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RAINWATER QUALITY IN SOUTHEASTERN ARIZONA RANGELAND

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INTRODUCTION

The effect of "acid rain" on the environment has become a concern in many parts of the world, particularly in the more industrialized nations. The effects have been studied extensively in Europe and, to a lesser extent, in the northeastern United States, but very little information on rainwater quality is available from the southwestern United States (Lewis and Grant 1980; Marsh 1977). This paper is based on precipitation samples collected since 1975 by the U.S. Department of Agriculture, Science and Education Administration (USDA-SEA), Southwest Rangeland Watershed Research Center, at the Walnut Gulch field station near Tombstone, Arizona. The purposes of the study were (1) to develop background rainwater quality information for input to other rangeland resource models, and (2) to determine what effect, if any, possible rainwater contamination would have on the Walnut Gulch experimental rangeland watershed in southeastern Arizona.

LOCATION

The rainwater samples were collected at a single raingage site near Tombstone, Arizona (Fig. 1). Possible sources of rainwater contamination include farmed land in the Sulfur Springs Valley, to the east and northeast, and the metropolitan Tucson area, about 95 km to the northwest. The most likely sources of contamination are the copper smelters at Douglas, about 65 km to the southeast (Fig. 1), at Cananea, about 80 km south-southwest, and at San Manuel, Hayden, Superior, and Miami, about 110 to 190 km to the northwest. Other possible sources are the copper smelters at Morenci, about 160 km to the northeast, and at Silver City, about 210 km to the northeast.

WATER QUALITY ANALYSIS

All parts of the precipitation collector that contact the atmospheric moisture are inert materials to minimize contamination of the collected sample. An automated cover for the collecting cone prevents contaminants from entering the system both before and after each event. Samples collected in plastic bags were removed soon after rainfall.

Immediately after the samples were collected, pH and electrical conductivity (EC) were determined. On weekends, the samples were collected and refrigerated and, measurements of pH and EC made on Monday morning. Immediately after sample collection, a 4-ml aliquot for NO_3-N analysis was placed in a 5-ml vial containing 20 microliters of chloroform, capped, and refrigerated at 4° C until analysis, usually within a month.

The sodium, potassium, calcium, and magnesium (Na^+, K^+, Ca^{++}, and Mg^{++}) cations were analyzed with a Perkin-Elmer 403 Spectrophotometer* using standard procedures as outlined in the Perkin-Elmer Methods Manual (Perkin-Elmer, 1976). Anions of sulfate and orthophosphate (SO_4 and PO_4) were determined with a Technicon Auto Analyzer Industrial 11 System.* For the SO_4, Industrial Method No. 226-72W, range 0-10 ppm (Technicon, 1972), was used, and for PO_4-P, range 0-300 ppb, Industrial Method No. 155-71W (Technicon, 1973), was used.

Analyses of rainwater samples are often uncertain because of possible contamination caused by temporarily suspended particulate matter falling into the sampler between rainstorms. For this reason, Bentz (1968) developed an inexpensive automatic cover for a standard raingage that would open when a sensor recorded precipitation and close when precipitation ended. In this study, a weighing-type recording raingage shell was converted to collect rainwater samples free of between-storm contamination (Schreiber et al. 1978) by using an automatic opening raingage lid similar to the one developed by Bentz (1968).

