RAINFALL pH IN TOMBSTONE, ARIZONA, 1968-81

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Abstract

Rainfall pH was measured at the Tombstone, Arizona, USDA-ARS station from 1968 to 1981. The summer rains were more acidic than the winter rains. The pH of the summer rains was about pH 5, the winter rains about pH 6, with considerable variation. The summer rain pH increased gradually over this period, coinciding with a general decrease of sulfur emissions from the nearest copper smelter at Douglas, Arizona, and from all smelters in Arizona. The ionic composition of the rainwater was quantitively uncertain due to numerous changes in analytical procedures. The acidity was very roughly related to sulfur content. The inverse relation between acidity and Ca and Na content was somewhat clearer.

The copper smelters of southern Arizona currently emit about 500,000 metric tons/yr of SO_2, down from the 1,300,000 metric tons/yr rate of 1969 (Anon. 1969; Walker, 1970) which is probably typical of the emission rates during the peak years of the 1960s and early 70s. Sulfur dioxide emissions decreased afterward due to decreased copper production and increased sulfur recovery from stack gases by the smelters. Figure 1 shows the locations of copper smelters in Arizona (circles), the average daily

1981 SO_2 emissions of copper smelters and, in parentheses, their average daily 1969 sulfur dioxide emission rates. The triangles are sites of coal-burning steam plants in and near Arizona with their daily or projected sulfur emissions, as SO_2. The squares are Tombstone and the three active National Atmospheric Deposition Program (NADP) precipitation sampling sites at Grand Canyon Natl. Park, Organ Pipe Natl. Monument, and Oliver Knoll.

The coal-burning steam plants, with the exception of the St. Joseph plant, (denoted by 60) are relatively new and the St. Joseph plant was only recently greatly expanded to its present output. The power plant emissions were calculated on the basis of full output, 35% thermal efficiency, and 0.5% sulfur content of the coal.

Rainfall measurements in Tucson do not seem to reflect acidity from this sulfur emission although the city is ringed by copper smelters. Dawson (1978), for example, found that the pH of rain in Tucson followed the general rainfall pattern of high acidity in the first 15 seconds or so, decreasing as the rain continues. The pH appeared to be more related to nitrate content rather than sulfate content.

Figure 2 shows the SO_2 emission rates of the Douglas, Arizona, smelter. The overall rate of decrease is probably representative of the industry in southern Arizona as a whole. This is the closest smelter to Tombstone, the site at which the rainfall was sampled.

The USDA-ARS research station at Tombstone, Arizona, began measuring rainfall pH in 1968. The sampling from 1979-81 continued with the cooperation of the Univ. of Arizona and NADP. This site sampled rainfall pH far from sources of urban dust and urban sources of nitrogen oxides and partially-oxidized hydrocarbons. The site is approximately 60 km northwest of Douglas, Arizona.

Method

The data from 1969-1979 was measured in samples of individual rainfall events. From 1979-81 the pH was measured in weekly composite samples, according to NADP recommendations. The pH of the weekly composite samples was measured at the site and several weeks later at the NADP central laboratory in Illinois. The agreement between local and central lab results was good although the central lab results were generally higher because of dust dissolution during the period between sampling and analysis.

Several periods were not sampled due to lack of personnel and lack of funds for NADP analysis. In order to present both sets of data on one graph, the USDA pH measurements were averaged over the weekly intervals that would have been corresponded to the later NADP sampling. An arithmetic average of log values such as pH is questionable, but Bartlett (1981) argued that pH averaging is valid for indicating environmental pH effects.

The rainwater samples were also analyzed for Ca^{2+}, NH_4^+, Na^+, SO_4^{2-}, and NO_3^-, but by several different methods, different technicians, two different laboratores, and by different samplers. Comparing these results is at best qualitative.

Results

The precipitation comes mainly in December-February as low-intensity frontal rain and snow and in July-August as high-intensity, short-duration thunderstorms. Figure 3 shows the weekly pH values measured over the period of 1968 to 1981. Although the variation was high, the variation within each rainy season was much less. The summer rains were more acidic than the winter rains. The pH of the summer rains increased slightly over the period 1969-81.

The winter rain and snow tended to be about pH 6 and the summer rains about pH 5. The early rain sampling was erratic and the pH measurements were few and tended to extremes, ranging from pH 3.6 to 9.2, perhaps because of experimental errors. After about 1972, the pH measurements of individual rainfall events ranged from 4.2 to 7.8. The relationship to the pH to other ions can only be judged qualitatively because of the analytical variance. The pH of the precipitation seemed directly related to its Ca^{2+} and Na^+ content and inversely roughly related to the sulfate content. Although nitrate contributes to the acidity of rainfall in Tucson (Dawson, 1978), nitrogen was not clearly related to pH in the Tombstone NADP analyses. The NADP samples were analyzed several weeks after sampling and perhaps long enough for microbial transformation of nitrate.

