THE CHEMICAL COMPOSITION OF RAINFALL IN THE SOUTHERN PLAINS AND IT'S IMPACT ON SOIL AND WATER QUALITY

TECHNICAL BULLETIN T-162
OCTOBER 1985

AGRICULTURAL EXPERIMENT STATION
DIVISION OF AGRICULTURE
OKLAHOMA STATE UNIVERSITY

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ACKNOWLEDGEMENTS

The assistance of USDA-ARS personnel at Chickasha, El Reno, and Woodward, Oklahoma and Bushland and Riesel-Temple, Texas in providing rainfall, runoff and groundwater samples is gratefully acknowledged.

Research was conducted in cooperation with the USDA-ARS Watershed and Water Quality Laboratory, Durant, Oklahoma 74702-1430, under State Project 1768.

The Chemical Composition of Rainfall in the Southern Plains and its Impact on Soil and Water Quality

Andrew N. Sharpley, Samuel J. Smith, Ron G. Menzel, and Robert L. Westerman. *

SUMMARY

Due to the ubiquitous nature of emissions that can affect the acidity and nutrient content of rainfall and the ease with which they are moved by air masses, the chemical composition of rainfall at several rural Oklahoma and north Texas locations was determined over a number of years (1972-1984). The chemical composition of agricultural watershed runoff, groundwater, and pond water collected from the same areas as rainfall, is included for comparison. The chemical analyses included pH, soluble and total P, nitrate-, ammonium-, nitrite-, and total N, chloride, sulfate, calcium, magnesium, potassium, and sodium content, and electrical conductivity.

Concentrations of soluble P in rainfall samples collected from chemical and open raingages were not significantly different. In contrast, total P, nitrate-N, and ammonium-N concentrations were significantly greater for open raingages due to a contribution of these chemicals in dust-fall to the open raingages during periods of no rain. The transport of soluble P in runoff (0.37 kg $ha^{-1}y^{-1}$) was on average similar to that input in rainfall (0.51 kg $ha^{-1}y^{-1}$), although nitrate-N (14.99 and 4.54 kg $ha^{-1}y^{-1}$) and ammonium-N (15.61 and 2.25 kg $ha^{-1}y^{-1}$) were conserved by the watersheds. The annual cation and chloride inputs in rainfall were generally in the order of 10 kg ha^{-1}, or less. Sulfate inputs, however, ranged from 37-89 kg ha^{-1}. The electrical conductivity of rainfall (39 µmhos cm^{-1}) was appreciably lower than that of groundwater at El Reno (1643 µmhos cm^{-1}), Little Washita (1106 µmhos cm^{-1}), and Woodward locations (816 µmhos cm^{-1}).

* Respectively, Research Soil Scientist; Soil Scientist, USDA-ARS; Soil Scientist, USDA-ARS; and Professor of Agronomy.

The mean annual pH of rainfall was consistently greater than that of "pure" rainfall (5.6). In fact, the average pH of rainfall for the Oklahoma and north Texas locations was 6.4 and 6.5, respectively. Thus, rainfall at these locations has not been acidified. In addition, the average pH of two farm ponds (7.8) was greater than that of rainfall in the same area (6.7). A similar occurrence was noted for surface runoff from the associated watershed soils. If a decrease in the pH of rainfall in the Southern Plains should occur in the future, the impact of the acidity will be reduced to a large extent by the buffering capacity of the area soils.

Appreciably more acid was added annually to the fertilized soil via fertilizer P and N than in rainfall. Under the present conditions it would take up to 1500 years rainfall to add as much acid as added in 1 year via fertilizer application (4.8 kg H ha^{-1} from 28 kg P and 124 kg N ha^{-1} added as diammonium phosphate and ammonium nitrate, respectively). Even with a dramatic decrease in rainfall pH to 4.0, this period would be 10 years. Consequently, rainfall acidity presents no immediate threat to detrimentally affecting the pH of agricultural soils in Oklahoma and north Texas under continuing normal management practices.

INTRODUCTION

The chemical composition of rainfall has become a controversial issue in recent years. In particular, the pH of rainfall has received considerable public attention due to acidification by sulfur and nitrogen gases emitted during the burning of fossil fuels and consequent detrimental effect of acid rain on both aquatic and terrestrial environments. Rainfall is considered acidic if the pH falls below 5.6, the normal equilibration value of carbon dioxide and water at 25° C (Barrett and Brodin, 1955). In many parts of the northeastern U.S., rainfall pH values average between 4.0 and 5.0, with values for some individual storms of less than 3.0 being recorded (Likens et al., 1979). Also, rainfall with pH below 4.0 is becoming increasingly frequent in the southeastern U. S. (EPA, 1980). Several studies have recently associated acid rain with the acidification of lakes and streams in Scandinavia (Wright et al., 1976), the Adirondack

Mountains of New York (Schofield, 1976), and southeastern Ontario (Beamish, 1976).

It has been shown that nutrients contributed in rainfall can play an important part in the nutrient cycle of ecosystems on oligotrophic sites (Carlisle et al., 1966; Miller, 1961). The amounts of nitrogen (N) and particularly phosphorus (P) in rainfall are small compared to the amounts of these elements frequently added annually in fertilizer to agricultural lands. Their direct addition to surface waters in rainfall, however, may be sufficient to enhance algae growth in certain situations. In a study of Lake Michigan, Murphy and Doskey (1975) reported a 30-fold greater total P (TP) concentration in rainfall than in lake water. In fact, the input of P in rainfall may contribute a significant proportion of the total P input in large lakes. For example, Elder (1975) estimated that rainfall P may account for up to 50% of the P entering Lake Superior. Since 25-50% of the TP in rainfall is soluble inorganic P, it is directly available to organisms in the lake (Delumyea and Petel, 1977; Murphy and Doskey, 1975; Peters, 1977). As a result, Schindler and Nighswander (1970) attributed most of the enrichment of Clear Lake, Ontario, to rainfall and similar observations have been made for several Wisconsin lakes by Lee (1973).

Due to the ubiquitous nature of the emissions increasing the acidity and nutrient content of rainfall and the ease with which they are moved by air masses, rainfall chemistry has become of increasing concern. At present little information exists on the chemical nature of rainfall in the Southern Plains area of Oklahoma and north Texas, although Smith et al. (1984) recently reported results of a preliminary survey of rainfall pH in this area. This report presents a chemical analysis of rainfall at several Oklahoma and north Texas locations over a number of years (1972-1984). The data were collected indirectly as a result of several different water quality monitoring studies and are, thus, a collation of that available. Associated watershed runoff, groundwater, and pond data are included for comparison.

MATERIALS AND METHODS

Study Area

Rainfall was collected on USDA watersheds at Chickasha, El Reno, Little Washita River Basin, and Woodward, Oklahoma, and at Bushland and Riesel, Texas (Fig. 1). The raingages were open, recording-type with galvanized metal containers (Nicks, 1971). Included, also, at Chickasha, El Reno, and Woodward was an automatic raingage with a plastic container. This type of raingage was covered between events to reduce "dry-fall" accumulation and automatically uncovered when rain began. Rainfall samples were stored in sealed glass 500 mL bottles and refrigerated at 0-4°C from the time of collection until analysis.

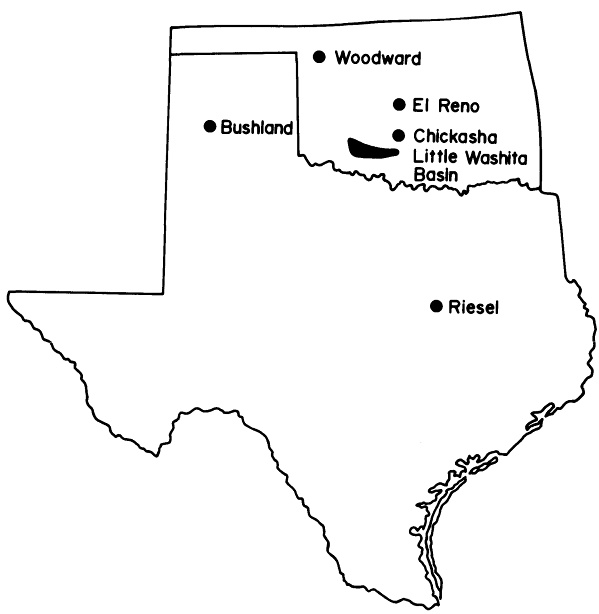

Figure 1. Map of collection sites.

Runoff from the watersheds was measured with precalibrated flumes equipped with FW-1 water-stage recorders. Automatic pumping samplers (Miller et al., 1969) collected from 5 to 15 samples during each runoff event. The samples were composited in proportion to flow, to provide a single representative sample of liquid for chemical analysis for each runoff event and watershed. In addition, groundwater samples were collected from a network of shallow wells (less than 20 m water table depth) at El Reno, Little Washita, and Woodward, Oklahoma (Naney and Smith, 1983). All samples were refrigerated at 0-4°C until analyzed.

The pH of 2 farm ponds in the Little Washita River Basin, southwest of Chickasha, Oklahoma, was measured on site (2-m mean depth) at monthly intervals from March 1980 to June 1981. A Martek[1] probe was used to measure pH and was standardized in the laboratory one to two days before field measurements were taken. The farm ponds are SCS flood detention ponds designated as site 11 (4.4 ha surface area) and 23 (3.7 ha surface area). The watershed of site 11 is 535 ha, primarily grassland with less than 10% of the area cropped. The watershed of site 23 is 250 ha, approximately half grassland and half cropland.

Chemical Analyses

Aliquots of each rainfall, runoff, groundwater, and pond water sample were centrifuged (266 km s^{-1} for 5 min) and filtered (0.45 µm) prior to pH, electrical conductivity (EC), soluble P (SP), nitrate-N (NO_3-N), ammonium-N (NH_4-N), nitrite-N (NO_2-N), chloride (Cl), sulfate (SO_4), and cation (Ca, Mg, K, and Na) determinations.

The pH and EC were measured using a glass electrode and Wheatstone bridge, respectively, on filtered samples at 25°C. Soluble P concentration was determined by the colorimetric method of Murphy and Riley (1962) as was TP following perchloric acid digestion of unfiltered samples (Olsen and Sommers, 1982). Analysis of NO_3-N, NH_4-N, and NO_2-N were conducted using standard methods as described in the Federal Water Pollution Control Administration Manual (USDI, 1971). Chloride was determined using a specific ion electrode, and sulfate by a turbidimetric method (HACH, 1973). The cations Ca, K, Na, and Mg were determined by atomic absorption spectrophotometry.

