Ammoniated Thermal Waters of Lake and Colusa Counties California

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By C. E. ROBERSON *and* H. C. WHITEHEAD

GEOCHEMISTRY OF WATER

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GEOCHEMISTRY OF WATER

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By C. E. Roberson and H. C. Whitehead

ABSTRACT

Thermal springs in two areas north of San Francisco, Calif., contain nitrogen occurring as ammonia, nitrite, and nitrate. The nitrogen compounds show, in general, progressive oxidation with increasing distance downchannel from spring orifices, and with exposure to air during storage of water samples. The resulting increase in content of nitrite and nitrate is accompanied by a decrease in bicarbonate. Oxidation of sulfides when they are present also occurs.

INTRODUCTION

Thermal springs in an area centered about 90 miles north of San Francisco, Calif. (fig. 1), are noted, among other things, for their high concentration of combined nitrogen. The general character of much of the spring water from that area has been discussed by D. E. White (1957). Studies of the unusual waters in the Sulphur Bank and Wilbur Springs areas, Lake and Colusa Counties, may solve some of the unanswered problems of nitrogen chemistry.

Data used in this paper are from analyses of samples collected by White and a series of samples collected by the authors in the fall of 1958, especially for a study of the behavior of combined nitrogen in these particular waters. All samples were analyzed by the U.S. Geological Survey in the laboratory at Menlo Park, Calif.

The results show that in some of these springs the nitrogen occurs at the orifice as ammonia.[1] However, oxidation occurs progressively downstream in runoff channels, and the nitrogen is present in the water both as nitrite and as nitrate. Furthermore, the results indicate with few exceptions, that nitrogen in water samples from springs with a high combined nitrogen content shows progressive oxidation with time of contact of the water with the air. Thus, if a sample is exposed to air and stored in the laboratory, the concentration of ammonia progressively decreases and the concentration of nitrite and (or) nitrate tends to increase. The progress of this oxidation is mediated in a large part, presumably, by bacteria.

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[1] The terms "ammonia" and "ammonia nitrogen as NH_4^{+1}" used in the text and in tables 1 and 2, respectively, refer to nitrogen in the form of $NH_3 \leftrightarrows NH_4^{+1}$. These forms of nitrogen occur in these waters primarily as ammonium (NH_4^{+1}).

