TABLE 1. Selected characteristics of the four lodgepole pine ecosystems, southeastern Wyoming, from which throughfall was collected (adapted from Knight et al. 1985)

Site	Elevation (m)	Age (year)	Stem density (stems/ha)	Aboveground biomass (Mg/ha)	Leaf area index
Nash Fork	2900	110	1850	174.7	9.9
French Creek	2950	240	420	174.8	4.5
Dry Park	2800	110	2217	171.7	7.3
Fox Park[1]	2775	85	2000	138.4	9.2

[1] D.H. Knight and T.J. Fahey, unpublished data.

evaporation), and because of moderate canopy surface area (Pearson et al. 1984). Finally, canopy leaching was expected to be moderate because of the moderate leaf biomass and the balancing effects of relatively poor foliar nutrition (Pearson et al. 1987) and synthesis of organic acids for osmotic adjustment (Kramer and Kozlowski 1979) during summer droughts (Fahey and Young 1984).

Study area

Precipitation and throughfall quantity and chemistry were measured at four sites in the lodgepole pine ecosystem of the Medicine Bow Mountains, southeastern Wyoming. Information about the location and biotic features of the sites is provided in Table 1, and more complete descriptions are available in Knight et al. (1985) and Fahey and Yavitt (1988). The climate in the study area is cold temperate, with about two thirds of the average annual precipitation coming in the form of snow from October to May. Most of the midwinter snowstorms in the study area follow the zonal flow of westerly winds, but wet spring storms may arise from "upslope" conditions from the east and southeast. Summer rainstorms usually are convective and local, but air masses usually arrive from the west; large, semi-arid basins are found to the west of the study area, and several large, coal-fired power plants also are located to the west, within 200 km of the site.

Methods

Precipitation and throughfall quantity

Rainfall magnitude was measured with static rain gauges positioned in large forest openings adjacent to four lodgepole pine stands from 1979 to 1982 and adjacent to two stands in 1983–1984. Measurements usually were made within 24 h of the end of each rainfall event. Throughfall quantity (net rainfall) was measured with 30 funnel collectors (15 cm diameter) at the Nash Fork stand (Table 1) for a total of 86 rainstorms during the study period.

Precipitation and throughfall chemistry

Bulk deposition was collected for several years using polypropylene funnel collectors (20 cm diameter) positioned about 1 m above the ground in large forest openings adjacent to several of the sites. From 1979 to 1982, the Nash Fork, French Creek, Dry Park, and Chimney Park sites were monitored, and in 1983–1984, collections were made at Nash Fork and Fox Park (Table 1). Samples usually were collected within 24h of the end of a rainfall event, and the funnels and polyethylene collection bottles were rinsed thoroughly with deionized water. These collectors remained open to the atmosphere between rain events. In addition, in 1983 and 1984 shielded precipitation collectors (Aerochem Metrics Inc.) were used to sample wetfall at the Nash Fork and Fox Park sites.

Throughfall was collected with networks of ten polypropylene funnel (20 cm diameter) collectors placed randomly in fixed positions beneath the forest canopy at the Nash Fork, Dry Park, and French Creek stands from 1979 to 1982 and the Nash Fork and Fox Park stands in 1983–1984. Samples usually were collected within 24h of the end of a rainfall event, and funnels and polyethylene bottles were rinsed thoroughly with deionized water. For small rainfall events (less than about 5mm) samples were pooled in the field or subsequent chemical analysis.

Atmospheric chemistry

Atmospheric particulates were sampled during the summer of 1984 at the Nash Fork site using a Hi-Vol air sampler positioned about 15m above ground level in a large opening surrounded by a 20-m tall forest. A constant flow rate of 0.84 m^3/min was maintained during six 1-week runs between 28 June and 17 September, and particulates were collected on pre-weighed and pre-ashed glass-fiber filters (effective pore size, 0.45 μm). Total particulate load was measured as increase in mass following drying to constant mass at 55°C. Each sample filter was quartered for measurement of chemical concentrations. Metal cations were extracted from the filters by shaking for 8 h in 0.1 M HCl and NH_4^+, NO_3^-, P_i, and SO_4^{2-} by shaking in 0.1 M HCl/1.0 M KCl.