Discussion

Some pH measurements below 4 and above 9 in 1969-70 were discounted as experimental or sampling error. The higher SO_2 production by the Douglas smelter in those years, Figure 2, however, suggests that these pHs may have been real. The pH > 9 measurements, however, are difficult to explain and made the very acidic measurements suspect also.

The rise in summer rain pH coincided with the decreased SO_2 emission from the Douglas smelter. Osborn, Cooper and Billings (1981) measured rain pH in Tombstone before and during the 1980 copper strike. Their seven rain samples that summer ranged from pH 6.2 to 7.35, averaging 6.8. Their average pH for individual summer rains in 1975-78 were 5.6, 5.4, 5.7, and 5.7, respectively. They also noted that pH tended to increase with the amount of rainfall. The first part of the rain "washes out" the atmosphere and tends to be more acidic than the remainder of the storm. The summer of 1980 was quite dry but the rains were still more alkaline than in the summers when the nearby smelter was operating. The high pH of the summer 1980 rains suggest that the smelter 150 km south in Cananea, Sonora, had a negligible effect on rain pH at Tombstone. Eldred, et al (1982) also concluded that smelter effects on rainfall composition decreased with distance.

The disappearance of sulfur and atmospheric acidity in Arizona has been attributed to the rapid removal of SO_2 and H_2SO_4 by soils (States, et al, 1976; Ferenbaugh, et al, 1979) and plants of desert regions. Many of the soils of the Southwest are calcareous and sorb SO_2 avidly (Yee, Bohn and Miyamoto, 1976). Plant cover is sparse and the soils are probably more important in SO_2 removal than in more humid regions (Chamberlain, 1960). Haase (1980-1983) concluded that 70 years operation and perhaps 20 million tons of SO_2 released by the Douglas smelter has not significantly affected soil pH in the surface 0 to 5 mm depth beyond 45 km from the smelter. At closer distances the change of surface soil pH km was small in these calcareous soils and negligible below 5 mm.

Acknowledgment

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Figures

Figure 1. Copper smelters (circles) and coal-burning power plants (triangles) in and near Arizona. The NADP sites are shown as squares. The values are the present sulfur emission in metric tons of SO_2 per day. The values in parentheses are the 1968 daily emission rates.

Figure 2. Daily emission from the Douglas, AZ smelter, 1972-82, in metric tons SO_2 per day.

Figure 3. Weekly average values of rainfall pH measured at Tombstone, AZ. The summer rains were more acidic averaging pH 5, than the winter rains which averaged about 6. The pH varation within each season was smaller than the annual variation.

