μeq/l				
Eastern US	Gorham et al. (1984)	0.34	24.0	0.28	7.8	0.72	55.0						
		(27.6)		(9.0)		(63.4)							
Southern coastal California	Schlesinger et al. (1982)	0.03	2.1	0.84†	23.6	0.20	12.5						
		(5.5)		(61.8)		(32.7)							
North central Minnesota	Verry (1983)	0.32	22.8	0.17	4.8	0.58	36.2						
		(35.6)		(7.5)		(56.6)							
Tallgrass prairie	Present study	0.31	22.8	0.13	3.7	0.52	32.4						
		(38.6)		(6.6)		(54.8)							

† Calculated from Na/Cl ratios (based on μeq/l) of seawater and Na concentration

that soil pH substantially influences  $\text{NH}_4^+$  in precipitation by controlling  $\text{NH}_3$  volatilization, both from native grassland soils and particularly from fertilized agricultural soils (Freney et al. 1983). Volatilization rates are high in the neutral soil pH range, a characteristic of tallgrass prairie soils and those of agricultural areas that are extensive in the central mid-west. Indeed, atmospheric  $\text{NH}_3$  in this region is one to two orders of magnitude higher than in regions to the east (Lau & Charlson 1977). Isoleths for atmospheric  $\text{NH}_3$  in the US are approximately coincident with those for  $\text{NH}_4^+$  concentrations in precipitation (Lau & Charlson 1977; Munger & Eisenreich 1983). Therefore,  $\text{NH}_3$  loss from mid-western soils indeed may be a predominant source of  $\text{NH}_4^+$  in precipitation over North America.

There are, however, some notable differences in wetfall acidity between the Minnesota and Kansas sites. Mean  $\text{H}^+$  concentration for Minnesota is five times that of Konza Prairie, presumably a result of  $\text{NO}_x$  emissions carried by air parcels from the east (Verry 1983). Furthermore,  $\text{Na}^+$  was the primary cation associated with net alkalinity in Minnesota wetfall, whereas all cations, particularly  $\text{Ca}^{2+}$ , contributed significantly to net alkalinity at Konza Prairie (Table 3).

Potentially deleterious effects of acid deposition do not appear prevalent for this mid-western site. Volume-weighted pH of wetfall for the study period was 4.79 (Table 1), which is within the range (pH 4.78 to 4.96) found for several remote areas of the world by Galloway et al. (1982). Although pH at Konza Prairie is below the reference pH of 5.65 for the  $\text{H}_2\text{O}/\text{CO}_2$  equilibrium (Reuss 1975), it is similar to the pH (5.0) of precipitation that is considered to be only slightly influenced by anthropogenic emissions (Charlson & Rodhe 1982).

Reuss (1975) argued that determination of net acidity/alkalinity (equation given in Table 3) is perhaps more meaningful than pH alone in considering effects of acidic deposition on ecosystems. Data in Table 3 indicate that acidity in wetfall of Konza Prairie was correlated significantly with all

*Table 3.* Contributions of ions to net acidity/alkalinity in wetfall at Konza Prairie. Values are Pearson product-moment correlation coefficients ( $r$ ). Net acidity is calculated from molar ion concentrations as  $e$ , where  $e = [\text{NO}_3^-] + [\text{Cl}^-] + 2[\text{SO}_4^{2-}] - (2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{K}^+] + [\text{Na}^+] + [\text{NH}_4^+])$ ;  $-e$  is net alkalinity.

Net	n	ion							
		$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{K}^+$	$\text{Na}^+$	$\text{NH}_4^+$	$\text{NO}_3^-$	$\text{Cl}^-$	$\text{SO}_4^{2-}$
Acidity	94						0.40***	0.22*	0.69***
Alkalinity	22	0.69***	0.47*	0.51*	0.57**	—			

n = Number of weeks in comparison

\*\*\*.\*\*\*.\*\*\* Indicate significant correlation of  $p < 0.05$ ,  $p < 0.01$ ,  $p < 0.001$  levels, respectively

anions, but was associated most strongly with  $\text{SO}_4^{2-}$ . Charlson and Rodhe (1982) concluded that precipitation pH of 4.5 to 5.6 could result solely from natural variations in the S cycle.

