RAINFALL AND WATER QUALITY IN THE SOUTHERN PLAINS

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ABSTRACT

The chemical composition of rainfall, agricultural runoff, groundwater, and pond water at several rural Oklahoma and north Texas locations was determined over a number of years (1972-1985). The inputs of acid, P, Cl, and cations in rainfall are not of major agronomic 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) averaging 6.5, while the average pH of two farm ponds (7.8) was even greater than that of rainfall. If a decrease in the pH of rainfall in the Southern Plains should occur in the future, the impact of the acidity on surface water will be reduced to a certain degree by the buffering capacity of the area soils. Appreciably more acid was added annually to the agricultural soils of the area via fertilizer P and N than in rainfall. Under present conditions it would take up to 1,500 years rainfall to add as much acid as added by fertilizer in one year. Even with a dramatic decrease in rainfall pH to 4.0, this period would be 10 years. Thus, rainfall acidity presents no immediate threat to agricultural soils, groundwater, or lakes in Oklahoma and north Texas under continuing management practices, although periodic monitoring is recommended due to an increasing number of coal-fired power stations located in this area.

INTRODUCTION

The acidification of rainfall has received considerable public attention due to increased amounts of sulfur and nitrogen gases emitted during the burning of fossil fuels and consequent detrimental effect of acid rain on both aquatic and terrestrial environments (Burns et al., 1981; Hileman, 1981). Rainfall is considered acidic if the pH falls below 5.6; the normal equilibration value of carbon dioxide and water at 25°C (Barett 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). 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).

The contribution of nutrients in rainfall can play an important part in the nutrient cycle of ecosystems in oligotrophic lakes (Carlisle et al. 1966; Miller, 1961). Their direct addition to surface waters in rainfall may be sufficient to enhance algal growth in certain situations. For example, Elder (1975) estimated that rainfall phosphorus may account for up to 50 percent of the Pentering Lake Superior. Since 25-50 percent of the TP in rainfall is soluble inorganic phosphorus (SP), 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. Relatively little attention has focused on the Southern Plains, but for several years we have participated in a series of cooperative studies to assess the impact of rainfall pH and nutrient contributions on agricultural lands and farm ponds (Sharpley et al. 1985; Smith et al. 1984). This paper presents an overview and update of the chemical analysis of rainfall at several Oklahoma and north Texas locations over a number of years (1972-1985). Associated watershed runoff, groundwater and pond water quality data at the same locations are included for comparison.

MATERIALS AND METHODS

Rainfall was collected on USDA grassed and cultivated watersheds at Chickasha, El Reno, Little Washita River Basin, and Woodward, Oklahoma, and Bushland and Riesel, Texas. The rain gauges 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, 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. No appreciable changes in pH (within $\pm$ 0.2 units) were measured during storage.

Runoff from the watersheds was measured with precalibrated flumes equipped with FW-1 water-stage recorders, with samples collected automatically (Miller et al. 1969). The samples were composited in proportion to flow, to provide a flow-weighted sample for analysis for each runoff event and watershed. 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 two 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 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 percent of the area cropped. The watershed of site 23 is 250 ha, approximately half grassland and half cropland.

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, nitrate-N (NO_3-N), ammonium-N (NH_4-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 phosphorus 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 and NH_4-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 means and significant differences between data sets are determined by analysis of variance for paired or unpaired data using a 5.0 percent level of significance. Amounts of chemicals input annually in rainfall were calculated from annual rainfall and mean concentrations.

RESULTS AND DISCUSSION

Nutrient Concentrations and Amounts

Mean annual SP, TP, NO_3-N, and NH_4-N concentration and inputs in rainfall are summarized in Table 1. The mean SP concentration for rainfall at Bushland (40 μg L^{-1}) averaged for the period of study was significantly greater than that for the other location, which did not differ significantly (3,9,6,7, and 6 μg L^{-1} for Chickasha, El Reno, Little Washita, Riesel, and Woodward, respectively). Similarly, the NO_3-N and NH_4-N concentration of rainfall at Little Washita (0.71 mg NO_3-N L^{-1}) and Bushland (0.70 mg NH_4-N L^{-1}), respectively, was significantly greater than at the other locations. The greater concentration of SP

Table 1.—Mean annual concentration and amount of soluble P, total P, nitrate-N, and ammonium-N in rainfall at several Southern Plains locatons.