In the following discussion, means are presented as geometric values and significant differences between data sets are determined by

[1]Mention of trade names or commercial products is for informational purposes only and does not constitute endorsement or preferential treatment by Oklahoma State Univ. or USDA.

analysis of variance for paired or unpaired data using a 5.0% level of significance, unless noted otherwise. Amounts of chemicals input annually in rainfall were calculated from annual rainfall and mean concentrations.

RESULTS

Acidity

The pH of rainfall at Bushland, El Reno, Little Washita, Riesel, and Woodward over a period of several years is summarized in Tables 1 and 2. The mean annual pH of rainfall was greater than that of "pure" rainfall (5.6) at each location and varied from 5.7 to 8.6 (Tables 1 and 2). The lowest pH recorded for an individual rainfall event was 5.2 at El Reno.

The pH of rainfall for individual events at El Reno, Riesel, and Woodward is presented in Figures 2, 3, and 4, respectively. No consistent seasonal variation in rainfall pH was apparent at these locations, or at Bushland, and Little Washita (data not shown). In a study of rainfall pH in Iowa, Tabatabai and Laflen (1976) similarly found no seasonal variation in pH values.

Nutrient Concentrations and Amounts

Phosphorus: Mean annual P concentrations and inputs in rainfall are summarized for Bushland (Table 3), Chickasha (Table 4), El Reno (Table 5), Little Washita (Table 6), Riesel (Table 7), and Woodward (Table 8). The mean annual P concentrations and amounts ranged from 1-81 $\mu g\ L^{-1}$ and 6-308 $g\ ha^{-1}\ y^{-1}$, respectively, with the TP values often several fold higher than SP. No consistent seasonal variation in SP concentration was observed (Fig. 5). Data for 1983 at El Reno and Woodward are given as examples, with the other locations behaving similarly.

The mean SP concentration for rainfall at Bushland (39 $\mu g\ L^{-1}$) averaged for the period of study was significantly greater than that for the other locations, which did not differ significantly (3, 7, 6, 7, and 8 $\mu g\ L^{-1}$ for Chickasha, El Reno, Little Washita, Riesel, and Woodward, respectively). No significant difference in SP concentration of individual rainfall events between years was observed at each location.

Table 1. pH of rainfall at Bushland, Texas and El Reno and Little Washita River Basin, Oklahoma.

Location	Year	Type of raingage[+]	Annual rainfall	Number of observ.[#]	pH Mean	pH Range	Acidity
			mm				g H ha^{-1} y^{-1}
Bushland	1982	O	484	5	6.2	6.0-6.3	3.05
	1983	O	380	8	6.4	6.3-6.6	1.51
	1984	O	488	16	6.5	6.4-6.7	1.54
	Average	O	451	29	6.4		1.80
El Reno	1981	C	906	9	7.5	6.7-8.3	0.29
	1982	C	822	8	5.9	5.2-6.3	10.35
		O		5	5.7	5.6-5.8	16.40
	1983	C	870	17	6.2	5.7-6.6	5.49
		O		8	6.0	5.6-6.3	8.70
	1984	C	735	7	6.4	6.1-6.4	2.93
		O		8	5.9	5.7-6.1	9.25
	Average	C	833	41	6.5		2.63
		O		21	5.9		10.49
Little Washita	1979	O	843	2	6.7	6.5-6.8	1.68
	1980	O	625	8	6.4	6.0-6.8	2.49
	1981	O	940	1	8.6	--	0.02
	Average	O	803	11	6.7		1.60

\+ C and O designate chemical and open raingages, respectively.

\# Number of rainfall events for which analyses were made.

Nitrogen: Mean annual NO_3-N and NH_4-N concentration and inputs in rainfall are summarized for Bushland (Table 9), Chickasha (Table 10), El Reno (Table 11), Little Washita (Table 12), Riesel (Table 13), and Woodward (Table 14). The mean annual NO_3-N and NH_4-N concentrations ranged from 0.21-1.03 and 0.16-1.47 mg L^{-1}, respectively, with amounts ranging from 1.34-7.57 and 1.08-5.95 kg ha^{-1} y^{-1}, respectively. No

Table 2. pH of rainfall at Riesel, Texas and Woodward, Oklahoma.

Location	Year	Type of raingage+	Annual rainfall	Number of observ.#	pH Mean	pH Range	Acidity
			mm				g H ha^{-1} y^{-1}
Riesel	1980	O	1213	9	6.3	5.7-6.8	6.08
	1981	O	1172	5	6.9	6.3-7.5	1.48
	1982	O	664	13	6.4	6.0-7.7	2.64
	1983	O	837	4	7.0	6.9-7.3	0.84
	Average	O	972	31	6.5		3.07
Woodward	1981	O	592	10	6.3	6.0-6.4	2.97
	1982	C	668	2	7.0	6.9-7.0	0.67
		O		12	6.0	5.3-7.0	6.68
	1983	O	640	25	6.8	6.2-7.4	1.01
	1984	O	568	8	6.3	6.1-6.7	2.85
	Average	C	617	2	7.0		0.62
		O		55	6.5		2.13

+ C and O designate chemical and open raingages, respectively.

\# Number of rainfall events for which analyses were made.

significant difference in NO_3-N or NH_4-N concentrations was found from year to year. However, the NO_3-N and NH_4-N concentration of rainfall at Little Washita and Bushland, respectively, was significantly greater than at the other locations. In addition, mean annual NH_4-N concentrations at Bushland were significantly greater than NO_3-N concentrations (Table 9), whereas at the other locations no significant difference between NO_3-N and NH_4-N concentration was observed. No consistent seasonal variation in NO_3-N (Fig. 6) and NH_4-N (Fig. 7) concentration of individual rainfall events was observed. Mean annual NO_2-N concentrations and inputs in rainfall are summarized in Table 15. Nitrite-N concentrations and amounts in rainfall ranged from 4-35 µg L^{-1} and 29-356 g ha^{-1} y^{-1}, respectively, and were approximately 1/30 of NO_3-N concentrations.

Table 3. Concentration and amount of soluble P in rainfall at Bushland, Texas, using an open raingage.

Year	Annual rainfall	Number of observations	Soluble P: Concentration Mean	Soluble P: Concentration Range	Soluble P: Amount
	mm		--- µg L^{-1} ---		g $ha^{-1} y^{-1}$
1978	571	3	13	4 - 27	74
1979	385	7	6	3 - 50	23
1980	353	12	44	3 -162	155
1981	692	18	32	14 - 96	221
1982	484	17	31	0 -142	150
1983	380	8	81	16-184	308
1984	488	16	45	4-158	220
Average	479	81	39		186

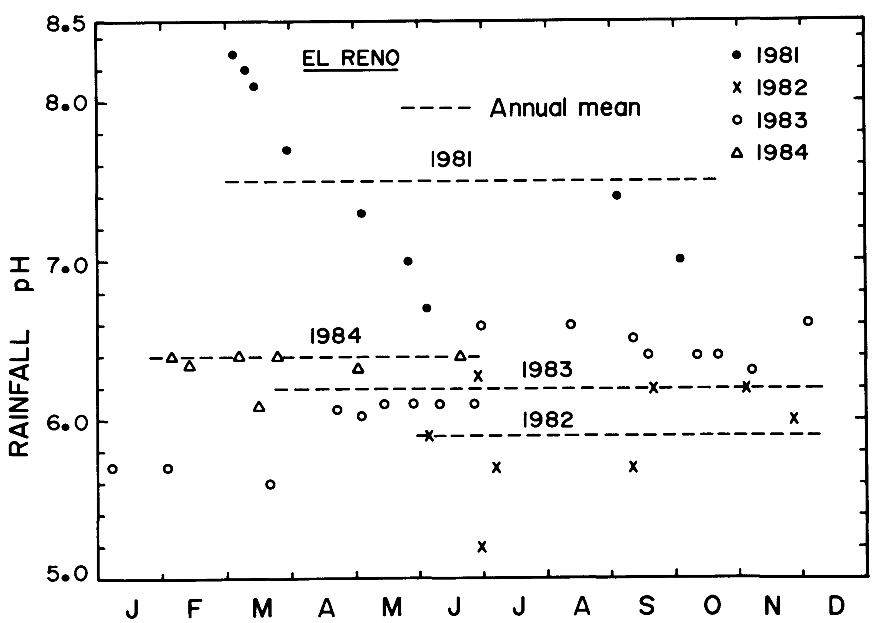

Figure 2. The pH of individual rainfall events at El Reno, Oklahoma.

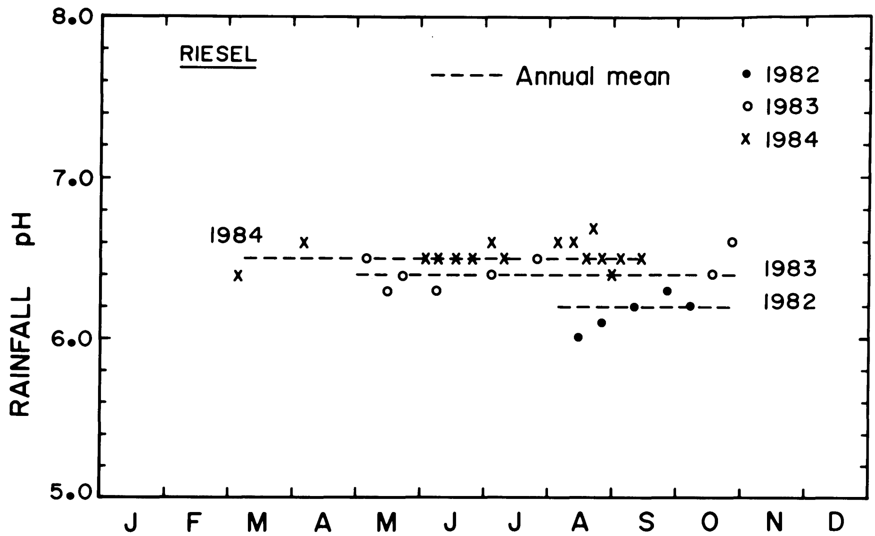

Figure 3. The pH of individual rainfall events at Riesel, Texas.