Altwicker and Mahar (1984) demonstrated the use of the  $\text{NH}_4^+/\text{Ca}^{2+}$  ratio to interpret data from studies of precipitation chemistry, eg relationships of wet/dry deposition and mechanistic (scavenging) processes. In general, lower  $\text{NH}_4^+/\text{Ca}^{2+}$  ratios indicate higher relative below-cloud scavenging and scavenging of primary ( $\text{Ca}^{2+}$ ) aerosols, as well as higher dryfall contributions to the wetfall sample. Higher ratios may represent in-cloud scavenging of  $\text{NH}_3$  and secondary ( $\text{NH}_4^+$ ) aerosols (Altwicker & Mahar 1984). Wetfall  $\text{NH}_4^+/\text{Ca}^{2+}$  ratios at Konza Prairie were low during small storms where washout (below-cloud scavenging) dominates and high during large storms where rainout (in-cloud scavenging) dominates (Fig. 1).

Monthly volume-weighted  $\text{NH}_4^+/\text{Ca}^{2+}$  ratios and  $\text{H}^+$  concentrations had similar seasonal patterns (Fig. 2), generally lower monthly values in spring and summer, and higher values in fall and winter. For the study period,  $\text{NH}_4^+/\text{Ca}^{2+}$  ratios and  $\text{H}^+$  concentrations in wetfall were correlated significantly ( $p < 0.05$ ). Scavenging of  $\text{Ca}^{2+}$  aerosols in the low-volume washout events of spring and summer storms (low  $\text{NH}_4^+/\text{Ca}^{2+}$ ) may tend to increase pH of wetfall (Reuss 1975; Pratt et al. 1984; see Table 3). Conversely, additional in-cloud  $\text{NH}_3$  uptake (high  $\text{NH}_4^+/\text{Ca}^{2+}$ ) can occur as pH drops

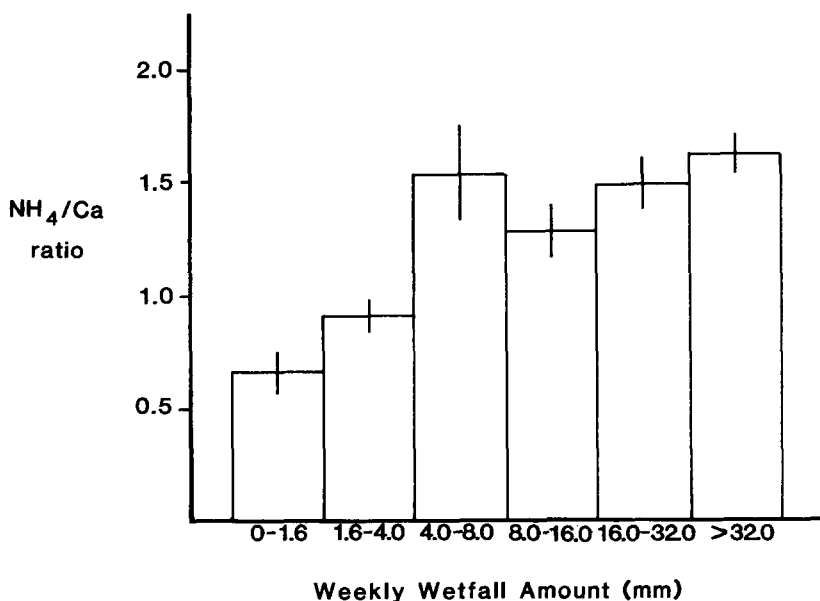


Fig. 1. Mean  $\text{NH}_4/\text{Ca}$  ratios for weekly wetfall amount classes. Ratios are based on ion concentrations in  $\mu\text{eq/L}$ . Error bars represent one standard error of the mean.



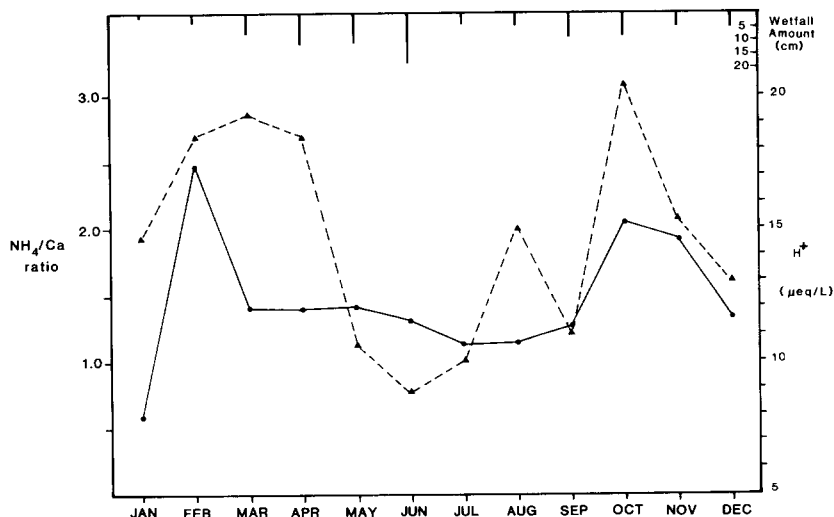


Fig. 2. Volume-weighted mean monthly  $\text{NH}_4^+/\text{Ca}$  ratios (solid lines) and  $\text{H}^+$  concentrations (dashed lines) in wetfall. Ratios are based on ion concentrations in  $\mu\text{eq/L}$ . Lines from top of figure are mean monthly wetfall amounts.

from absorption and rapid subsequent oxidation of  $\text{SO}_2$  (Lazrus et al. 1983; Altwicker & Mahar 1984).