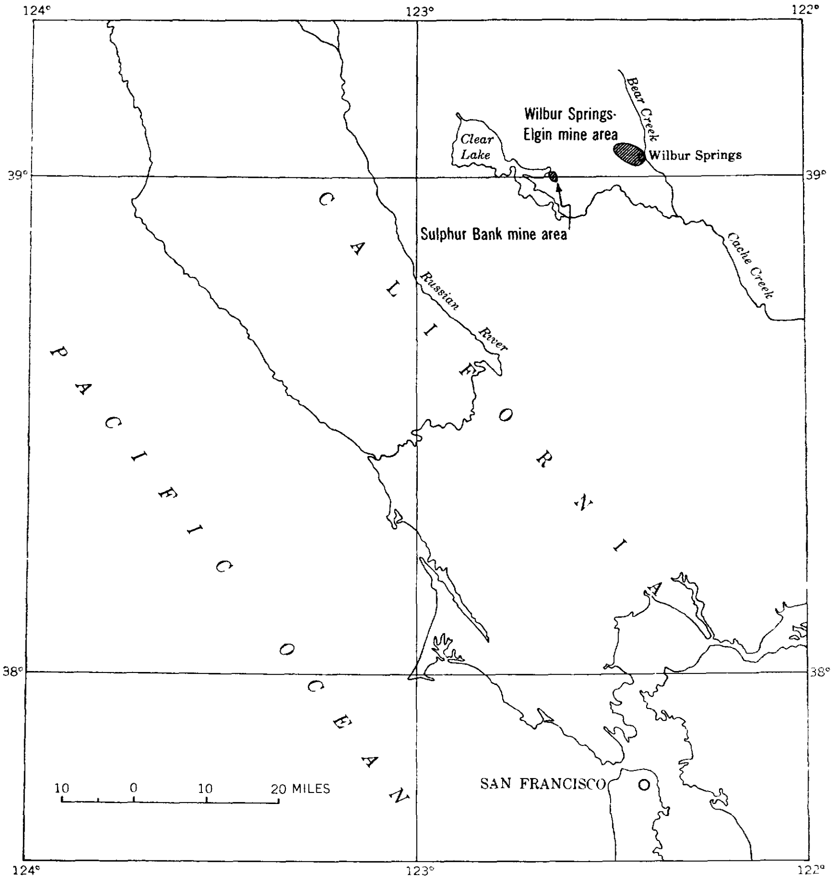

FIGURE 1.—Map of part of California showing location of Sulphur Bank and Wilbur Springs-Elgin min areas.

THERMAL SPRINGS

Thermal springs in two areas (fig. 1) furnished the water samples discussed in the present study. These areas are the Sulphur Bank mine area, located on the shore of Clear Lake, and the Wilbur Springs area, about 15 miles east of Sulphur Bank.

SULPHUR BANK MINE AREA

The Sulphur Bank mine is on the southeast edge of the east arm of Clear Lake. The mine was first worked for sulfur, and later it became one of the largest producers of quicksilver in the United States (White, 1955; 1957). Outcrops near Sulphur Bank consist mainly of sedimentary rocks of Jurassic(?) age overlain near the mine by Quaternary lake sediments and altered pyroxene andesite (White, 1955, p. 117). Water samples (table 1, Nos. 180, 181) of two of the

TABLE 1.—*Partial chemical analyses of water from the Sulphur Bank area*

Sample	Source of water	Date		Temperature at time of collection (° F)	Upper number, parts per million Lower number, equivalents per million						Hardness as $CaCO_3$	Specific conductance (micromhos at 25° C)	pH	Sulfides as H_2S
		Collection	Analysis		Ammonia nitrogen as (NH_4^{+1})	Nitrate (NO_2^{-1})	Nitrite (NO_3^{-1})	Bicarbonate (HCO_3^{-1})	Sulfate (SO_4^{-2})	Chloride (Cl^{-1})				
108	Sulphur Bank, spring on north wall.	10–56	4–23–57	--------	--------	--------	--------	[1]2,590 [1]42.45	[1]1,430 [1]29.77	695 19.60	780	7,670	6.8	1.4
			2– 7–57	--------	276 15.30	--------	--------	--------	--------	--------	--------	--------	--------	--------
			3– 8–57	--------	230 12.75	--------	--------	--------	--------	--------	--------	--------	--------	--------
			3–11–57	--------	223 12.36	470 10.22	0.0 .00	--------	--------	--------	--------	--------	--------	--------
			3–14–57	--------	209 11.58	--------	--------	--------	--------	--------	--------	--------	--------	--------
180	Spring 1	3–26–57	7–18–57	156	464 25.72	.00 .00	.0 .00	3,290 53.92	598 12.45	644 18.16	276	7,430	6.8	12
181	Spring 2	3–26–57	7–18–57	170	476 26.38	.00 .00	.0 .00	2,960 48.51	454 9.45	690 19.46	108	7,060	7.5	3.6
834	Thermal spring, southwest wall	9–17–58	9–30–58	105	59 3.27	.07 .00	4.0 .06	1,470 24.09	279 5.81	13 .37	990	2,400	6.9	(2)
835	Cold acid spring, southwest wall.[3]	9–17–58	9–30–58	60	13 .72	.00 .00	24 .34	0 .00	4,870 101.39	8 .23	--------	4,990	3.5	(2)
836	Mixture of 834 and 835	9–17–58	9–30–58	(4)	60 3.33	.16 .00	4.0 .06	1,480 24.26	272 5.66	11 .31	990	2,400	6.8	(2)
838	Bubbling thermal spring, north wall.	9–17–58	9–30–58	128	460 25.50	.00 .00	2.0 .03	4,060 66.54	31 .64	760 21.43	82	7,760	7.2	9.4
839	Standing pool from 838	9–17–58	9–30–58	95	430 23.83	1.5 .03	2.0 .03	4,020 65.89	57 1.19	814 22.95	88	7,790	7.7	.2
840	Runoff from 838 and 839	9–17–58	9–30–58	79	485 26.88	5.6 .12	6.0 .10	4,030 66.05	114 2.37	866 24.42	102	7,840	8.0	0