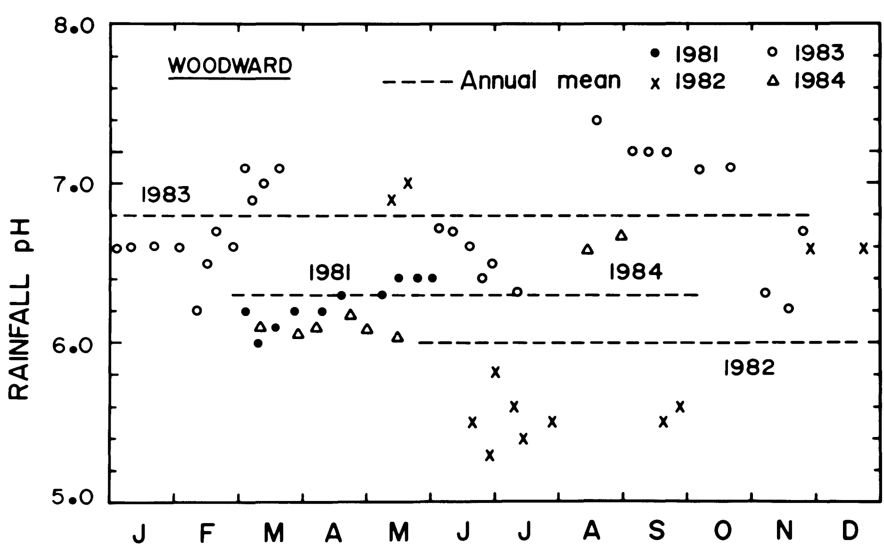

Figure 4. The pH of individual rainfall events at Woodward, Oklahoma.

Table 4. Concentration and amount of soluble and total P in rainfall at Chickasha, Oklahoma.

Year	Type of raingage[+]	Annual rainfall	Number of observ.[#]	Soluble P Concentration Mean	Soluble P Concentration Range	Soluble P Amount	Number of observ.[#]	Total P Concentration Mean	Total P Concentration Range	Total P Amount
		mm		--- $\mu g\ L^{-1}$ ---		$g\ ha^{-1}\ y^{-1}$		---- $\mu g\ L^{-1}$ ----		$g\ ha^{-1}\ y^{-1}$
1972	C	632	3	1	0-4	6	4	21	10-56	133
	O		2	2	0-5	13	4	28	22-42	177
1973	C	1080	25	2	0-10	22	21	16	6-42	173
	O		17	3	1-34	32	13	30	16-122	324
1974	C	727	20	3	1-11	22	19	13	3-110	95
	O		15	5	2-19	36	12	22	5-92	160
1975	C	903	11	4	1-17	36	12	12	2-117	108
	O		9	10	6-25	90	17	18	4-336	163
1976	C	675	4	4	3-5	27	4	15	13-16	101
	O		4	9	3-125	61	4	21	8-205	142
Average	C	803	63	3		18	60	15		120
	O		47	5		24	50	23		185

[+] C and O designate chemical and open raingages, respectively.

[#] Number of rainfall events on which analyses were made.

Table 5. Concentration and amount of soluble P in rainfall at El Reno, Oklahoma.

Year	Type of raingage+	Annual rainfall	Number of observations#	Soluble P: Concentration Mean	Soluble P: Concentration Range	Soluble P: Amount
		mm		--- $\mu g\ L^{-1}$ ----		$g\ ha^{-1}\ y^{-1}$
1978	C	624	19	5	0-86	31
1979	C	939	20	7	1-45	66
1980	C	642	13	6	0-67	39
1981	C	906	23	10	3-60	91
1982	C	822	8	6	0-17	49
	O		11	5	0-52	41
1983	C	870	16	7	0-46	61
	O		8	8	0-21	70
1984	C	735	7	14	6-42	103
	O		8	4	0-34	29
Average	C	791	106	7		55
	O		27	6		47

+ C and O designate chemical and open raingages, respectively.

Number of rainfall events for which analyses were made.

Table 6. Concentration and amount of soluble P in rainfall at the Little Washita River Basin, Oklahoma, using an open raingage.

Year	Annual Rainfall	Number of observations	Soluble P: Concentration Mean	Soluble P: Concentration Range	Soluble P: Amount
	mm		--- $\mu g\ L^{-1}$ ----		$g\ ha^{-1}\ y^{-1}$
1978	709	34	6	1-81	43
1979	843	18	7	1-58	59
1980	625	7	2	1-5	13
1981	940	5	10	3-16	94
Average	779	64	6		47

Table 7. Concentration and amount of soluble and total P in rainfall at Riesel, Texas, using an open raingage.

Year	Annual rainfall	Number of observ.+	Soluble P			Number of observ.+	Total P		
			Concentration				Concentration		
			Mean	Range	Amount		Mean	Range	Amount
	mm		----μg L^{-1}---		g ha^{-1} y^{-1}		---μg L^{-1}---		g ha^{-1} y^{-1}
1977	591	12	4	0-46	24	12	16	6-75	95
1978	885	42	4	0-80	36	--	--	--	--
1979	1122	58	4	1-35	45	--	--	--	--
1980	1213	35	4	0-49	49	--	--	--	--
1981	1172	46	11	0-40	129	--	--	--	--
1982	664	35	12	0-136	80	--	--	--	--
1983	837	4	3	1-9	25	--	--	--	--
Average	926	232	7		65		--		--

+ Number of rainfall events for which analyses were made.

Table 8. Concentration and amount of soluble and total P in rainfall at Woodward, Oklahoma.

Year	Type of raingage[+]	Annual rainfall	Number of observ.[#]	Soluble P Concentration Mean	Soluble P Concentration Range	Soluble P Amount	Number of observ.[#]	Total P Concentration Mean	Total P Concentration Range	Total P Amount
		mm		---μg L^{-1}---		g ha^{-1} y^{-1}		---μg L^{-1}---		g ha^{-1} y^{-1}
1977	C	701	1	6	--	42	--	--	--	--
	O		1	35	--	245	--	--	--	--
1978	C	572	24	5	1-50	29	16	21	7-102	120
1979	C	803	21	5	2-11	40	--	--	--	--
	O		20	3	1-11	24	--	--	--	--
1980	C	636	21	3	0-17	19	--	--	--	--
	O		12	9	0-38	57	--	--	--	--
1981	C	592	10	36	25-56	213	--	--	--	--
	O		10	4	3-6	24	--	--	--	--
1982	C	668	9	4	0-50	27	--	--	--	--
	O		22	4	1-30	27	--	--	--	--
1983	O	640	25	5	0-35	32	--	--	--	--
1984	O	568	8	11	8-17	62	--	--	--	--
Average[++]	C	662	86	8		53		--		--
	O	658	98	4		26		--		--

[+] C and O designate chemical and open raingages, respectively.

[#] Number of rainfall events for which analysis were made.

[++] Mean concentration and amount for 1977 thru 1982 for C and 1979 thru 1984 for O.

Table 9. Concentration and amount of nitrate- and ammonium -N in rainfall at Bushland, Texas, using an open raingage.

Year	Annual rainfall	Number of observ.+	Nitrate-N Concentration Mean	Nitrate-N Concentration Range	Nitrate-N Amount	Ammonium-N Concentration Mean	Ammonium-N Concentration Range	Ammonium-N Amount
	mm		----mg L^{-1}----		kg ha^{-1} y^{-1}	----mg L^{-1}----		kg ha^{-1} y^{-1}
1978	571	3	0.41	0.39-0.41	2.34	0.98	0.95-0.98	5.60
1979	385	12	0.49	0.14-1.07	1.89	0.80	0.27-1.23	3.08
1980	353	7	0.38	0.15-0.19	1.34	1.13	0.00-2.75	3.99
1981	692	18	0.23	0.04-0.75	1.59	0.83	0.33-3.45	5.74
1982	484	12	0.46	0.21-4.20	2.23	0.84	0.30-3.04	4.07
1983	380	8	0.56	0.15-1.02	2.13	1.47	0.30-5.25	5.59
1984	488	16	0.58	0.15-1.68	2.83	1.22	0.58-4.65	5.95
Average	479	76	0.44		2.11	1.01		4.84

+ Number of rainfall events for which analyses were made.

Table 10. Concentration and amount of nitrate- and ammonium-N in rainfall at Chickasha, Oklahoma.

Year	Type of raingage[+]	Annual rainfall	Number of observ.[#]	Nitrate-N Concentration Mean	Nitrate-N Concentration Range	Nitrate-N Amount	Number of observ.[#]	Ammonium-N Concentration Mean	Ammonium-N Concentration Range	Ammonium-N Amount
		mm		----mg L^{-1}----		kg $ha^{-1}y^{-1}$		----mg L^{-1}----		kg $ha^{-1}y^{-1}$
1972	C	632	9	0.24	0.13-0.50	1.52	7	0.21	0.13-0.39	1.33
	O		2	0.49	0.46-0.57	3.10	2	0.22	0.24	1.39
1973	C	1080	34	0.28	0.09-0.57	3.02	34	0.22	0.06-0.84	2.38
	O		32	0.39	0.14-1.03	4.21	30	0.47	0.21-1.01	5.08
1974	C	727	23	0.25	0.08-1.31	1.82	23	0.21	0.08-0.55	1.53
	O		20	0.45	0.15-1.40	3.27	21	0.32	0.10-0.85	2.33
1975	C	903	28	0.22	0.06-0.71	1.99	27	0.22	0.04-0.83	1.99
	O		30	0.46	0.13-1.52	4.15	31	0.36	0.10-1.19	3.25
1976	C	675	14	0.24	0.10-1.50	1.62	14	0.16	0.01-0.54	1.08
	O		12	0.55	0.22-1.25	3.71	12	0.29	0.01-0.74	1.96
Average	C	803	108	0.25		2.01	105	0.21		1.69
	O		96	0.45		3.61	96	0.37		2.97

+ C and O designate chemical and open raingages, respectively.

Number of rainfall events for which analyses were made.

Table 11. Concentration and amount of nitrate- and ammonium-N in rainfall at El Reno, Oklahoma.