LOCATION	PERIOD	MEAN ANNUAL RAINFALL	OBS.	SOLUBLE P CONC MEAN	SOLUBLE P CONC RANGE	SOLUBLE P AMOUNT	TOTAL P CONC MEAN	TOTAL P CONC RANGE	TOTAL P AMOUNT
		mm		μg L^{-1}		g ha^{-1} yr^{-1}	μg L^{-1}		g ha^{-1} yr^{-1}
Bushland	1978-1985	490	101	40	0-184	196	—	—	—
Chickasha	1972-1976	803	63	3	0-125	24	15	2-336	120
El Reno	1978-1985	809	135	9	0-241	73	—	—	—
L. Washita	1978-1981	779	64	6	1-81	47	—	—	—
Riesel	1977-1983	926	232	7	0-136	65	—	—	—
Woodward	1977-1985	680	138	6	0-241	41	—	—	—

and NH_4-N at Bushland compared to the other locations may result from an increased amount of airborne soil material from a large commercial cattle feedlot located 1 km southwest of the sampling site.

Mean annual concentrations and inputs in rainfall of the anions Cl and SO_4 and EC are summarized in Table 2. The cations Ca, Mg, K and Na are summarized in Table 3. Agronomically the inputs of P, N, 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, which is 100-fold lower than annual fertilizer phosphorus applications frequently used in the Southern Plains area (20 kg phosphorus 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 (Woodmansee, 1978). In addition, the input of SO_4 (41-44 kg ha^{-1}) may be agronomically significant in some cases. For example, this is an annual sulphur (S) input of 13-15 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.)

Acidity

The pH of rainfall at each location is summarized in Table 4. The mean annual pH of rainfall was greater than that of "pure" rainfall (5.6) at each location and varied from 6.6. to 6.8. The lowest pH recorded for an individual rainfall event was 5.2 at El Reno. No consistent seasonal variation in rainfall pH was apparent at any of the locations. In a study of rainfall pH in Iowa, Tabatabai and Laflen (1976) similarly found no seasonal variation in pH values.

A statistically significant decrease in the mean annual pH of rainfall was measured for both 1982 (5.9) and 1983 (6.2) compared to 1981 (7.5) at El Reno. 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). Conse-

Table 2.—Mean annual concentration and amount of chloride, sulfate, and electrical conductivity of rainfall at several Southern Plains locations.

LOCATION	PERIOD	MEAN ANNUAL RAINFALL	OBS.	CHLORIDE CONC MEAN	CHLORIDE CONC RANGE	CHLORIDE AMOUNT	SULFATE CONC MEAN	SULFATE CONC RANGE	SULFATE AMOUNT	ELECTRICAL CONDUCTIVITY MEAN	ELECTRICAL CONDUCTIVITY RANGE
		mm		mg L^{-1}		kg ha^{-1} yr^{-1}	mg L^{-1}		kg ha^{-1} yr^{-1}	μmhos cm^{-1}	
Bushland	1982-1985	479	49	—	—	—	—	—	—	35	10-76
El Reno	1983-1985	845	33	1.1	0.6-2.3	9	4.9	0.0-10.6	41	36	17-89
L. Washita	1978-1981	779	4	8.9	2.7-27.4	69	5.7	4.8-10.5	44	47	26-84
Riesel	1983	837	3	1.1	0.9-1.7	9	—	—	—	—	—
Woodward	1982-1985	705	67	1.4	0.6-5.0	10	5.9	0.0-23.5	42	35	17-109

Table 3.—Mean annual concentration and amount of calcium, magnesium, potassium and sodium in rainfall at several Southern Plains locations.

LOCATION	PERIOD	MEAN ANNUAL RAINFALL	OBS.	CATION	CONCENTRATION MEAN	CONCENTRATION RANGE	AMOUNT
		mm			mg L^{-1}		kg ha^{-1} yr^{-1}
Bushland	1982-1985	479	62	Ca	4.11	0.38–27.00	19.7
				Mg	0.55	0.06–3.98	2.6
				K	0.52	0.06–5.67	2.5
				Na	0.38	0.08–2.80	1.8
El Reno	1982-1985	839	65	Ca	1.56	0.12–24.40	13.1
				Mg	0.19	0.07–0.87	1.6
				K	0.38	0.04–4.76	3.2
				Na	3.57	0.17–9.84	30.0
Woodward	1983-1985	717	86	Ca	2.19	0.43–8.58	15.7
				Mg	0.22	0.05–3.21	1.6
				K	0.58	0.06–5.32	4.2
				Na	0.80	0.32–11.20	5.7

Table 4.—Mean annual pH of rainfall at several Southern Plains locations.