[1] Determined 3–11–57.

[2] Qualitative test; results negative.

[3] Flow contribution from cold spring is negligible.

[4] Warm.

springs discharging from the north wall of Hermann pit at Sulphur Bank were analyzed in July 1957. These waters are representative of the mineralized springs in the area.

Sample 108, collected in October 1956 from a spring on the north side of the pit at Sulphur Bank, was analyzed 4 times for ammonia in a period of 35 days, early in 1957. It was found that the ammonia content had dropped from 276 ppm (parts per million) to 209 ppm over a period of 35 days (fig. 2).

Another determination for nitrite made on water from the same source, but taken from a small bottle which was only about one-fourth full and which had been opened several times during the course of analysis, contained 880 ppm nitrite. Thus this sample, which had been repeatedly exposed to the air, had the greater opportunity for obtaining the oxygen needed for oxidation; hence, the more rapid change of ammonia to nitrite.

The nitrate found in the sample was less than 10 ppm. A more specific value cannot be assigned because in the determination of nitrate, the nitrate and nitrite are reduced together and distilled as ammonia. The total so obtained is corrected by using a separate method to determine the amount of nitrite. Because the determination of nitrite is very sensitive, small samples of water are used when the concentration of nitrite is high and any error in the determination, however small, is magnified by the computation factor. And because the value for nitrate is obtained by difference, a small percentage error in the determination of nitrite would introduce a much larger percentage error for nitrate when these constituents are present in high and low concentrations, respectively. However, the nitrate content of the samples mentioned above is relatively low, indicating that nitrite was not being rapidly oxidized to nitrate.

Two series of samples (834–836 and 838–840) in the Sulphur Bank area contained high concentrations of ammonia that exhibited various degrees of stability. These samples were collected in the fall of 1958. The amount of nitrite was determined in the field immediately upon sampling, and samples preserved with formaldehyde were brought back to the laboratory for further study of the nitrogen compounds.[2] The nitrite content of the preserved samples was again determined after return to the laboratory, and the laboratory values are reported in the tables. These values confirm the results obtained in the field within the sensitivity limits of the field procedure.

A thermal spring on the southwest wall of Hermann pit (834) had one of the lowest values for ammonia obtained in this area. Hydrogen sulfide was conspicuously absent. The sulfate content, notably

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[2] The amount of ammonia was determined by distillation as NH_3 and titration with acid. The Griess reaction was used for determining the amount of NO_2^{-1} both in the field and in the laboratory.