Year	Type of raingage	Annual rainfall	Number of observ.#	Nitrate-N Concentration Mean	Nitrate-N Concentration Range	Nitrate-N Amount	Number of observ.#	Ammonium -N Concentration Mean	Ammonium -N Concentration Range	Ammonium -N Amount
		mm		----mg L^{-1}----		kg ha^{-1} y^{-1}		-----mg L^{-1}----		kg ha^{-1} y^{-1}
1977	C	785	7	0.84	0.52-1.08	6.59	7	0.37	0.30-0.53	2.90
1978	C	624	22	0.42	0.18-1.16	2.62	18	0.40	0.20-0.96	2.50
1979	C	939	20	0.31	0.16-0.82	2.91	20	0.29	0.13-0.87	2.72
1980	C	642	13	0.41	0.21-0.84	2.63	13	0.43	0.10-1.03	2.76
1981	C	906	24	0.31	0.13-1.10	2.81	24	0.22	0.00-1.46	1.99
1982	C	822	8	0.33	0.18-0.56	2.71	8	0.44	0.25-0.83	3.62
	O		11	0.48	0.26-1.29	3.95	11	0.34	0.15-0.64	2.79
1983	C	870	17	0.28	0.10-0.69	2.44	17	0.32	0.10-1.08	2.78
	O		8	0.37	0.05-0.71	3.22	8	0.25	0.01-0.65	2.18
1984	C	735	7	0.67	0.44-2.00	4.92	7	0.30	0.10-0.45	2.21
	O		8	1.03	0.24-1.42	7.57	8	0.72	0.23-1.35	5.29
Average	C	790	118	0.37		2.92	114	0.33		2.61
	O	809	27	0.61		4.93		0.43		3.48

+ C and O designate chemical and open raingages, respectively.

Number of rainfall events for which analyses were made.

Table 12. Concentration and amount of nitrate- and ammonium-N in rainfall at the Little Washita River Basin, using an open raingage.

Year	Annual rainfall	Number of observ.+	Nitrate-N Concentration Mean	Nitrate-N Concentration Range	Nitrate-N Amount	Number of observ.+	Ammonium-N Concentration Mean	Ammonium-N Concentration Range	Ammonium-N Amount
	mm		----- $mg\ L^{-1}$ ----		$kg\ ha^{-1}\ y^{-1}$		---- $mg\ L^{-1}$ ----		$kg\ ha^{-1}\ y^{-1}$
1978	709	33	0.78	0.33-3.38	5.53	29	0.41	0.16-1.45	2.91
1979	843	54	0.69	0.13-1.64	5.82	54	0.43	0.07-1.90	3.62
1980	625	8	0.85	0.54-1.19	5.31	8	0.32	0.24-0.67	2.00
1981	940	5	0.21	0.08-0.42	1.97	5	0.22	0.20-0.53	2.07
Average	779	100	0.71		5.53	96	0.40		3.12

+ Number of rainfall events for which analyses were made.

Table 13. Concentration and amount of nitrate- and ammonium-N in rainfall at Riesel, Texas, using an open raingage.

Year	Annual rainfall	Number of observ.[+]	Nitrate-N Concentration Mean	Nitrate-N Concentration Range	Nitrate-N Amount	Number of observ.[+]	Ammonium-N Concentration Mean	Ammonium-N Concentration Range	Ammonium-N Amount
	mm		-----mg L^{-1}----		kg ha^{-1} y^{-1}		-----mg L^{-1}----		kg ha^{-1} y-1
1977	591	12	0.33	0.13-1.70	1.95	12	0.40	0.22-2.08	2.36
1978	885	42	0.32	0.11-1.20	2.83	40	0.33	0.10-1.46	2.92
1979	1122	59	0.30	0.10-1.29	3.37	55	0.24	0.09-1.11	2.69
1980	1213	38	0.44	0.18-1.19	5.34	37	0.34	0.16-0.58	4.12
1981	1172	46	0.27	0.07-1.80	3.16	46	0.25	0.07-1.58	2.93
1982	664	35	0.32	0.07-1.72	2.12	35	0.22	0.06-1.31	1.46
1983	837	4	0.44	0.19-0.66	3.68	4	0.20	0.12-0.54	1.67
Average	926	236	0.33		3.05	229	0.28		2.59

[+] Number of rainfall events for which analyses were made.

Table 14. Concentration and amount of nitrate- and ammonium-N in rainfall at Woodward, Oklahoma.

Year	Type of raingage[+]	Annual rainfall	Number of observ.[#]	Nitrate -N: Concentration Mean	Nitrate -N: Concentration Range	Nitrate -N: Amount	Number of observ.[#]	Ammonium-N: Concentration Mean	Ammonium-N: Concentration Range	Ammonium-N: Amount
		mm		-----mg L^{-1}-----		kg ha^{-1} y^{-1}		-----mg L^{-1}-----		kg ha^{-1} y^{-1}
1977	C	701	4	0.21	0.61-0.41	1.47	4	0.52	0.12-0.56	3.65
	O		6	0.50	0.10-1.02	3.51	6	0.31	0.09-1.04	2.17
1978	C	572	23	0.41	0.14-1.47	2.35	21	0.48	0.20-1.48	2.75
1979	C	803	21	0.31	0.08-0.85	2.49	21	0.41	0.09-0.95	3.29
	O		19	0.56	0.24-1.31	4.50	19	0.54	0.28-1.30	4.34
1980	C	636	21	0.34	0.14-0.84	2.16	20	0.45	0.11-0.89	2.86
	O		12	0.71	0.34-3.35	4.52	12	0.56	0.15-1.23	3.56
1981	C	592	10	0.31	0.15-0.60	1.84	10	0.39	0.25-0.76	2.31
	O		10	0.60	0.27-1.65	3.55	10	0.59	0.36-1.04	3.49
1982	C	668	9	0.33	0.23-0.68	2.20	9	0.29	0.23-1.08	1.93
	O		22	0.52	0.22-2.40	3.47	22	0.22	0.09-0.74	1.47
1983	O	640	25	0.58	0.21-2.59	3.71	25	0.40	0.13-2.98	2.56
1984	O	568	8	1.10	0.40-2.18	6.25	8	0.51	0.40-0.57	2.90
Average[++]	C	662	88	0.34		2.25	85	0.43		2.85
	O	658	102	0.59		3.88	102	0.43		2.83

\+ C and O designate chemical and open raingages, respectively.

\# Number of rainfall events for which analyses were made.

++ Mean concentration and amount for 1977 thru 1982 and 1979 thru 1984 for C and O respectively.

Table 15. Concentration and amount of nitrite-N in rainfall at several locations.

Location	Year	Type of raingage[+]	Annual rainfall	Number of observ.[#]	Nitrite-N Concentration Mean	Range	Amount
			mm		$\mu g L^{-1}$		$g\ ha^{-1}\ y^{-1}$
Chickasha	1972	C	632	7	8	5 - 17	51
		O		7	35	9 - 114	221
	1973	C	1080	31	5	0 - 16	54
		O		31	33	7 - 79	356
	1974	C	727	23	4	1 - 23	29
		O		23	18	7 - 63	131
	1975	C	903	27	16	2 - 66	144
		O		32	23	8 - 141	208
	1976	C	675	14	6	1 - 14	41
		O		14	27	16- 71	182
Average[¶]		C	803	102	8		64
		O		107	26		209
El Reno	1978	C	624	14	10	4 - 173	62
Riesel	1977	O	591	12	10	3 - 35	59
	1978	O	885	14	8	2 - 19	71
Average		O	738	26	9		66
Woodward	1977	C	701	4	10	10- 10	70
		O		6	30	20- 60	210
	1978	C	572	15	10	10- 50	57
Average		C	637	19	10		64
		O	701	6	30		191

[+] C and O designate chemical and open raingage, respectively.

Anions and Cations: Mean annual concentrations and inputs in rainfall of the anions Cl and SO_4 and cations Ca, Mg, K, and Na are summarized in Tables 16 and 17, respectively, for locations where these parameters were measured. Mean annual concentrations of Cl and SO_4 ranged from 0.8-27.4 and 5.2-16.4 mg L^{-1}, respectively, with amounts ranging from 7-258 and 37-89 kg ha^{-1} y^{-1}, respectively (Table 16). Mean annual Ca concentration of rainfall ranged from 1.04-6.09, Mg 0.16-0.77, K 0.10-0.51, and Na 0.30-9.05 mg L^{-1}, with amounts ranging from 9.0-29.7, 1.4-3.8, 0.8-3.3, and 1.1-78.7 kg ha^{-1} y^{-1} for Ca, Mg, K, and Na, respectively (Table 17). The concentrations of Na observed in 1983 at El Reno were markedly higher than other years and locations and, thus, the samples may have been contaminated.

Electrical Conductivity: The EC of rainfall at Bushland, El Reno, Little Washita, and Woodward locations is summarized in Table 18. Mean annual EC values ranged from 22-89 µmhos cm^{-1}. No significant variation in EC of rainfall was found between locations. Observed EC values are higher than that of distilled water (4 µmhos cm^{-1}) but appreciably lower than tap water at the Durant Laboratory (400-3400 µmhos cm^{-1}).

DISCUSSION

Comparison of Chemical and Recording Raingages

The pH of rainfall collected by the chemical raingages was significantly greater than that collected by the open raingages at El Reno only (mean values of 6.18 and 5.87 for chemical and open raingages, respectively, Table 19). Concentrations of SP in samples collected from chemical and open raingages were not significantly different. In contrast, TP, NO_3-N, and NH_4-N concentrations were significantly greater for the open raingage (Table 19 and 20). This results from a contribution of these chemicals in dustfall to the open raingages during periods of no rain. Since the contribution from dustfall is a natural occurrence, the open raingages may represent a more realistic chemical input from the atmosphere.

Table 16. Concentration and amount of chloride and sulfate in rainfall at several locations.

Location	Year	Type of raingage[+]	Annual rainfall	Number of observ.[#]	Chloride Concentration Mean	Chloride Concentration Range	Chloride Amount	Number of observ.[#]	Sulfate Concentration Mean	Sulfate Concentration Range	Sulfate Amount
			mm		----mg L^{-1}----		kg ha^{-1} y^{-1}		----mg L^{-1}----		kg ha^{-1} y^{-1}
El Reno	1983	C	870	16	0.8	0.7 - 1.5	7	8	5.4	0 - 10.6	47
		O		7	0.8	0.6 - 1.3	7	-	--	--	--
Little Washita	1978	O	709	--	--	--	--	23	5.2	4.8 - 9.9	37
	1979	O	843	2	3.2	2.7 - 3.8	27	2	7.7	5.7 - 10.5	65
	1980	O	625	1	1.6	1.6	10	1	9.5	9.5	59
	1981	O	940	1	27.4	27.4	258	1	9.5	9.5	89
Riesel	1983	O	837	3	1.1	0.9 - 1.7	9	--	--	--	--
Woodward	1982	C	668	2	2.1	1.8 - 2.5	14	2	13.2	12.6 - 13.9	88
	1983	O	640	11	1.8	0.8 - 5.0	12	--	--	--	--
	1984	O	317	2	3.0	1.7 - 4.2		2	16.4	16.3 - 16.5	52

[+] C and O designate chemical and open raingages, respectively.