LOCATION	PERIOD	MEAN ANNUAL RAINFALL	OBS.	pH		
				MEAN	RANGE	AMOUNT
		mm				g H ha^{-1}yr^{-1}
Bushland	1982-1985	479	49	6.7	6.0–7.3	0.96
El Reno	1981-1985	853	58	6.7	5.2–8.3	1.70
L. Washita	1979-1981	803	11	6.7	6.0–6.8	1.60
Riesel	1980-1983	972	31	6.5	5.7–7.7	3.07
Woodward	1981-1985	682	107	6.8	5.3–7.4	1.08

quently, the drier soil was more susceptible to wind erosion and since the pH of the prairie soils in 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. The risk in obtaining misleading estimates of rainfall pH by collecting infrequent samples is thus emphasized.

Comparison of Rainfall and Runoff Chemistry

The above discussion is limited to the chemical composition of rainfall; however, contact with soil changes 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: Due to the greater volume of rainfall than surface runoff, amounts of SP contributed annually in rainfall were greater than those lost in runoff for El Reno and Woodward locations (Fig. 1). At Riesel, however, the opposite was true (Fig. 1). Both NO_3-N and NH_4-N were conserved at each location and watershed (Fig. 1.).

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} yr^{-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.

Groundwater: An increase in pH of groundwater compared to rainfall was measured at El Reno but at Woodward a decrease occurred (Fig. 2). These chemical changes result from passage of groundwater through differing subsoil and geologic deposits. The SP, NO_3-N and NH_4-N concentration

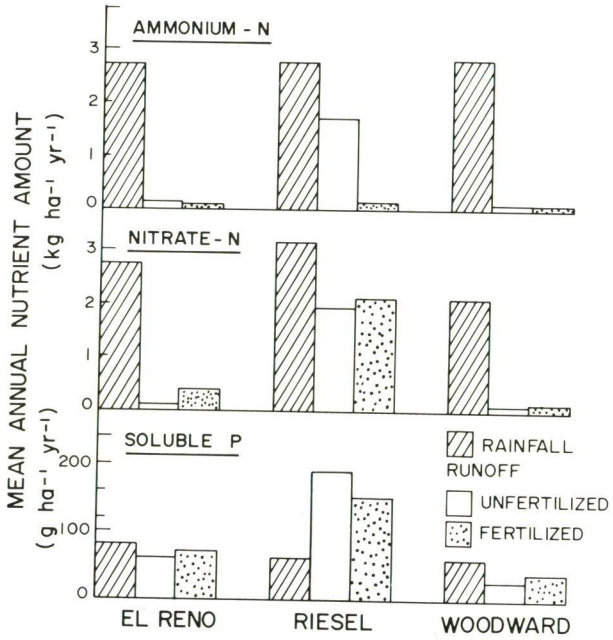

Figure 1.—Mean annual input of soluble P, nitrate-N, ammonium-N in rainfall and runoff from unfertilized and fertilized watersheds at El Reno (1981 to 1985), Riesel (1981 to 1983), and Woodward (1981 to 1985).

of rainfall increased on passage through the soil profile at each location, except for NH_4-N at Woodward (Fig.2.). The EC of groundwater was appreciably greater than that of rainfall at El Reno, Little Washita, and Woodward locations (Fig. 2). Electrical conductivity is frequently used as an index of total soluble salt concentration, an important criterion of irrigation water quality, because high salinity levels (generally when EC exceeds 8,000 μmhos cm^{-1}) can reduce crop yields (Branson et al. 1975; U.S. Salinity Laboratory, 1954). 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.