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*Trade names are included for information of the reader, and do not constitute endorsement by the U.S. Department of Agriculture.
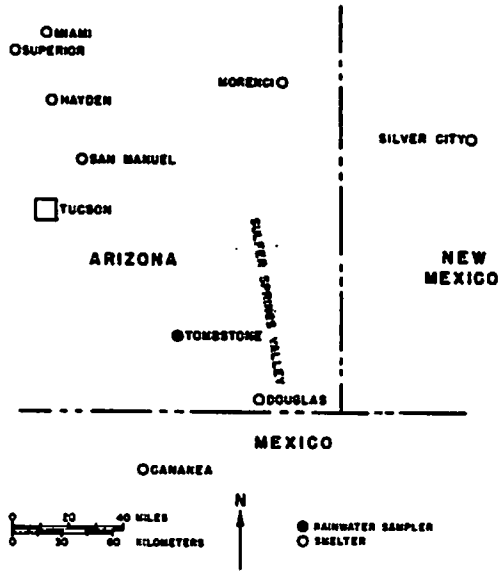
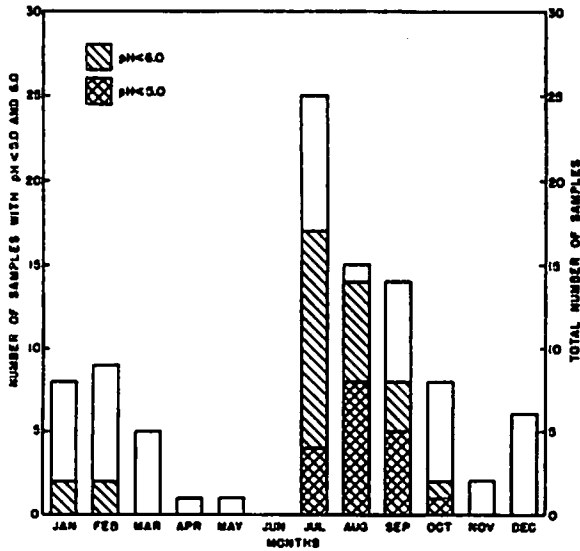Figure 1. Location of rainwater sampler and possible sources of pollution.

Figure 2. Total number of rainwater samples collected per month and samples with pH of less than 6.0 and 5.0, Tombstone, Arizona (1975-1978).

Water quality samples were collected from 1975 to the present. Average rainfall for the 4 years (1975 through 1978) was about that of the 25-yr average on Walnut Gulch but below the long-term mean for the Tombstone gage near the watershed center. The summer of 1979 was extremely dry and the winter unusually wet, while the summer of 1980 was not only dry, but the copper smelters were closed by a strike. Therefore, the principal analyses were based on the 1975 through 1978 data. Also, initial analyses indicated seasonal differences in some of the contaminant concentrations, so the data were divided into seasonal components. Calcium, PO_4, and SO_4 were the major contaminants. The summer events consistently yielded the lower values of pH (Fig. 2). Of the compounds analyzed, NO_3, SO_4, and PO_4 were best correlated with pH. For 1975 through 1978, the NO_3-N and SO_4 ions yielded a correlation coefficient (r) of -.36 with pH. Orthophosphate concentration evaluations in the rainwater were begun in 1977. When the combined concentrations of NO_3-N, SO_4, and PO_4 were correlated with pH for the 1977 and 1978 samples, the correlations improved to -.53.

Summer precipitation is dominated by high-intensity, short-duration thunderstorm rainfall. Most winter precipitation is low-intensity frontal rain or snow (Osborn and Hickok, 1968). Most of the compounds, with the exception of sulfate, had no general trend in their seasonal variation. High values of sulfate were recorded in the summer months with the lower values being noted in the winter months (Table 1). The SO_4 values ranged from 1.4 to 4.7 kg/ha in the winter and from 7.3 to 13.0 kg/ha in the summer. While at first glance it may seem that the difference in summer and winter values for sulfate resulted from differences in the length of the two periods, the data in Table 1 show that the trend toward lower concentrations in winter and higher in summer was also evident in the average SO_4 concentrations in winter and summer storms. While summer rainfall for the period was only 25% higher than winter rainfall, accumulation of SO_4 in the summer was 4 times that in the winter. This trend compares well with that observed by Tabatabai and Laflen (1976) for Iowa. Their sulfate accumulations for October through March averaged 2.5 kg/ha, and for April through September averaged 9.0 kg/ha, compared to our seasonal averages of 2.9 kg/ha for the winter and 9.4 kg/ha for the summer. Tabatabai and Laflen's data for nitrate also compared well with our data. For the months of October through March, they reported a value of 0.7 kg/ha for NO_3-N, while for the summer (April through September) they reported a value of 2.8 kg/ha. Our average values were 0.85 kg/ha in the winter and 1.8 kg/ha in the summer. Annual rainfall in Iowa is over twice that of Walnut Gulch, so individual sample concentrations were generally much higher at Tombstone than Iowa. Part of this difference can be accounted for by greater "washout" from more rainfall in Iowa, but even so, the contaminant concentrations in the air are probably greater over Walnut Gulch than over Iowa.

Table 1. Estimated average precipitation and precipitation contaminants on Walnut Gulch based on rainwater samples collected near Tombstone, Arizona (1975 through 1978).