Sample handling and chemical analysis

Water samples were returned to the laboratory the same day as collected and analyzed for pH by glass electrode. From 1979 to 1981, total alkalinity was estimated by titration to pH 4.5 with carefully standardized HCl (Golterman et al. 1978). From 1982 to 1984, a Gran titration to pH 3.5 was used to estimate total alkalinity (Stumm and Morgan 1981), and "nonvolatile alkalinity" was estimated by back-titration under N_2 to the original pH with NaOH after purging samples of CO_2. Purged samples were titrated under N_2 to pH 8.3 with NaOH to provide an estimate of "nonvolatile acidity."

Samples were then filtered through a prerinsed, glass-fiber filter on the day of collection and stored at 4 ± 2°C for up to 72 h before being analyzed for NH_4^+ (phenol hypochlorite method; Solorzano 1969) and NO_3^- (cadmium reduction; Rand 1976) on a continuous-flow analyzer (CFA, Scientific Instruments) and for orthophosphate (molybdate blue method; Murphy and Riley 1962) on a Beckman model 25 UV/VIS spectrophotometer. In 1982 and 1983 a variety of organic fractions was analyzed. Dissolved organic carbon was measured by CO_2 coulometry following sealed ampule oxidation (Huffman 1976). Background leaching tests of funnels and collection bottles indicated no contamination at our levels of detection (0.2 mg/L). Colorimetric methods were used to estimate dissolved carbohydrates (Handa 1966), polyphenolics (Rand 1976), free amino acids (Satake et al. 1960), and proteins (Bradford 1976). For selected samples, an organic fractionation was performed using a liquid chromatography procedure (Leenheer and Huffman 1976). Subsamples for this analysis were stored in glass containers with minimal head space at 4°C prior to analysis. Low molecular weight organic acids were separated by gas–liquid chromatography of both nonderivatized samples (C_2–C_5 acids; DiCorcia and Samperi 1974) and trimethylsilyl derivatives (phenolic acids; Kaminsky and Muller 1977).

Filtered subsamples were stored for up to 3 months (usually less than 6 weeks) at 4 ± 2°C before being analyzed for major cations, SO_4^{2-}, Cl^-, and total N and P. Ca^{2+}, Mg^{2+}, K^+, Na^+, and Mn^{2+} were analyzed by atomic absorption spectrophotometry (Perkin-Elmer model 560), with 1% (M/V) lanthanum added to

TABLE 2. Volume-weighted mean chemistry of wetfall (1983–1984), bulk rainfall, and throughfall (1979–1983) in lodgepole pine ecosystems, southeastern Wyoming. In columns, numbers with the same superscript letter were not significantly different ($p > 0.05$)

	Concn. (μequiv.$\cdot$L^{-1})																Concn. (mg$\cdot$L^{-1})		
	n	pH	Ca	Mg	K	Na	Mn	NH_4	Total cations	SO_4	Cl	NO_3	HCO_3	p-alk*	Total anions	CBD†	DOC	org. N	TP
Wetfall	68	4.7*a*	26*a*	8*a*	7*a*	9*a*	1*a*	14*ab*	85	36*a*	14*a*	20*a*	10*ab*	17	97	−12	2.8*a*	0.16*a*	0.016*a*
Bulk deposition	365	5.24*a*	49*b*	9*a*	7*a*	13*a*	1*a*	20*b*	105	47*a*	9*a*	18*a*	18*b*	29	121	−16	3.3*a*	0.15*a*	0.034*a*
Throughfall	1130	4.63*a*	112*c*	40*b*	30*b*	29*b*	2*a*	10*a*	246	85*b*	25*b*	20*a*	5*a*	29	164	82	13.5*b*	0.44*b*	0.055*a*

NOTE:
*Alkalinity of samples purged of CO_2.
†Charge-balance deficit.