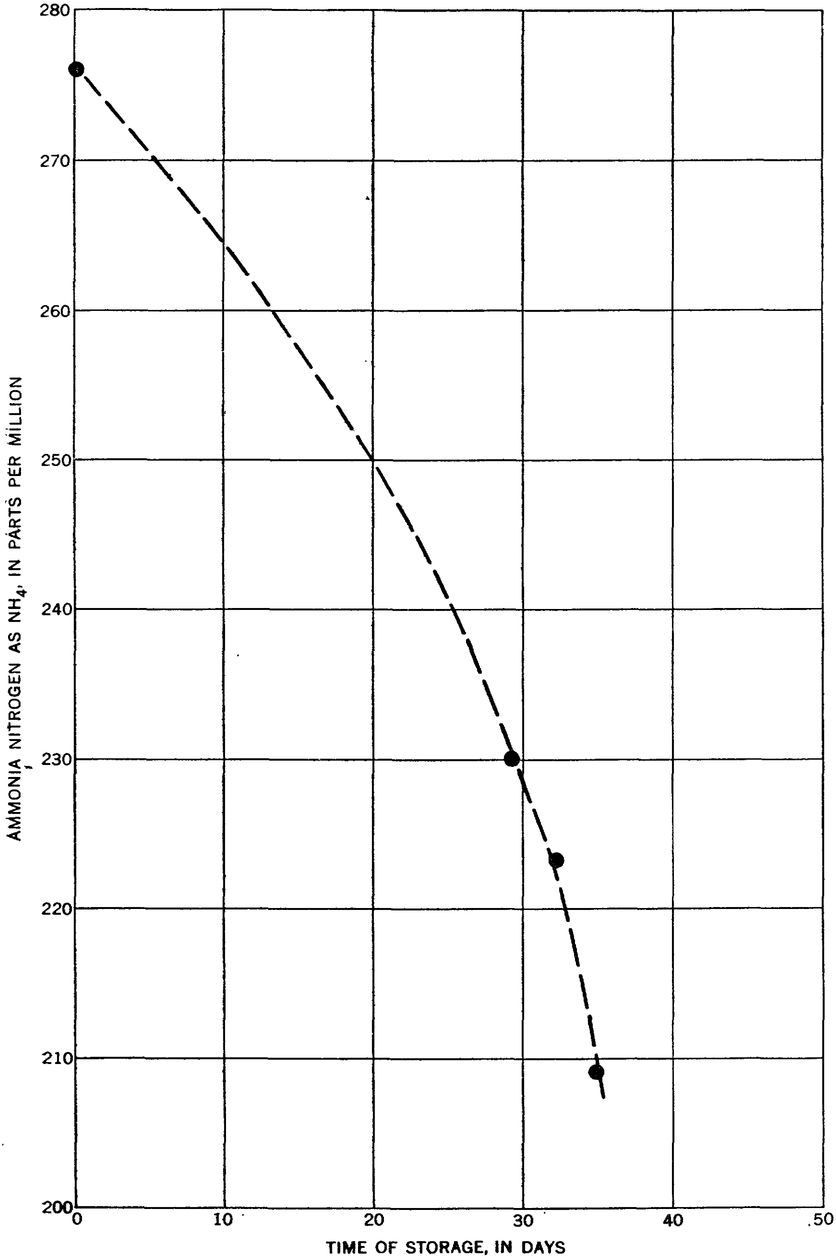

FIGURE 2.—Graph showing change in ammonia nitrogen as NH_4^{+1} during storage of a water sample. Sample from a thermal spring at Sulphur Bank (table 1, No. 108).

greater than that of the other thermal springs sampled at Sulphur Bank by the authors, suggests that any hydrogen sulfide present at depth must be oxidized to sulfate during passage of the water toward the earth's surface. This change suggests a loss of the reducing environment that seems prevalent at many other springs in the area. The ammonia, characteristic of water from nearby springs, has presumably been partly lost. There seems to be no concurrent rise in the oxidized forms of nitrogen.

The decrease in ammonia content of water at higher rates than the increase in nitrite and nitrate is a well-known phenomenon (Hutchinson, 1957, p. 864). Presumably nitrogen is lost as nitrogen gas or ammonia gas and by metabolic processes in which nitrate is assimilated.

In another thermal spring, on the north wall of Hermann pit (838) about 100 yards down the road leading into the pit, there was considerable bubbling in the spring pool caused by gas evolution and the odor of hydrogen sulfide was easily detected. The ammonia content in a sample from the center of the bubbling water was found to be high (460 ppm), but very little nitrate and no nitrite were present. The spring water flowed 2 or 3 feet away into a small depression in the road and was ponded. A sample from this small pool (839) had lower concentrations of ammonia and hydrogen sulfide and higher concentrations of chloride, sulfate, and nitrite than the sample from the spring.