	Average sample	Accumulated amount	Average sample	Accumulated amount	Average sample	Accumulated amount	Average sample	Accumulated amount
	(ppm)	(kg/ha)	(ppm)	(kg/ha)	(ppm)	(kg/ha)	(ppm)	(kg/ha)
	---(1975)---		---(1976)----		---(1977)----		---(1978)----	
Summer (May through September)								
NO_3	2.3	5.2	1.9	4.0	0.4	0.8	0.5	0.6
SO_4	5.7	13.1	6.3	12.9	3.6	8.0	5.4	7.3
Cl	0.8	1.9	0.5	1.0	0.2	0.6	1.0	1.4
Na	0.2	0.5	0.1	0.2	0.2	0.4	0.3	0.4
Ca	1.2	2.8	1.3	2.8	1.4	3.0	2.5	3.4
K	0.2	0.4	0.1	0.2	0.2	0.3	0.8	1.0
Mg	0.04	0.1	0.1	0.2	0.04	0.1	0.2	0.2
PO_4	---	---	---	---	---	---	4.5	6.1
H_2O	---	1.93×10^6	---	2.05×10^6	---	2.21×10^6	---	1.42×10^6
Winter (October through April)								
NO_3	2.1	1.2	---	---	0.1	0.3	0.4	1.0
SO_4	2.4	1.4	3.2	2.8	1.3	2.9	2.0	4.7
Cl	0.6	0.3	0.4	0.3	0.3	0.6	0.4	0.9
Na	0.2	0.1	0.1	0.1	0.2	0.5	0.3	0.7
Ca	5.2	3.0	4.2	3.6	0.7	1.5	1.8	4.3
K	0.3	0.2	0.1	0.1	0.2	0.5	0.5	1.2
Mg	0.1	0.1	0.2	0.1	0.01	0.02	0.2	0.4
PO_4	---	---	---	---	1.9	4.2	4.9	11.6
H_2O	---	5.57×10^5	---	8.53×10^5	---	2.22×10^6	---	2.36×10^6

A comparison of ion concentration versus rainfall amount yielded envelope curves such as those obtained in Fig. 3. These curves indicate a logarithmic decline in ionic concentration with increasing precipitation amount. In general, the smaller the rainfall amount, the more acidic the rain. As the rain continues, it eventually "washes out" the air, with the concentration of the contaminant decreasing at an exponential rate.
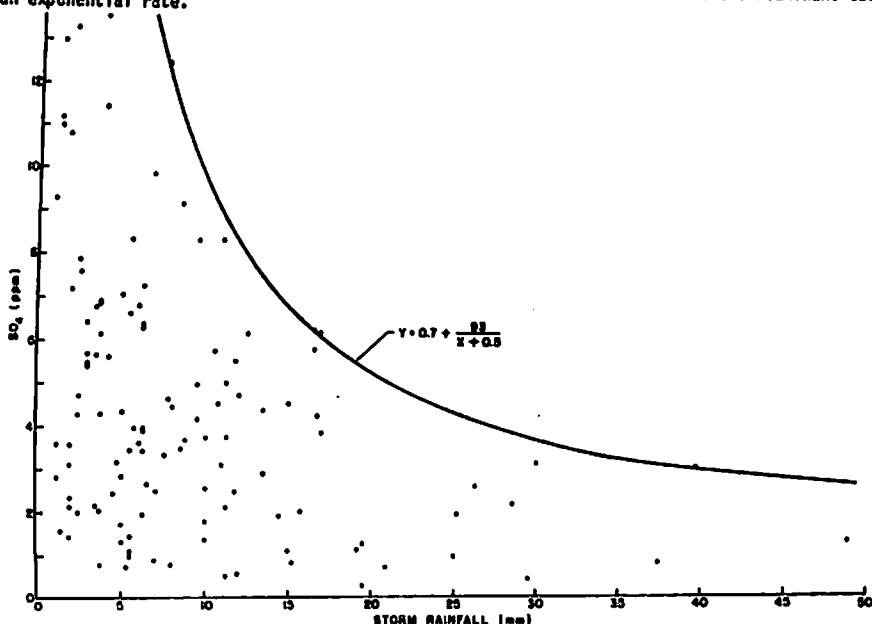

$$Y = 0.7 + \frac{83}{X + 0.5}$$

Figure. 3. Sulfate concentration in precipitation samples collected at Tombstone, Arizona, 1975-1978.