Wetfall and bulk deposition chemistry

Chemical concentrations in rainfall and throughfall are expressed in Table 2 as volume-weighted means which were calculated as the quotient of chemical flux and water flux. The chemistry of wetfall (shielded collector) was significantly different from bulk deposition (continuously open collector) during the snow-free period (Table 2). Total ionic strength of wetfall (0.110 mM) averaged about 74% that of bulk deposition (0.148 mM), with concentrations of Ca^{2+} and Na^+ much higher in the latter. In a summary of North American precipitation chemistry data, Munger and Eisenreich (1983) noted that base cation and SO_4^{2-} and NO_3^- concentrations generally are higher in bulk precipitation than wetfall. Our data supported this pattern, although statistically significant differences were measured only for Ca^{2+}. The lower concentrations of base cations in wetfall than in bulk deposition were offset somewhat by the higher H ion concentrations in wetfall and no significant differences were observed for NH_4^+, NO_3^-, and Cl^-. Apparently, metal carbonates and sulfates, deposited by dryfall into the open funnels, reacted with H ions in the rainfall resulting in higher pH in bulk deposition than wetfall. For bulk deposition these ionic strength values are similar to statewide average values for Colorado in 1982–1983 (0.132 mM, not including NH_4^+ and Mn^{2+}; Lewis et al. 1984).

Measured anion equivalence exceeded cation equivalence in bulk deposition and wetfall (Table 2). This anomaly could be explained in part by overestimation of bicarbonate and organic anions with our simple titration procedures that are subject to a variety of errors (Barnard 1985). Grant and Lewis (1982) observed a similar imbalance of cations and anions for bulk deposition and also attributed this error to difficulties in quantifying bicarbonate.

Bulk deposition chemistry varied markedly among storm events but differences between four collection sites were not consistent between events. Although there were no significant seasonal patterns in bulk deposition chemistry at any of the sites, rain had consistently higher solute concentrations than did snow (Knight et al. 1985).

A detailed analysis of bulk deposition chemistry in 1982–1983 for a network of 42 sites in Colorado (Lewis et al. 1984) provides a basis for comparison of our values with regional trends; however, in that study annual mean values were reported, including winter snow. To facilitate comparison we calculated annual mean bulk deposition chemistry for our study area by assuming that 68% of annual precipitation comes as snow and by weighting bulk deposition (Table 2) and snowpack concentrations (Knight et al. 1985) accordingly. Concentrations of base cations were very similar in our site and a nearby station at Steamboat Springs, Colorado (elevation 2090 m); however, our values were much lower than for a high-elevation site in northern Colorado at Rabbit Ear's Pass (2910 m), which received high annual precipitation (about 75 cm in 1982–1983). As detailed by Lewis et al. (1984), spatial variation in bulk deposition in Colorado depends upon proximity to large anthropogenic sources of strong acid anions (power plants and urban areas) as well as to low elevation sources of cations and carbonates from windblown soil particles. The low ratio of NO_3^- to SO_4^{2-} in our study area is similar to values for rural locations downwind of power plants in Colorado which are much lower than values in urban areas of that State (Lewis et al. 1984). Both of these strong acid anions were found in much lower concentrations in the Rocky Mountains than in more polluted areas such as the northeastern United States (Likens et al. 1977). Moreover, neutralization by Ca^{2+} and other base cations resulted in very low H^+ loading via bulk precipitation in these lodgepole pine ecosystems.