The overflow from the standing pool (840) was sampled 20 feet farther down the slope and found to contain more nitrite. No hydrogen sulfide was noticed and the sulfate content was greater. The lower concentrations of ammonia and nitrite found in the samples collected from both the bubbling and the standing pools may result from lack of mixing in these pools.

WILBUR SPRINGS-ELGIN MINE AREA

The Wilbur Springs-Elgin mine area (fig. 3) is in the valley of Sulphur Creek in southwestern Colusa County, Calif., about 15 miles east of the Sulphur Bank area. The springs at the Elgin mine at the time of the investigation constituted virtually the entire flow of the headwaters of Sulphur Creek. The creek flows past Wilbur Springs and joins Bear Creek 1 mile below Wilbur Springs.

Both the springs in and the surface waters draining the Wilbur Springs-Elgin mine area were sampled to show changes in combined nitrogen. Sampling points are shown on figure 3 and analyses on table 2. A thermal spring (845) at the Elgin mine had a high content of ammonia, of sulfide as H_2S, and of bicarbonate. No nitrite was found in this water and there was only 2 ppm of nitrate. Sulphur Creek was sampled about a mile down the hillside from the Elgin mine (846). The stream at this point was receiving most of its flow from the springs at the Elgin mine. The analysis, however, especially values for hardness and sulfate, implied mixing of water from the creek with water of undetermined chemical quality from other sources.

The water from the stream contained considerably less ammonia (68 ppm) than that from the Elgin mine (271 ppm). Similarly, the bicarbonate concentration was lower, sulfide was absent, and the sulfate concentration (648 ppm) was much greater. The nitrite content (55 ppm) was high, compared to none found for the spring at the Elgin mine. The nitrate content (15 ppm) was also greater than in the sample from the mine.

In terms of nitrogen (N), the thermal spring (845), at its source had 210 ppm of nitrogen (N) occurring predominantly as NH_4^{+1}, whereas the runoff (846) had only about 73 ppm of nitrogen (N) occurring as NH_4^{+1}, NO_2^{-1}, and NO_3^{-1}.

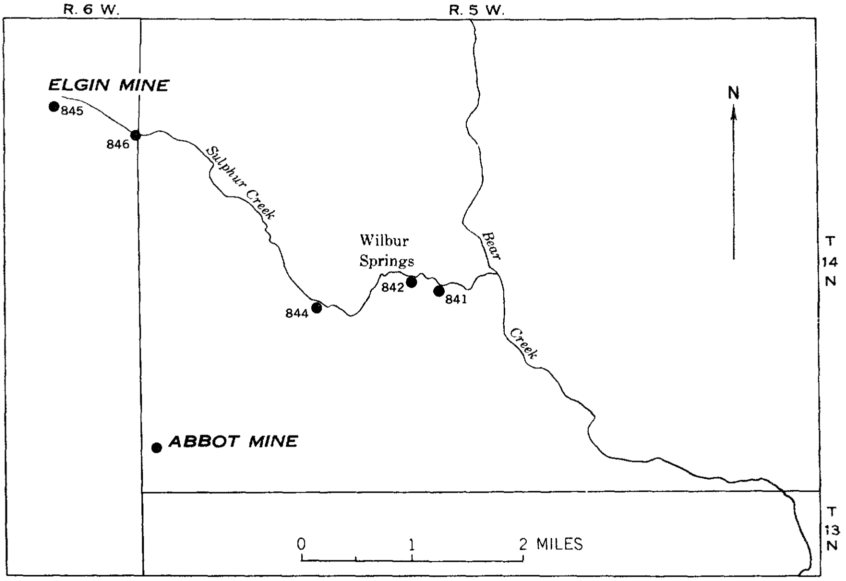

FIGURE 3.—Map of Wilbur Springs-Elgin mine area showing location of water-sample points. Numbers refer to analyses reported in table 2.