### Nutrient inputs

Wetfall nutrient inputs at Konza Prairie were relatively high for  $\text{Ca}^{2+}$ ,  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N, and  $\text{SO}_4^{2-}$ -S (Table 4). Inputs were virtually identical for both  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N, approximately  $2.5 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ . Inputs at Konza Prairie contrasted sharply with inputs at the coastal California site,

Table 4. Wetfall amounts and nutrient inputs for different sites.

Site	Amount cm	$\text{kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$							
		$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{K}^+$	$\text{Na}^+$	$\text{NH}_4^+$ -N	$\text{NO}_3^-$ -N	$\text{Cl}^-$	$\text{SO}_4^{2-}$ -S
Coastal California*	93.5	0.25	0.55	0.13	4.40	0.20	0.30	8.40 <sup>§</sup>	1.90
Central Minnesota†	70.1	2.01	0.34	0.47	2.35	2.03	2.13	1.14	3.86
North-central Kansas‡	80.7	3.18	0.34	0.29	0.78	2.49	2.48	1.12	4.14

\* Schlesinger et al. (1982)

† Verry (1983); Pratt et al. (1984)

‡ Present study

§ Calculated from seawater dilution (see Table 3)

where dominant inputs were the primary constituents of sea water aerosols, ie  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{Cl}^-$ . Inorganic N inputs at Konza Prairie were only slightly higher than those for central Minnesota. Organic N input in wetfall was  $1.4 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ . Differences in wetfall inputs at these two midwestern sites were primarily in the balance between  $\text{Ca}^{2+}$  (higher for Konza Prairie) and  $\text{Na}^+$  (higher for Minnesota), probably reflecting different relative amounts of these ions in soils at each site (Verry 1983).

Although precipitation sampled with continuously open collectors (bulk precipitation) is now widely accepted to underestimate total atmospheric inputs (Lindberg et al. 1986), bulk inputs may provide a lower level estimate of dry deposition when compared with wetfall inputs. Indeed, N input estimates for North American prairies in the literature, ranging from 10.0 to  $16.6 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ , have been based on bulk precipitation sampling (Woodmansee 1979; Seastedt 1985). Bulk inputs of  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N, and organic N in this study were 5.1, 4.5, and  $6.4 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ , respectively, for a total N input of  $16.0 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ . Compared with a mean wet deposition of N of  $6.4 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ , these bulk estimates suggest that dry deposition may contribute at least 60% of total N inputs to this tallgrass prairie, particularly in the form of organic N.

#### *Interception of N by prairie canopies*

In contrast to the predominance of inorganic N in wetfall, organic N was the major form of N in throughfall, particularly for unburned prairie. Inorganic and organic N concentrations in unburned and burned prairie throughfall were 0.55 and 1.28 mg/L, and 0.70 and 0.91 mg/L, respectively. Total N concentrations were higher in unburned prairie throughfall than in burned prairie throughfall, a result of much higher organic N content of unburned prairie samples, but possibly also from higher throughfall amounts ("dilution" effect) in burned prairie samples. Annual amounts of burned prairie throughfall exceeded that of unburned prairie by 20% (Table 5).

Of 81.1 cm of incident precipitation annually, 42.4 cm reached unburned prairie soil, whereas 50.8 cm reached burned prairie soil. A similar proportion of total N was intercepted by the prairie canopy, confirming conclusions of Seastedt (1985) that this canopy can act as a "filter" for N. Lower inorganic N concentrations in throughfall compared to bulk precipitation suggest that N, to some degree, is taken up by canopy leaves and immobilized by epiphyllic microbial populations. Lower inorganic and higher organic N inputs in unburned prairie throughfall compared to burned prairie throughfall further suggest that much of the immobilization is associated with standing dead canopy material. This standing dead plant bio-