[#] Number of rainfall events for which analyses were made.

Table 17. Concentration and amount of calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na) in rainfall.

Location	Year	Type of raingage[+]	Annual rainfall	Cation	Number of observ.[#]	Concentration Mean	Concentration Range	Amount
			mm			------mg L^{-1}------		kg ha^{-1} y^{-1}
Bushland	1982	O	484	Ca	5	2.06	1.49 - 2.83	10.0
				Mg		0.43	0.24 - 0.71	2.1
				K		0.22	0.10 - 0.76	1.1
				Na		0.32	0.14 - 0.54	1.6
	1983	O	380	Ca	8	2.79	0.92 - 4.55	10.6
				Mg		0.55	0.18 - 1.05	2.1
				K		0.20	0.08 - 0.45	0.8
				Na		0.30	0.08 - 0.45	1.1
	1984	O	488	Ca	29	6.09	0.38 - 27.00	29.7
				Mg		0.77	0.18 - 3.98	3.8
				K		0.41	0.06 - 5.67	2.0
				Na		0.46	0.12 - 2.80	2.2
El Reno	1983	C	870	Ca	16	1.91	0.70 - 24.20	16.6
				Mg		0.23	0.08 - 0.87	2.0
				K		0.37	0.05 - 1.09	3.2
				Na		9.05	8.33 - 9.84	78.7
	1983	O		Ca	7	1.04	0.12 - 24.40	9.0
				Mg		0.16	0.08 - 0.44	1.4
				K		0.27	0.05 - 0.56	2.3
				Na		8.90	8.13 - 9.32	77.4
	1984	C	735	Ca	25	1.85	0.34 - 4.87	13.6
				Mg		0.16	0.07 - 0.30	1.2
				K		0.10	0.04 - 0.21	0.7
				Na		0.48	0.17 - 0.84	3.5
Woodward	1983	O	640	Ca	9	2.47	1.15 - 5.70	15.8
				Mg		0.43	0.13 - 3.21	2.8
				K		0.51	0.15 - 5.32	3.3
				Na		0.87	7.24 - 11.20	5.6
	1984	O	568	Ca	25	3.16	0.68 - 8.58	17.9
				Mg		0.29	0.09 - 0.81	1.7
				K		0.16	0.06 - 0.50	0.9
				Na		0.81	0.37 - 1.99	4.6

[+] C and O designate chemical and open raingages, respectively.

[#] Number of rainfall events for which analyses were made.

Table 18. Electrical conductivity of rainfall at Bushland, Texas and El Reno, Little Washita River Basin, Woodward, Oklahoma.

Location	Year	Type of raingage+	Annual rainfall	Number of observ.#	Electrical conductivity Mean	Electrical conductivity Range
			mm		------ μmhos cm^{-1} -----	
Bushland	1982	0	484	5	42	28 - 93
	1983	0	380	8	44	18 - 81
	1984	0	488	16	39	18 - 76
	Average			29	41	
El Reno	1983	C	870	1	41	---
	1984	C	735	7	43	23 - 87
		0		8	58	17 - 94
	Average	C	866	8	43	
		0		8	58	
Little Washita	1979	0	843	4	50	26 - 84
	1980	0	625	1	59	---
	1981	0	940	1	22	---
	Average	0	803	6	47	
Woodward	1984	0	568	2	89	84 - 94

\+ C and 0 designate chemical and open raingages, respectively.

Number of rainfall events for which analyses were made.

Table 19. Comparison of mean pH and soluble and total P in rainfall collected by chemical and open raingages. Number of observations is in parenthesis.

Location	Type raingage[+]	pH	Soluble P	Total P
			---------μg L^{-1}--------	
Chickasha	C	--	10 (47)	11 (50)[a]
	O	--	29	23
El Reno	C	6.18 (41)[a]	7 (106)	--
	O	5.87 (21)	9 (27)	--
Woodward	C	6.95 (53)	8 (86)	--
	O	6.42 (14)	4 (86)	--

+ C and O designate chemical and open raingages, respectively. Significant difference (5.0% level) between C and O as identified by a, was determined by analysis of variance for paired data for Chickasha, and unpaired data for the El Reno and Woodward locations.

Table 20. Comparison of mean nitrate-, ammonium-, and nitrite-N in rainfall collected by chemical and open raingages. Number of observations is in parenthesis.

Location	Type of raingage[+]	Nitrate-N	Ammonium-N	Nitrite-N
		--------mg L^{-1}----------		--μg L^{-1}--
Chickasha	C	0.28 (96)[a]	0.10 (102)[a]	8 (102)[a]
	O	0.45	0.37	26
El Reno	C	0.37 (118)[a]	0.33 (114)	--
	O	0.71 (27)	0.53 (27)	--
Woodward	C	0.34 (88)[a]	0.43 (85)	10 (19)[a]
	O	0.59 (102)	0.43 (102)	30 (6)

+ C and O designate chemical and open raingages, respectively. Significant difference (5.0% level) between C and O as identified by a, was determined by analysis of variance for paired data for Chickasha, and unpaired data for the El Reno and Woodward locations.

Chemical Composition of Rainfall

Although the pH of rainfall at all locations was not acidic compared to "normal" values (5.6), a statistically significant decrease in the mean annual pH of rainfall was measured for both 1982 and 1983 compared to 1981 at El Reno (Table 1). This decrease may be attributed to the fact that 1980 had a lower than average amount of rainfall (642 mm, 105 mm below annual average). Consequently, the drier soil was more susceptible to wind erosion and since the pH of the prairie soils in the El Reno area is generally greater than the pH of "pure" rain (5.6), the airborne material probably increased the pH of subsequent rainfall. In other words, the pH of rainfall in 1982 and 1983 is considered close to normal and that in 1981 elevated by the preceding dry year (Table 1). The risk in obtaining misleading estimates of rainfall pH by collecting infrequent samples is, thus, emphasized.

In the case of the nutrient content of rainfall, average concentrations of SP over the study period at Bushland (39 $\mu g\ L^{-1}$) was greater than the critical value associated with eutrophication (10 ug L^{-1}, Sawyer, 1947). Consequently, inputs of P in rainfall can contribute to the nutrient enrichment of surface waters (Elder, 1975; Lee, 1973; Schindler and Nighswander, 1970). The fact that concentrations of SP in rainfall can be higher than the critical value associated with eutrophication, indicates that it is unrealistic to attempt to attain or maintain P concentrations in many relatively pristine surface waters below these levels.

Agronomically, however, the inputs of acid, P, Cl, and cations are not of major importance. For example, the maximum annual TP input was 0.324 kg $ha^{-1}\ y^{-1}$ at Chickasha in 1973, Table 4), which is 100-fold lower than annual fertilizer P applications frequently used in the Southern Plains area (30 kg $ha^{-1}\ y^{-1}$). In contrast, the input of N (NO_3-N and NH_4-N) in rainfall was up to 10 kg $ha^{-1}\ y^{-1}$, which may be of considerable importance to grass production. In addition, the input of sulfate (37-89 kg ha^{-1}) may be agronomically significant in some cases. For example, this is an annual sulphur (S) input of 12-30 kg ha^{-1} and annual crop requirements of S can vary from 11 to 49 kg ha^{-1} for a 3.36 Mg ha^{-1} soybean (50 bushels $acre^{-1}$) and 12.54 Mg ha^{-1} corn (200 bushels $acre^{-1}$) yield, respectively (Bixby and Beaton, 1970).

The greater concentration of SP and NH_4-N at Bushland compared to the other locations may result from an increased amount of airborne soil material from the close proximity to the sampling location of a large commercial cattle feedlot . No consistent seasonal variation in SP, NO_3-N, and NH_4-N concentration of rainfall was observed at Woodward and El Reno during 1983 (Figs. 5, 6, and 7). The other locations and years also showed no seasonal trends.

It is apparent that nutrient concentrations in rainfall can vary according to the geography of the collection site and human activities. Olson et al. (1973) observed that the amounts of total N (TN) in rainfall ranged from 5.6 to 15.7 kg ha^{-1} y^{-1} from west to east in an area of intensive livestock farming in Nebraska. In contrast, Taylor et al. (1971) attributed an increase in the nutrient concentration of rainfall at Coshocton, Ohio, over a ten-year period to an increase in automobile traffic in the several major population centers located within a 400-500 km distance from Coshocton. Although variations in the concentration of P and N in rainfall during the year were measured by Allen et al. (1968) and Schuman and Burwell (1974), no seasonal trends were observed. In addition, these workers reported no consistent relationship between the quantity of rainfall and the concentrations of P and N in rainfall.

Mean pH, SP, TP, NO_3-N, NH_4-N (Table 21), EC, SO_4, Cl, and cation concentration (Table 22) of rainfall at the Oklahoma and north Texas locations for each study period, are compared with rainfall concentrations at other geographic locations. The pH of rainfall in Oklahoma and north Texas is not as acidic as that of the Midwestern and Southeastern states (Table 21). This is consistent with earlier reports which have indicated the industrialized Midwestern states as possible sources of acid rain (Cogbill and Likens, 1974; NADP, 1981; National Research Council, 1981) and with prevailing winds which transport these atmospheric chemicals away from Oklahoma.