Pond Water: The pH of the two small farm ponds (2-m average depth) during 1980 and 1981 is shown in Fig. 3. A decrease in the pH of water from both ponds was observed during the cooler winter months with a corresponding increase in the warmer

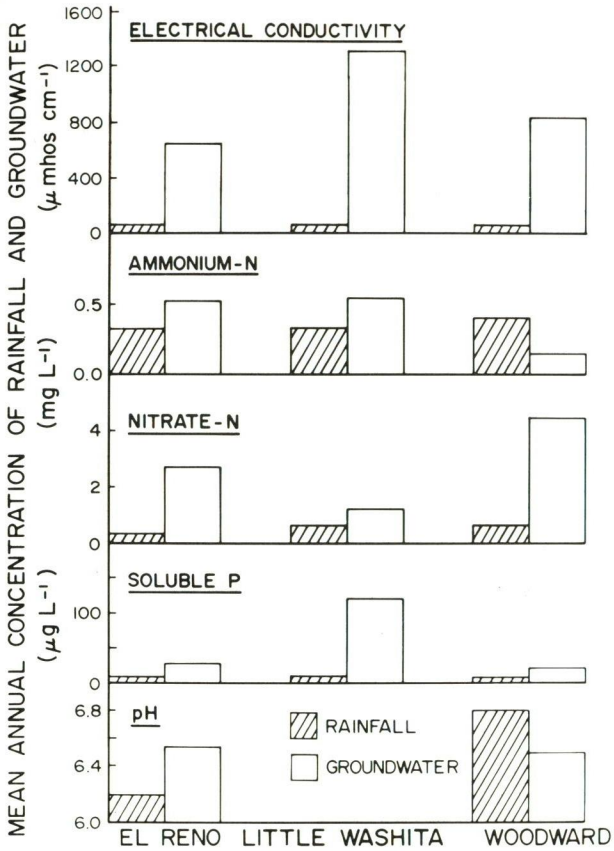

Figure 2.–Mean annual pH and concentrations of soluble P, nitrate-N, ammonium-N, and electrical conductivity in rainfall and groundwater at El Reno (1983 to 1985), Little Washita (1980 to 1982), and Woodward, Oklahoma (1983 to 1985).

months (Fig. 3). 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 carbon dioxide

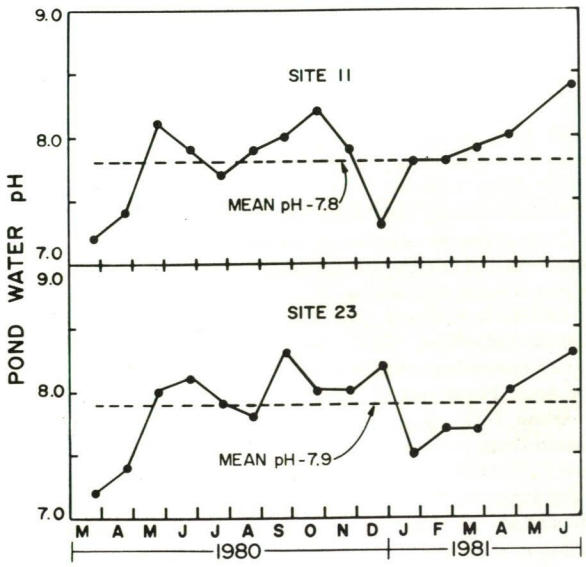

Figure 3.–The pH of water from two ponds near Chickasha, Oklahoma, at monthly intervals from March 1980 to June 1981.

by respiring aquatic biota exceeds photosynthetic oxygen production. The carbon dioxide produced dissolves in the pond water and reduces the pH (Fig. 3). During the warmer months, photosynthetic oxygen production dominates and the pH of pond water tends to increase.

The lowest pH recorded at both pond sites during the study period was 7.2 (Fig. 3). Since the pH of rainfall in the area (Little Washita) averaged 6.6 for the same period, 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 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 phosphorus and N applications to El Reno and Woodward watersheds was calculated from the amount of fertilizer phosphorus 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 ammomium nitrate, 12 g H kg^{-1}. The amount of acid contributed by rainfall (2.8 to 103 x 10^{-4} kg H ha^{-1} yr^{-1}) was very small compared to that added in fertilizer material (2.3 to 5.1 kg H ha^{-1} yr^{-1}). 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,). 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 phosphorus and N acidity (1 kg of H ion is chemically equivalent to 50 kg $CaCO_3$).

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 1979-1985. 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 on a water body 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 phosphorus and N than in the 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 and subsequently surface water in Oklahoma and north Texas under continuing normal management practices.

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