Concentrations of dissolved organic carbon (DOC) in summer wetfall and bulk deposition in our study area (Table 2) were higher than annual mean values for bulk precipitation at a mountain station in northcentral Colorado (1.52 mg/L; Grant and Lewis 1982). This difference is probably explained in part by higher DOC concentrations in rain than snow (our unpublished data), as the Colorado study included year-round, weekly collections. However, our values for dissolved organic N were very similar to the annual mean (0.18 mg/L) reported by Lewis and Grant (1982), suggesting the possibility of some bias in the DOC analysis in one of these two studies.

Concentrations of DOC in summer wetfall in our study area (2.8 mg/L; Table 2) were higher than those reported by Likens et al. (1983) for central New York State (summer mean, 2.2 mg/L) and central New Hampshire (1.4 mg/L); however, the higher rainfall amounts in those areas led to higher summer deposition of DOC than for our study site. Some slight addition of DOC to our samples from plastic storage bottles may have occurred, although we could not detect any such contamination with our analytical methods.

Atmospheric chemistry

Concentrations of soluble cations in the atmosphere during the growing season (Table 3) were comparable to values reported for other areas of North America. For

TABLE 4. Dissolved organic carbon (DOC) fractions in throughfall for six storm events in 1982 at the Fox Park lodgepole pine stand, southeastern Wyoming

		% of total DOC					
		Hydrophobic			Hydrophilic		
Date	DOC ($mg \cdot L^{-1}$)	Acid	Base	Neutral	Acid	Base	Neutral
26 June	29.2	38.1	0.7	7.2	39.0	5.8	9.2
27 July	30.1	24.2	0.3	23.2	49.0	2.3	1.0
17 Aug.	11.7	42.7	0.8	1.9	46.1	5.1	3.4
6 Sept.	18.8	31.9	0	7.6	48.9	2.6	9.0
13 Sept.	23.1	40.2	0	1.3	39.8	16.4	1.7
16 Sept.	6.5	49.2	0	6.1	0	43.2	1.5

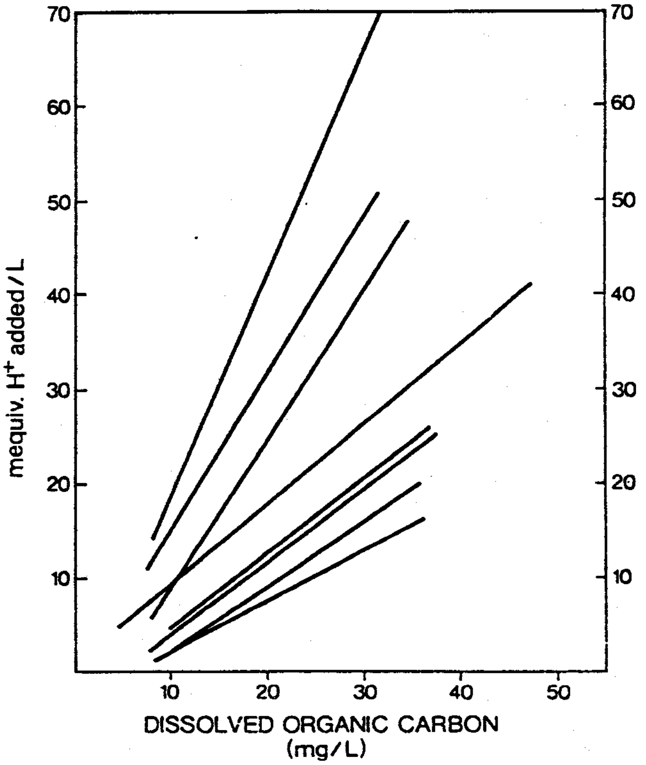

FIG. 2. Relationship between dissolved organic carbon concentration in throughfall and the increase in H^+ concentration of bulk rain during passage through the canopy. Each line represents a linear regression of the 8 to 10 collectors for individual rainfall events (r^2 ranged from 0.85 to 0.99).

Because of these low regression coefficients, the application of the method of Lovett and Lindberg (1984) for estimating dry deposition was not possible for this study. We suspect that the poor explanatory behavior of this regression model in the lodgepole pine ecosystems resulted from high temporal variation in atmospheric chemistry in the study area (Table 3) and the highly variable intensity–duration characteristics of individual summer rain events.