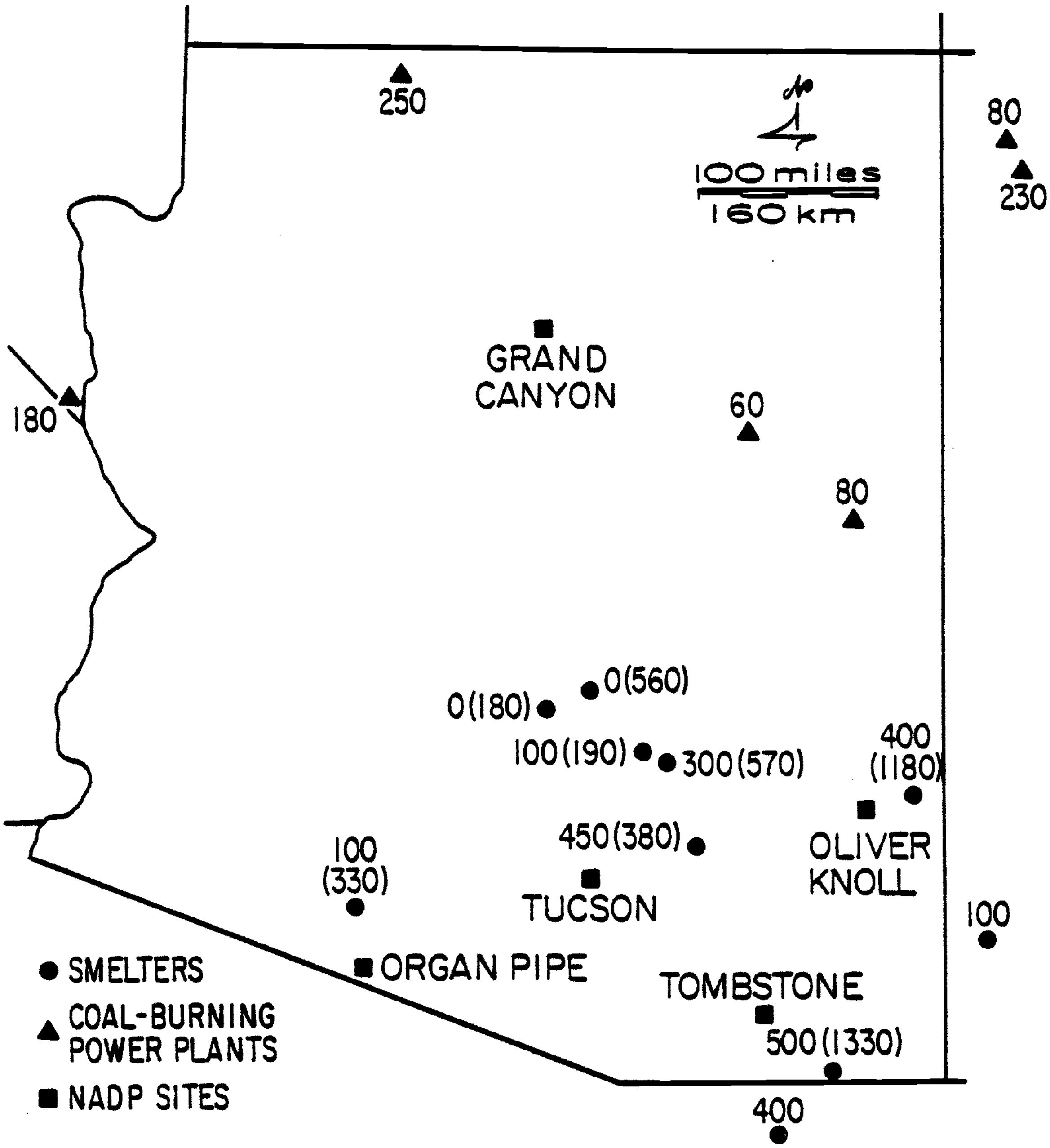
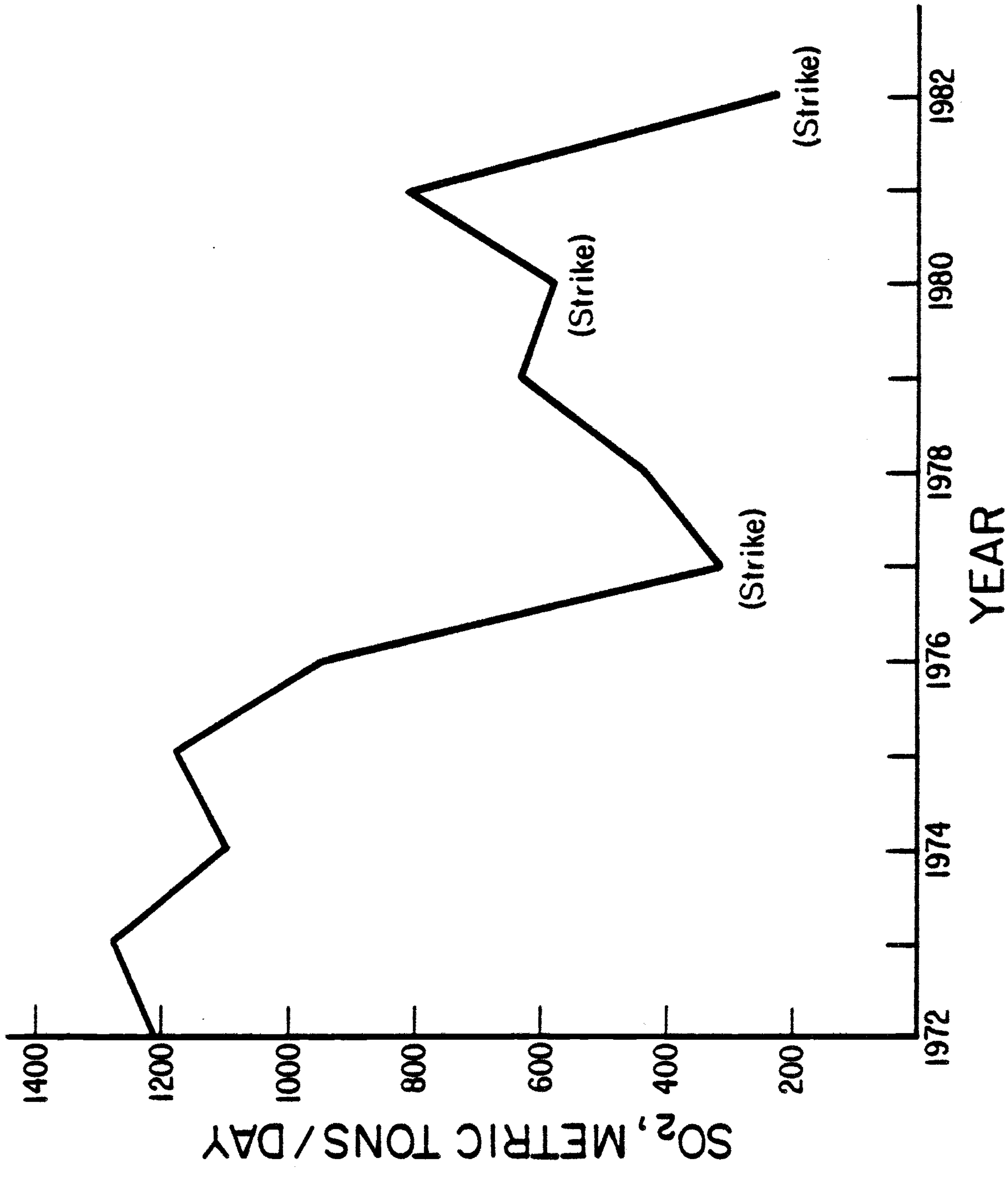