Overall, SP and TP concentration in rainfall in Oklahoma and north Texas is lower than at the other locations reported, although no consistent differences were apparent (Table 21). Electrical conductivity and concentrations of Ca and SO_4 of rainfall in Oklahoma were slightly greater than those reported for other locations with

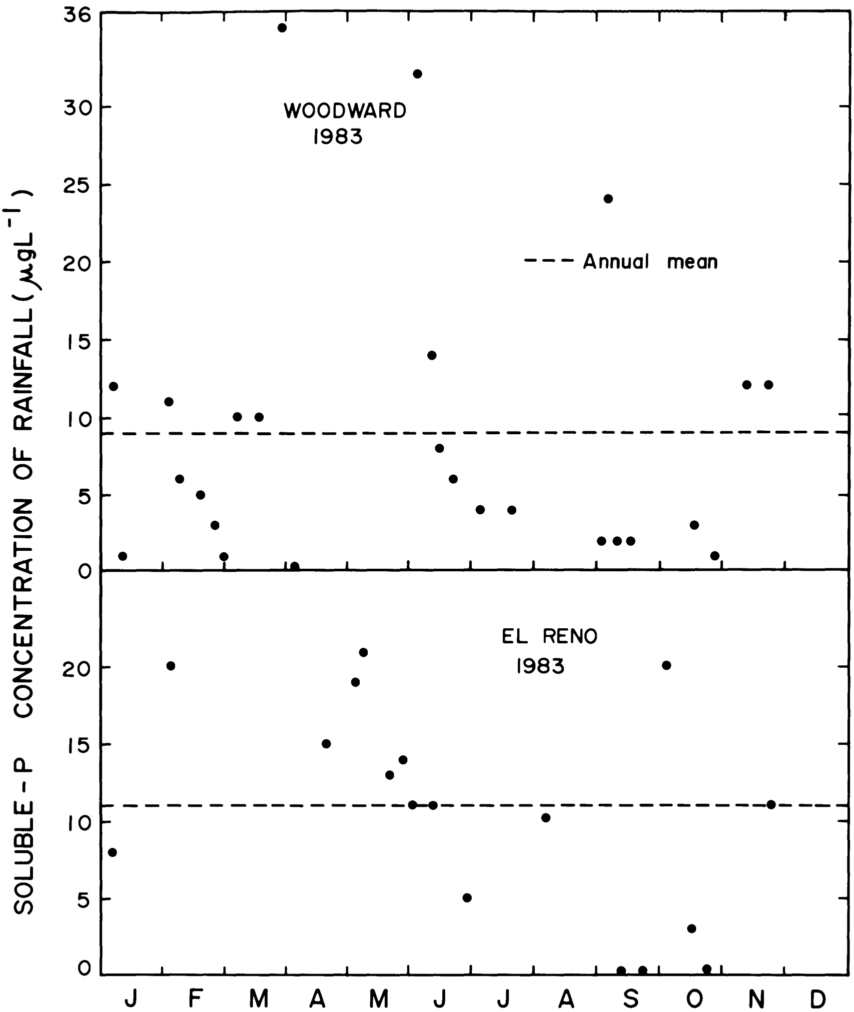

Figure 5. The soluble P concentration of individual rainfall events at Woodward and El Reno, Oklahoma.

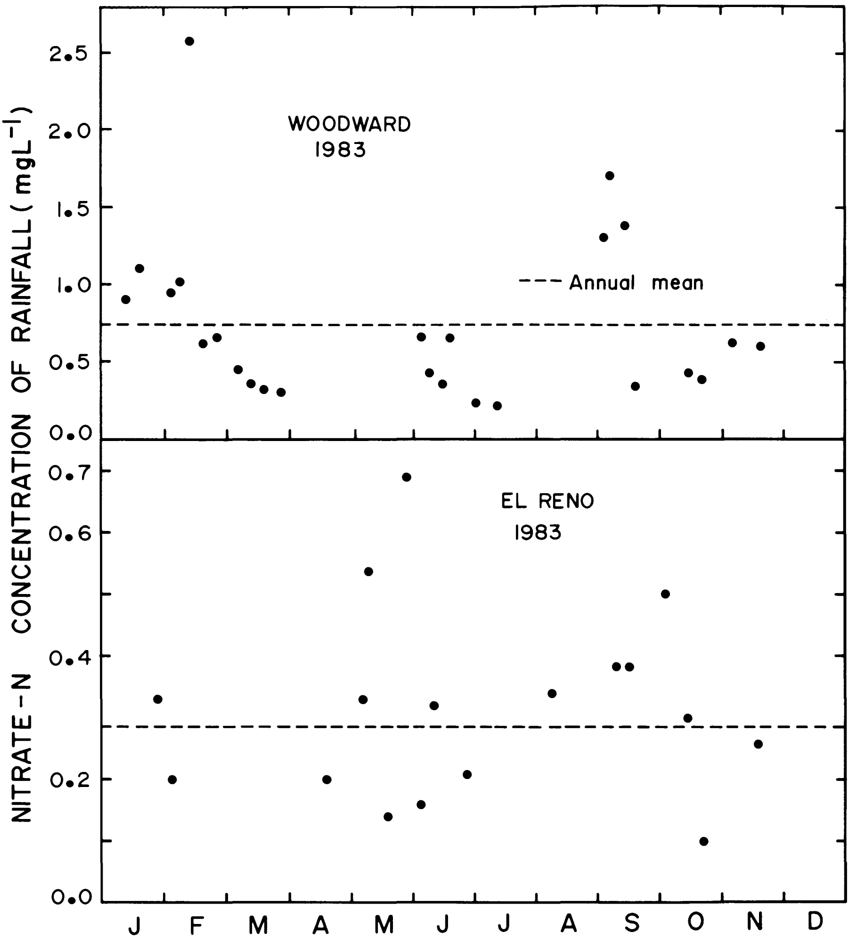

Figure 6. The nitrate-N concentration of individual rainfall events at Woodward and El Reno, Oklahoma.

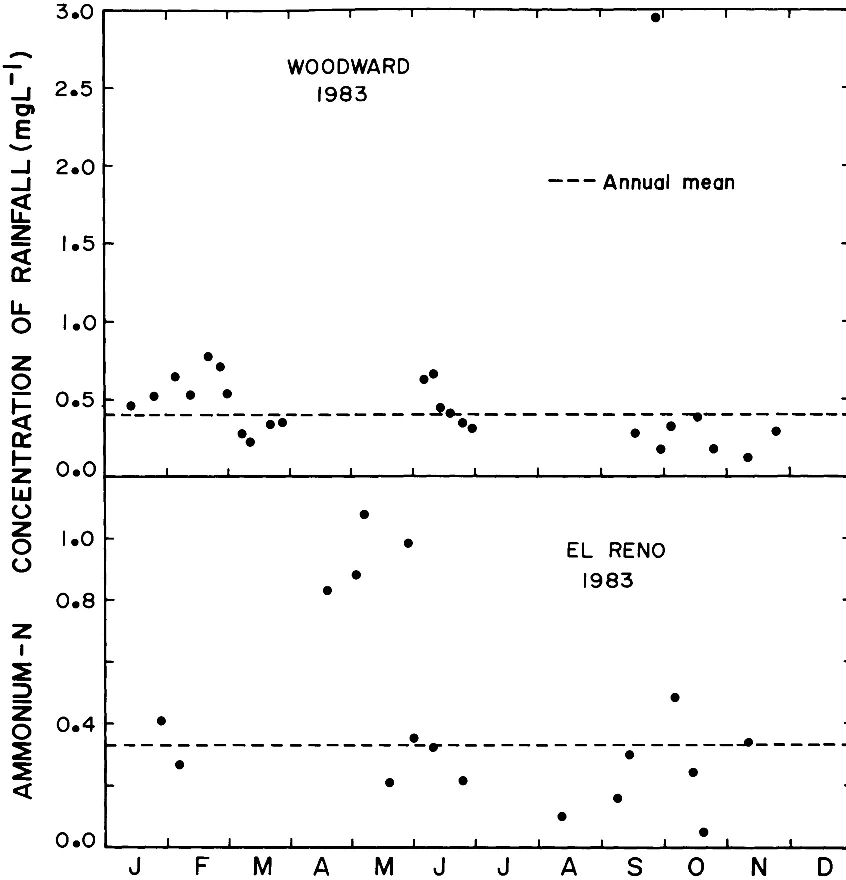

Figure 7. The ammonium-N concentration of individual rainfall events at Woodward and El Reno, Oklahoma.

Table 21. Mean pH, soluble and total P, and nitrate- and ammonium-N concentrations in rainfall in Oklahoma and North Texas in comparison with several other locations.

Location	Period of study	Rain amount	pH	Soluble P	Total P	Nitrate N	Ammonium N	Reference
		mm		---------------mg L^{-1}			--------------	
Oklahoma								
Chickasha	1972-1976	803	--	0.003	0.015	0.25	0.24	Present study
El Reno	1978-1984	791	6.47	0.007	--	0.37	0.33	Present study
L. Washita	1978-1981	779	6.65	0.006	--	0.71	0.40	Present study
Woodward	1977-1983	662	6.46	0.008	0.021	0.34	0.43	Present study
Texas								
Bushland	1978-1984	479	6.42	0.030	--	0.46	1.04	Present study
Riesel	1977-1983	926	6.53	0.007	0.016	0.33	0.28	Present study
Georgia	1979-1981	1162	4.50	0.060	--	1.30	0.36	Walker (1982)
Iowa	1971-1973	887	6.27	--	--	0.51	0.47	Tabatabai et al. (1981)
Indiana	1974-1976	849	--	0.045	0.413	1.13	0.43	Tabatabai et al. (1981)
Michigan	1972	775	4.54	0.028	0.043	0.44	0.29	Tabatabai et al. (1981)
Minnesota	1971-1974	775	5.63	0.009	0.060	0.29	0.36	Tabatabai et al. (1981)
Nebraska	1970-1972	460	5.99	0.051	--	0.75	1.37	Tabatabai et al. (1981)
Ohio	1975-1977	996	4.32	0.036	0.190	0.80	0.39	Tabatabai et al. (1981)
New Zealand	1974-1976	970	--	0.008	0.037	0.23	--	Sharpley and Syers (1979)
New York	1970-1971	981	--	0.005	0.020	0.27	0.29	Klausner et al. (1974)

little difference apparent for Cl, Mg, K, and Na concentrations (Table 22). Apart from pH, SP, Ca, and SO_4 concentrations, therefore, the chemical composition of rainfall in Oklahoma and north Texas is similar to that for other geographical locations.

Comparison of Rainfall and Runoff Chemistry

The above discussion is limited to the chemical composition of rainfall, however, contact with soil may change its composition. The chemical composition of rainfall and runoff, groundwater and pond water at each location was compared to evaluate the changes occurring after contact.

Surface runoff: Native soil P and applied fertilizer resulted in an appreciable increase in SP concentration in surface runoff from El Reno, Riesel, and Woodward watersheds compared, with rainfall at these locations (Table 23). In the case of N, however, concentrations of NO_3-N and NH_4-N in rainfall were greater than in surface runoff from the unfertilized watersheds (Table 23, FR1, Y14, and W2). Fertilizer N application resulted in an increased transport of N as NO_3-N and NH_4-N in surface runoff.