Cation–anion balance and nature of DOC

In contrast to wetfall and bulk deposition, for which cation and anion charges were nearly in balance (Table 2), a large anion deficit usually was observed for throughfall. Based upon the volume-weighted mean, the anion deficit comprised one third of the total ionic charge in throughfall. Assuming that this deficit represents unmeasured organic anions (Hoffman et al. 1980*a*), and adding this deficit to the analytically determined, weak organic acid anions (nonvolatile alkalinity), we calculated that organic anions contributed about 42% of the total anions in throughfall in these lodgepole pine ecosystems. This value compares with about 12% for bulk deposition (Table 2).

The predominance of organic anions which were not detected by our acidimetric titration procedure indicates that most of the organic acids behaved as rather strong acids that remain dissociated at the acidimetric titration end point. Among the low molecular weight organic acids with low pK_a values, citric acid and *p*-hydroxybenzoic acid were identified by gas–liquid chromatography as important components of these throughfall samples; however, the amounts measured were not sufficient to account for the high observed organic anion concentrations. The ratio of organic anion equivalence (80 μequiv./L) to DOC (13.5 mg/L) indicates about 6 μequiv./mg DOC for throughfall, somewhat lower than the commonly cited value of about 10 μequiv./mg DOC for natural waters (Oliver et al. 1983). This result suggests a greater importance of nonionic organic constituents in throughfall than in bog, stream, and lake waters.

Fractionation of DOC (Leenheer and Huffman 1976) of pooled samples from six rainfall events in the Nash Fork stand in 1982 provided an index of the nature of the dissolved organic compounds. Throughfall DOC usually was predominantly acidic but the proportions of hydrophobic and hydrophilic compounds varied markedly among the six events (Table 4). Organic fractions of forest floor leachate in these ecosystems also were acidic but, as expected, the hydrophobic to hydrophilic ratio (1.4; Yavitt and Fahey 1985) was higher than for throughfall (0.85 for five events, Table 4). In one of the fall rain events (16 September), hydrophilic bases replaced acids as components of throughfall DOC.

Other chemical fractionations further elucidated the nature of the DOC in throughfall. Concentrations of a carbohydrate fraction (Handa 1966) were always quite high in throughfall, and based upon simple comparison with glucose standards, this fraction constituted an average 60% of total DOC. Polyphenolics, as indexed by a colorimetric procedure (Rand 1976), were always present at high concentrations in throughfall. The linear correlation between polyphenolics and nonvolatile acidity was high ($r = 0.86$), and some overlap between these analyses seems likely. Malcolm and McCracken (1968) demonstrated the importance of polyphenols and reducing sugars as components of aqueous leaf leachates in pine and oak. In contrast, mobile ions (Parker 1983; Lovett et al. 1985). In contrast, litterfall accounted for much more Ca^{2+} and Mg^{2+} recycling than did canopy leaching, reflecting the lower mobility of these ions in plants (Pate 1975). Future studies of precipitation and throughfall chemistry in these ecosystems could profitably focus upon (*i*) improving estimates of dry deposition, an important vector of element input and (*ii*) identifying the causes of high between-storm variability in canopy leaching, including the physiological explanations for the observed patterns in organic and inorganic fluxes from foliage.

Acknowledgements

We thank the following associates for field and laboratory assistance: R. Campbell, T. Clarke, J. Marshall, J. Pearson, and P. Schwarz. Dr. Dennis Knight provided valuable support throughout the duration of the study, and Drs. W.M. Lewis, Jr. and G.M. Lovett reviewed earlier drafts of the manuscript. This research was supported by grants to D. Knight and T. Fahey from the National Science Foundation (DEB 78-05311, DEB 80-11024, DEB 81-13546, BSR 83-01842).

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