250
80
230
100 miles
160 km
GRAND
CANYON
180
60
80
0(560)
0(180)
100(190)
300(570)
400
(1180)
OLIVER
KNOLL
450(380)
100
(330)
TUCSON
100
SMELTERS
ORGAN PIPE
TOMBSTONE
COAL-BURNING
POWER PLANTS
500(1330)
NADP SITES
400

Figure 1



SO_2, METRIC TONS / DAY
1400
1200
1000
800
600
400
200
YEAR
1972
1974
1976
1978
1980
1982
(Strike)
(Strike)
(Strike)

Figure 2

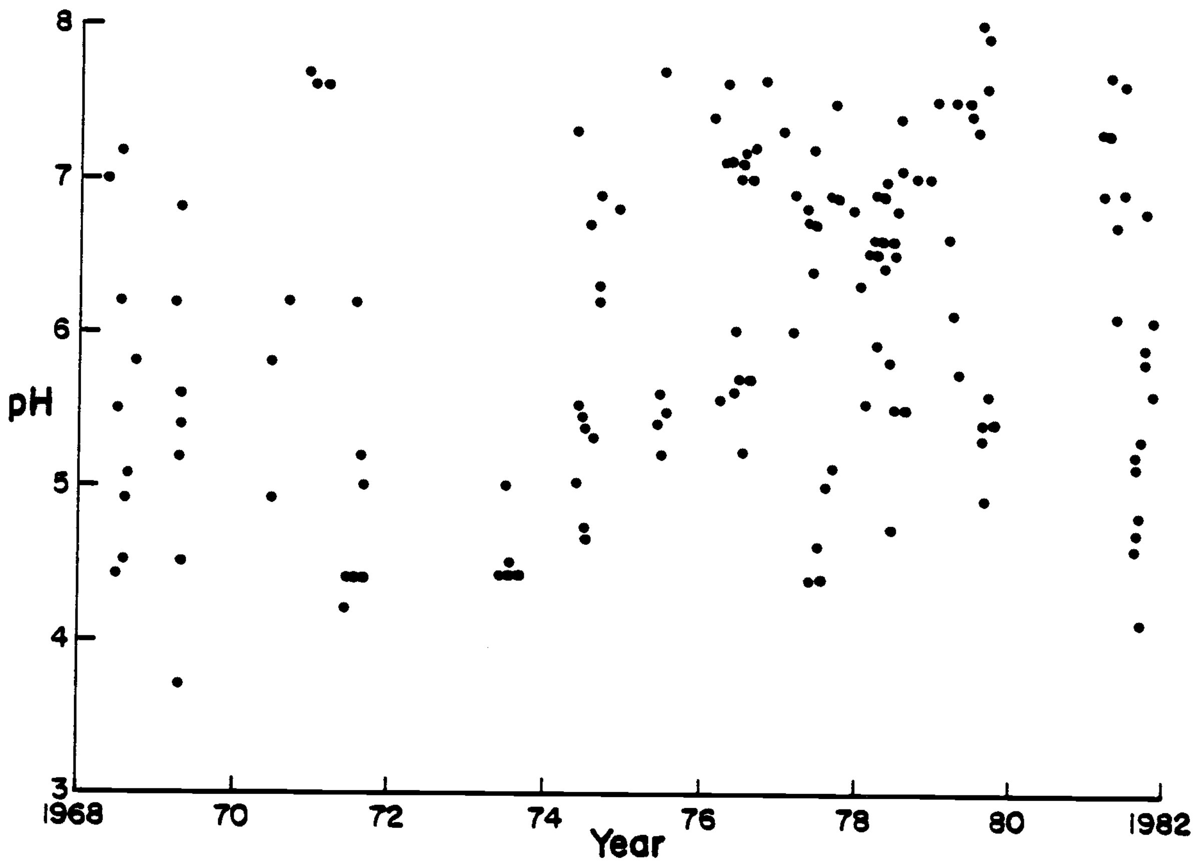


Figure 3