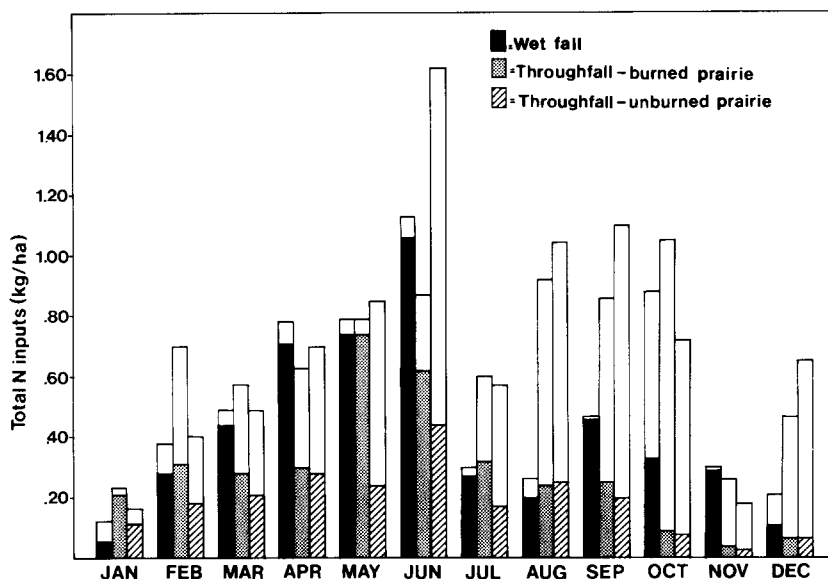


Fig. 3. Monthly inorganic ( $\text{NO}_3^- \text{-N} + \text{NH}_4^+ \text{-N}$ ) and organic N inputs for wet deposition and throughfall in burned and unburned prairie. Organic N inputs for each sample type represented by open bars. Inorganic N inputs represented as follows: wet deposition — solid bars, burned prairie throughfall — dotted bars, unburned prairie throughfall — slashed bars.

mass is present throughout the year in unburned prairie, but is removed by fire in burned prairie.

Seasonal patterns of N inputs in wet deposition and throughfall of burned and unburned prairie illustrate the influence of prairie canopies on the N chemistry of throughfall (Fig. 3). There was a relatively consistent predominance of organic N in throughfall throughout the year, contrasting with wet deposition, which showed minor, inconsistent changes in organic N throughout the year. Increases in organic N in throughfall were in late summer to autumn. These increases were accompanied by sharp decreases in  $\text{NO}_3^- \text{-N}$  and  $\text{NH}_4^+ \text{-N}$  (Fig. 3).

Whereas organic N inputs were relatively high for much of the year in unburned prairie throughfall, they remained somewhat low through the growing season in burned prairie throughfall, increasing sharply in the autumn (Fig. 3). This pattern appeared to be related to phenological changes that are more pronounced in burned prairie. As grass leaves senesce, N is retranslocated into storage organs, and C:N ratios of the current year's standing dead material can reach 110:1 (Dahlman et al. 1969). This ratio is well above the critical levels (20 to 30:1) for net N mineralization, and thus, assuming sufficient moisture, rapid N immobilization would be expected (Alexander 1977).

Table 5. Throughfall amounts, weighted N concentrations, and annual N inputs in throughfall of burned and unburned prairie. Values in parentheses are percentages of wetfall amounts.

Throughfall	Amount cm/yr	NO <sub>3</sub> <sup>-</sup> -N mg/L	kg·ha <sup>-1</sup> ·yr <sup>-1</sup>	NH <sub>4</sub> <sup>+</sup> -N mg/L	kg·ha <sup>-1</sup> ·yr <sup>-1</sup>	Organic N mg/L	kg·ha <sup>-1</sup> ·yr <sup>-1</sup>	Total N mg/L	kg·ha <sup>-1</sup> ·yr <sup>-1</sup>
Burned prairie	50.8(63%)	0.33	1.74	0.37	2.09	0.91	5.42	1.60	9.25
Unburned prairie	42.4(50%)	0.27	1.04	0.28	1.16	1.28	6.05	1.83	8.25

Although it is impossible from the data presented here to determine the relative contributions of wet and dry deposition of N in throughfall, it is important to consider the potential significance of dry deposition of N to prairie canopies. The leaf area index of prairie canopies may be as high as 4.2 (Knapp 1985), resulting in a much more efficient collection surface for dry deposition than artificial collectors. Indeed, the estimates of N input by dry deposition discussed here probably greatly underestimate actual dry inputs of N to the prairie canopy. Furthermore, the residence time of dry-deposited N compounds would be greater than that of wet-deposited N, such that microbial immobilization may be acting primarily on N from dry deposition. Similarities in inorganic N concentrations in wetfall and throughfall (Tables 1, 5) further suggest this possibility.

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