Due to the greater volume of rainfall at these locations than surface runoff, amounts of SP contributed annually in rainfall were greater than those lost in runoff for El Reno and Woodward locations (Fig. 8 and Table 24). At Riesel, however, the opposite was true (Fig. 8). Both NO_3-N and NH_4-N were conserved at each location and watershed, such that amounts input annually in rainfall were greater than those lost in surface runoff from unfertilized and fertilized watersheds (Fig. 8 and Table 24).

In other areas of the country, Burwell et al. (1975) found less SP and more NO_3-N and NH_4-N in rainfall than was lost annually in surface runoff in Minnesota. Taylor et al. (1971) reported that N in rainfall at Coshocton, Ohio, averaged 20.3 kg ha^{-1} y^{-1} for a 2-year period and exceeded by 6 times the average annual N in runoff. During a 2-year period, Schuman and Burwell (1974) found that rainfall in Iowa contributed an average of 7.26 kg $ha^{-1}y^{-1}$ inorganic N. This was four to seven times greater than the average annual surface runoff N from the high- and normal-fertility watersheds, respectively.

Table 22. Mean electrical conductivity, sulfate, chloride, and cation concentration of rainfall in Oklahoma and north Texas in comparison with several other locations.

Location	Period of study	Rain amount	Elect. cond.	SO_4	Cl	Ca	Mg	K	Na	Reference
		mm	μmhos cm^{-1}	------------------mg L^{-1}------------------						
Oklahoma										
El Reno	1983-1984	866	43	5.4	0.8	1.91	0.16	0.19	3.95	Present study
L. Washita	1979-1981	803	47	8.6	8.8	--	--	--	--	Present study
Woodward	1982-1984	542	49	13.2	1.2	1.61	0.18	0.14	0.45	Present study
Texas										
Bushland	1982-1983	478	41	--	--	2.38	0.33	0.17	0.20	Present study
England										
Abbots Moss	1965-1966	950	--	--	--	1.50	0.30	0.60	1.50	Allen et al. (1968)
Grindale	1962-1065	1690	--	--	--	0.73	0.35	0.20	2.63	Allen et al. (1968)
Kerloch	1965-1966	950	--	--	--	0.70	0.40	0.40	1.50	Allen et al. (1968)
Merlewood	1965-1966	1500	--	--	--	0.80	0.20	0.20	1.50	Allen et al. (1968)
Silpho	1965-1966	1160	--	--	--	0.90	0.40	0.40	3.10	Allen et al. (1968)
Georgia	1979-1981	1162	28	3.0	0.5	0.24	0.13	0.18	0.47	Walker (1982)
Michigan	1972	775	23	3.2	--	0.46	0.13	--	--	Walker (1982)
Minnesota	1972-1974	775	12	2.2	--	0.45	0.09	0.14	0.14	Tabatabai et al. (1981)
Ohio	1975-1977	996	44	--	--	0.80	0.20	0.60	0.20	Tabatabai et al. (1981)

Table 23. Average chemical concentration of rainfall (geometric) and runoff (flow-weighted) at El Reno, Riesel, and Woodward locations for 1982 and 1983.

Location	Year	pH		Soluble P		Nitrate-N		Ammonium -N		Chloride	
		Rain	Runoff	Rain	Runoff	Rain	Runoff	Rain	Runoff	Rain	Runoff
El Reno[+]				----ug L^{-1}----		----------mg L^{-1}----------					
FR1	1982	5.90	--	6	113	0.33	0.03	0.44	0.22	--	--
FR5			--		353		3.59		0.50		--
FR1	1983	6.20	6.42	7	90	0.28	0.01	0.32	0.14	0.8	1.6
FR5			6.48		248		0.86		0.93		2.8
Riesel[#]											
Y	1982	6.40	--	12	329	0.32	4.75	0.22	0.12	--	--
Y14			--		93		0.31		0.08		--
Y	1983	7.00	--	3	346	0.44	0.51	0.20	0.24	1.1	--
Y14			--		168		0.06		0.04		--
Woodward[¶]											
W2	1982	7.00	--	4	151	0.33	0.29	0.29	0.12	2.7	--
W4			--		192		0.48		0.11		--
W2	1983	6.80	6.32	5	239	0.58	0.92	0.40	0.29	1.8	--
W4			6.95		173		0.94		0.05		--

[+] Watershed management is - FR1, native grass, no fertilizer P or N added; FR5, Wheat with 20 kgP and 96 kgN $ha^{-1}y^{-1}$ broadcast in Sept.

[#] Y, 60% bermuda grass and 40% a 3-year rotation of cotton, oats, sorghum with 36 kgP and 90 kgN $ha^{-1}y^{-1}$ for grass, 40 kgP and 90 kgN $ha^{-1}y^{-1}$ for sorghum, 40 kgP and 45 kgN $ha^{-1}y^{-1}$ for cotton and 27 kgP and 54 kgN $ha^{-1}y^{-1}$ for oats broadcast in May; Y14, Klein grass receiving no P or N.

[¶] W2, native grass receiving no P or N; W4, wheat with 55 kgN $ha^{-1}y^{-1}$ applied in March and 25 kgP and 56 kgN $ha^{-1}y^{-1}$ in Sept.

Table 24. Amount of soluble P, nitrate-N, and ammonium-N in rainfall and runoff at El Reno, Riesel and Woodward locations.

Location		Years of study	Soluble P		Nitrate-N		Ammonium-N	
			Rain	Runoff	Rain	Runoff	Rain	Runoff
	TOTAL INPUT ($kg\ ha^{-1}$)							
El Reno+	FR1	5	0.39	0.26	13.68	0.25	13.59	0.51
	FR5			0.34		1.93		0.51
Riesel#	Y	6	0.36	0.87	18.77	12.75	16.46	1.71
	Y14			1.16		11.59		10.35
Woodward¶	W2	6	0.37	0.18	12.51	0.30	16.79	0.15
	W4			0.25		0.42		0.26
	AVERAGE ANNUAL INPUT ($kg\ ha^{-1}y^{-1}$)							
El Reno	FR1	5	0.08	0.06	2.74	0.06	2.71	0.13
	FR5			0.07		0.39		0.10
Riesel	Y	6	0.06	0.15	3.13	2.13	2.74	0.19
	Y14			0.19		1.93		1.72
Woodward	W2	6	0.06	0.03	2.09	0.05	2.80	0.03
	W4			0.04		0.07		0.04

Watershed Management:

+ FR1, native grass, no fertilizer P or N added; FR5, Wheat with 20 kgP and 96 kgN $ha^{-1}y^{-1}$ broadcast in Sept.

Y, 60% bermuda grass, and 40% a 3-year rotation of cotton, oats, sorghum with 36 kgP and 96 kg N $ha^{-1}y^{-1}$ for grass, 40 kgP and 90 kgN $ha^{-1}y^{-1}$ for sorghum, 40 kgP and 45 kgN $ha^{-1}y^{-1}$ for cotton, and 27 kgP and 54 kgN $ha^{-1}y^{-1}$ for oats broadcast in May; Y14, Klein grass receiving no P or N.

¶ W2, native grass receiving no P or N; W4, wheat with 55 kgN $ha^{-1}y^{-1}$ applied in March and 25 kgP and 56 kgN $ha^{-1}y^{-1}$ in Sept.

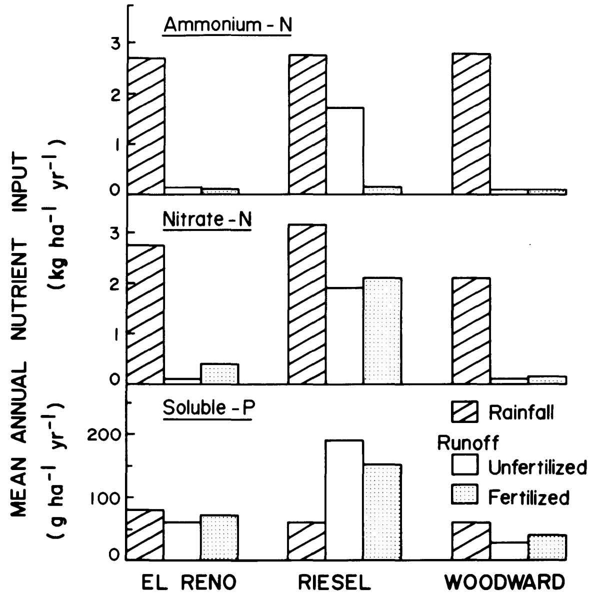

Figure 8. Mean annual input of soluble-P, nitrate-N, and ammonium-N in rainfall and runoff from unfertilized and fertilized watersheds at El Reno, Riesel, and Woodward for 1981 and 1982.

Groundwater: An increase in pH of groundwater compared to rainfall was measured at El Reno but at Woodward a decrease occurred (Fig. 9 and Table 25). These chemical changes result from passage of groundwater through differing subsoil and geologic deposits. The SP, NO_3-N, and NH_4-N concentration of rainfall increased on passage through the soil profile at each location (Fig. 9 and Table 25). The EC of groundwater was appreciably greater than that of rainfall at El Reno, Little Washita, and Woodward locations (Fig. 9 and Table 25). Electrical conductivity is frequently used as an index of total soluble salt concentration, an important criterion of irrigation water quality, because its salinity level can produce yield-limiting soil salinity values under general field conditions (Branson et al., 1975). For example, if the EC is less than 4000 µmhos cm^{-1}, no crop is likely to suffer from general salt injury, but when EC exceeds 8000 µmhos cm^{-1}, only tolerant crops will give satisfactory yields (US Salinity

Table 25. Average chemical composition of rainfall and groundwater at El Reno, Little Washita, and Woodward, Oklahoma.

Parameter	El Reno[+]			Little Washita			Woodward	
		Groundwater			Groundwater			Groundwater
	Rain	Pasture	Wheat	Rain	Pasture	Wheat	Rain	Sorghum
pH	6.20	6.70	6.54	6.64	--	--	6.80	6.54
Electrical conductivity (µmhos cm^{-1})	41	629	1643	41	1307	1106	35	815
Soluble P (µg L^{-1})	7	191	22	5	25	115	5	14
Nitrate-N (mg L^{-1})	0.28	0.47	2.72	0.60	0.46	1.15	0.58	4.41
Ammonium-N (mg L^{-1})	0.32	0.57	0.52	0.33	0.28	0.54	0.40	0.15
Chloride (mg L^{-1})	1	49	258	15	28	28	2	118
Sulfate (mg L^{-1})	5	199	192	10	575	146	--	103

[+] El Reno, Little Washita, and Woodward data for 1983, 1980 to 1982, and 1983, respectively, with rainfall data from chemical, open, and open raingages.