We attempted to verify the expected correlations between the sum of the contaminants Na, Ca, K, and Mg and the electrical conductivity of the rainwater. The winter storms yielded a strong correlation of $r = 0.92$, but the summer correlation of $r = 0.70$ was much weaker. For the summer rains, we can only say that the relationship between ion concentrations and EC is in the right direction.

Our data indicate that pH and concentrations of NO_3-N, SO_4, and Ca in rainwater collected at Tombstone are approaching some of the values reported for Michigan and New York in the early 1970's (Richardson,1976). For Michigan, Richardson (1976) reported values for SO_4 of 18.25 kg/ha/yr; for New York, in 1970-71, he reported values for SO_4 of 39.49 kg/ha/yr, for NO_3-N of 4.22 kg/ha/yr, and for Ca of 6.48 kg/ha/yr. Our report indicates yearly SO_4 averages of 12.3 kg/ha/yr, NO_3-N averages of 2.70 kg/ha/yr, and Ca averages of 6.20 kg/ha/yr. Again, there is much more precipitation in Michigan, so concentrations from individual samples at Tombstone, generally, must be greater than those collected in Michigan.

DISCUSSION

Studies by Eriksson (1958) indicated that the composition of rainwater contamination might be affected by both marine and terrestrial sources. Hutton and Leslie (1958) and Aggarwal et al. (1980) found that terrestrial, rather than marine, salts predominate at increasing distances from the sea. In southeastern Arizona, prevailing winds are generally from the west in the winter and the southeast in the summer; thus, air masses must cross considerable land surfaces before reaching southeastern Arizona. This suggests that almost all rainwater contamination at Tombstone originates from terrestrial sources, including the contribution from the copper smelters.

Ammonia may contribute a significant part of the nitrogen in rainwater samples. West (1978) found that NH_3 exceeded NO_3 at two of the four arid land sites in the western United States. Eriksson (1952) found, for a site near Salt Lake City, Utah, that NH_3 accounted for 90 percent of the total nitrogen in the rainwater sample. Ammonia has not been measured at Tombstone, and if the program is to be continued, it should be. The high incidence of lightning during the summer may contribute appreciably to the nitrogen balance in the area.

In the summer of 1980, a labor strike closed down all Arizona copper smelters. Although it was a very dry summer, seven rainwater samples were collected with pH ranging from 6.2 to 7.35, with an average pH of 6.8. For the summers of 1975 through 1978, the average summer season pH was 5.6, 5.4, 5.7, and 5.7, respectively. Five consecutive rainwater samples, in late August and early September of 1977, yielded pH readings of 4.0 to 4.6. Even with the dryer summer, the pH readings in 1980 were significantly higher than those for four earlier years, suggesting that the copper smelters may be contributing to the production of "acid" rain.

However, most of the southeastern Arizona rangeland soils are basic, and the overall effect of acidic precipitation, in most cases, would be to neutralize the soil. In general, the contaminants are probably beneficial to soils and vegetation in southeastern Arizona, although the concentrations and amounts are probably too small to significantly improve rangeland vegetation.

An effort was made to correlate wind direction and smelter location with the quality of rainwater samples. Unfortunately, the only dependable wind data were from twice daily radiosonde measurements at Tucson, 65 miles to the northwest of Tombstone. Although there appeared to be some correlation for certain periods or selected events, no significant overall correlations could be found. If an effort to identify the source and disposition of rainwater contaminants is undertaken, better wind data would be needed.

CONCLUSIONS

Conclusions were based on one sampling site at Tombstone, Arizona. Although other sites could indicate very different values, the samples collected at Tombstone were comparable with those from some other sampling sites in the United States. The study indicated that:

a. Apparently, most rainwater contamination in the area results from terrestrial sources, primarily the nearby copper smelters.

b. In general, the contaminants are probably beneficial to rangeland soils in southeastern Arizona, but amounts are too small to significantly improve the rangelands.

c. In future studies, NH_3 should be measured as well as NO_3 for a quantitative survey of the effect of rainwater quality on soil nutrients or as back ground for other modeling efforts.

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