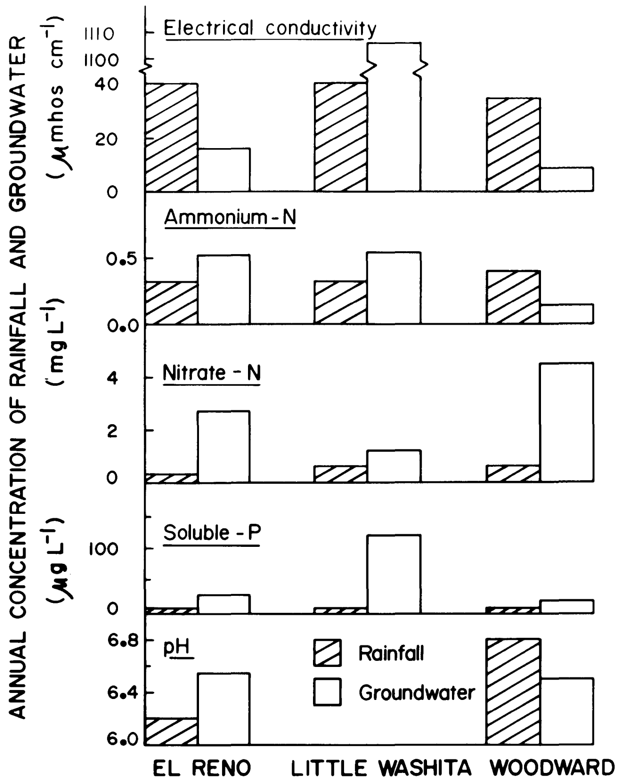

Figure 9. Mean annual pH and concentration of soluble-P, nitrate-N, and ammonium-N in rainfall and groundwater at El Reno (1983), Little Washita (1980-1982), and Woodward, Oklahoma (1983).

Laboratory, 1954). When EC exceeds 16000 μmhos cm^{-1}, only a few very tolerant crops are likely to give economic yields. Consequently, at the present time, groundwater at El Reno, Little Washita, and Woodward will not result in salt damage to crops if used as irrigation water.

An increase in Cl and especially SO_4 concentration in groundwater occurred after rainfall had passed through the soil profile (Table 25), as a result of geologic salt and gypsum deposits (Naney and Smith, 1983). Little information has been published previously comparing the chemical composition of rainfall and groundwater. Consequently, comparison of the present results with other geographic locations cannot be made.

Pond Water: The pH of the two small farm ponds (2-m average depth) during 1980 and 1981 is shown in Fig. 10. A decrease in the pH of water from both ponds was observed during the cooler winter months with a corresponding increase in the warmer months (Fig. 10). These seasonal fluctuations in pH result in part from changes in the biological productivity of the farm ponds. In the cooler winter months with less daylight, the production of CO_2 by respiring aquatic biota exceeds photosynthetic O_2 production. The CO_2 produced dissolves in the pond water and reduces the pH (Fig. 10). During the warmer months, photosynthetic O_2 production dominates and the pH of pond water tends to increase.

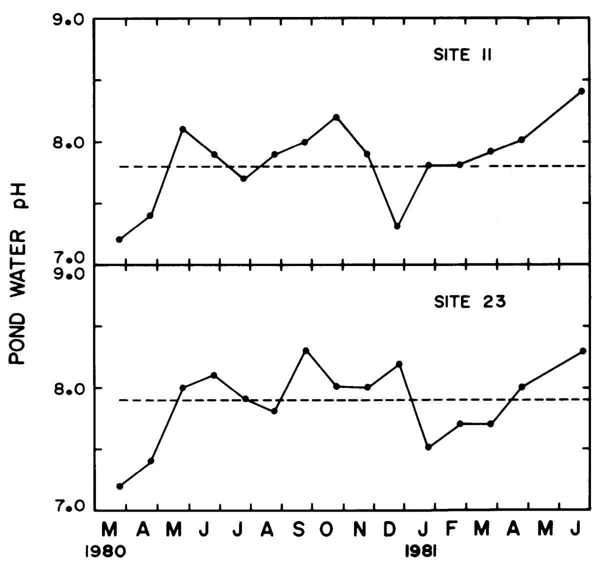

Figure 10. The pH of water from two ponds near Chickasha, Oklahoma, at monthly intervals from March 1980 to June 1981.

The lowest pH recorded at both pond sites during this period was 7.2 (Table 26). Since the pH of rainfall in the area (Little Washita) averaged 6.7 for 1981 (Table 1), the associated watershed soils increased the pH of surface and subsurface runoff. For instance, the mean pH range of surface runoff from subwatersheds contributing to the ponds in 1981 was 7.1 to 7.3. Although the pH of only two farm ponds

Table 26. pH of rainfall and 2 farm ponds in the Little Washita River Basin, Oklahoma, for the period March 1980 to June 1981.

Location	Number of observations	pH	
		Mean	Range
Rainfall	11	6.6	6.0 - 8.6
Pond 11	15	7.8	7.2 - 8.4
Pond 23	15	7.9	7.2 - 8.3

was monitored a similar situation is expected at other locations where alkaline soils predominate.

Comparison of Rainfall and Fertilizer Acidity

The acid equivalent of annual fertilizer P and N applications to El Reno and Woodward watersheds was calculated from the amount of fertilizer P and N added and potential acidity of fertilizer material used (Slack, 1976). The following acid equivalents were used - monoammonium phosphate, 13 g H kg^{-1}, diammonium phosphate, 14 g H kg^{-1}; and ammonium nitrate, 12 g H kg^{-1}. Annual acidic inputs from rainfall and fertilizer material are presented for fertilized El Reno and Woodward watersheds during 1981 and 1982 in Table 27. The amount of acid contributed by rainfall was very small compared to that added in fertilizer material. Even if the pH of rainfall at Woodward decreased from the present average of 6.5 to 4.0, with an average annual rainfall of 660 mm, it would still take almost 10 years to add as much acid as added in fertilizer material in 1981 (4.8 kg H ha^{-1}, W3 and W4, Table 27). Thus, the amount of acidity in rainfall is small in comparison with the potential of soils to neutralize incoming acidity. Furthermore, lime is frequently added to agricultural soil to negate fertilizer P and N acidity (1 kg of H ion is chemically equivalent to 50 kg $CaCO_3$).

A similar situation is evident at other geographic locations. For example, the average annual application of fertilizer N in the U.S. is about 56 kg ha^{-1} for cropland (CAST, 1984). If applied as

Table 27. Acid equivalent (kg H ha^{-1}) added in rainfall and fertilizer to watersheds at El Reno and Woodward in 1981 and 1982.

Location	Year	Fertilizer applied+		Acid input	
		P	N	Fertilizer	Rain
		-----kg P ha^{-1}-----		-------kg H ha^{-1}-------	
El Reno					
FR5	1981	20	92	3.6	$2.8x10^{-4}$
FR6		20	92	3.6	
FR7		20	58	2.4	
FR8		20	58	2.4	
FR2	1982	20	57	2.3	$103x10^{-4}$
FR4		20	57	2.3	
FR5		20	134	5.1	
FR6		20	134	5.1	
FR7		20	134	5.1	
FR8		20	134	5.1	
Woodward					
W3	1981	28	124	4.8	$29.6x10^{-4}$
W4		28	124	4.8	
W3	1982	21	98	3.8	$6.6x10^{-4}$
W4		21	98	3.8	

+ Fertilizer applied as monoammonium phosphate (1 kg P = 0.013 kg H) and ammonium nitrate (1 kg N = 0.036 kg H) to El Reno and diammonium phosphate (1 kg P = 0.014 kg H) and ammonium nitrate at Woodward watersheds.

anhydrous ammonia, urea, or ammonium nitrate - three commonly used N fertilizers - 2 kg H would be produced (as nitric acid) and require 100 kg $CaCO_3$ for neutralization. Some crops are fertilized much more heavily. Corn commonly receives upwards of 112 kg fertilizer N ha^{-1}. A good crop of alfalfa that fixes 270 kg of atmospheric N ha^{-1} would produce an acid equivalent of 11 kg H ha^{-1} requiring more than 550 kg Ca CO_3 ha^{-1} (CAST, 1984).

For the production of optimum crop yields, soil pH values are maintained high enough for good growth by lime applications. As the additions of acidity from rainfall are small relative to additions from management practices and internal sources in the soil and lime is frequently added, rainfall acidity will not have a measureable effect on the pH of cropped soils subject to normal management practices (CAST, 1984; McFee, 1977; Reuss, 1977).

CONCLUSIONS

In general, rainfall inputs of SP, NO_3-N and NH_4-N to the watersheds studied, were greater than those lost in runoff for both unfertilized and fertilized soils. Therefore, input of these nutrients in rainfall represents a net addition to the soil. From an agronomic standpoint, the inputs of acid, P, Cl, and cations in rainfall are not of major importance, although inputs of N (as NO_3-N and NH_4-N) and S (as SO_4) in rainfall can contribute a significant proportion of the uptake of these elements by grasses or crops.

The mean annual pH of rainfall was consistently greater than that of "pure" rainfall (5.6) for the Oklahoma and north Texas agricultural locations for periods covering 1972-1984. In fact, the average pH of rainfall for the Oklahoma and north Texas locations was 6.4 and 6.5, respectively. Obviously therefore, rainfall at these locations has not been acidified. In addition, the average pH of two farm ponds (7.8) was greater than that of rainfall in the same area (6.7). A similar occurrence was noted for surface runoff from the associated watershed soils. Therefore, if a decrease in the pH of rainfall in the Southern Plains should occur in the future, the impact of the acidity will be reduced to a certain degree by the buffering capacity of the area soils. This would be especially so in those areas containing soils with considerable calcium carbonate, such as the Blackland Prairie and Grand Prairie.

Appreciably more acid was added annually to the fertilized soils via fertilizer P and N than in rainfall. Under present conditions it would take up to 1500 years rainfall to add as much acid as added in 1 year via fertilizer application. Even with a dramatic decrease in rainfall pH to 4.0, this period would be 10 years. Consequently, rainfall acidity presents no immediate threat to detrimentally affecting the pH of agricultural soils in Oklahoma and North Texas under continuing normal management practices.

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