TABLE 2.—*Partial chemical analyses of waters from the Wilbur Springs-Elgin mine area*

Sample	Source of water	Date		Temperature (° F)	Upper number, parts per million Lower number, equivalents per million						Hardness as $CaCO_3$ (ppm)	Specific conductance (micromhos as 25° C)	pH	Density at 20° C	Sulfides as H_2S (ppm)
		Collection	Analysis		Ammonia nitrogen as NH_4^{+1}	Nitrite (NO_2^{-1})	Nitrate (NO_3^{-1})	Bicarbonate (HCO_3^{-1})	Sulfate (SO_4^{-2})	Chloride (Cl^{-1})					
845	Elgin mine, Judge Moore tunnel(?).	9/18/58	9/30/58	148	271 15.02	0.00 .00	2.0 .03	7,320 119.97	69 1.44	11,200 315.84	118	36,300	7.8	1.018	110
846	Sulphur Creek, 1 mile downstream from 845.	9/18/58	9/30/58	80	68 3.77	55 1.20	15 .24	[1]3,790 [1]62.12	648 13.49	11,200 315.84	413	35,000	8.7	1.017	([2])
844	Sulphur Creek above Wilbur Springs.	9/18/58	9/30/58	72	3.9 .22	0.10 .00	1.6 .03	1,520 24.91	161 3.35	2,990 84.32	----------	10,500	8.1	--------	0
842	Wilbur Springs 22	9/18/58	9/30/58	121	266 14.74	.00 .00	2.0 .03	6,910 113.25	110 2.29	9,790 276.08	207	32,600	7.3	1.016	190
841	Sulphur Creek 0.4 mile below Wilbur Springs.	9/18/58	9/30/58	65	80 4.43	.91 .02	2.1 .03	[3]4,640 76.05	237 4.93	7,220 203.60	544	24,500	8.3	1.011	0

[1] CO_3: 991 ppm, 33.03 epm.

[2] Qualitative test; results negative.

[3] CO_3: 185 ppm, 6.17 epm.

Sulphur Creek was sampled farther downstream, about a mile above Wilbur Springs (844). The creek at this point seems to have been diluted fourfold, as shown by a decrease in the chloride content from 11,200 ppm to 2,990 ppm. Although a fourfold dilution would normally yield 50 ppm of nitrogen, only 3 ppm were found.

The Wilbur Springs sample (842) had the highest amount of ammonia, sulfide, and bicarbonate. Here, Sulphur Creek was receiving one-fourth to one-half of its flow from the springs. About 0.4 mile below Wilbur Springs, the creek water (841) had a lower content of ammonia and bicarbonate, and no sulfide was present.

ANALYTICAL PROBLEMS IN NITROGEN DETERMINATION

In all cases cited there has been an oxidation of ammonia, an oxidation of sulfide, a loss of bicarbonate, and a gain in nitrite and (or) nitrate. The mechanism of the oxidation of ammonia to nitrite and finally to nitrate has been discussed by Cooper (1937, p. 183–204) and others. From the equation

$$NH_4^{+1}+OH^{-1}+3/2\ O_2 \longrightarrow H^{+1}+NO_2^{-1}+2\ H_2O$$

three principal conditions are necessary: (a) A positive oxidation potential (that is, a loss of reducing conditions); (b) an external source of oxygen, whether from dissolved oxygen, atmospheric oxygen, or release of combined oxygen by bacterial or other action; and (c) a production of hydrogen ions from the oxidation process. The hydrogen ions then react with, and decrease the content of, bicarbonate and (or) carbonate. W. L. Lamar (oral communication, 1958) has studied the decrease of bicarbonate during the oxidation of ammonia. This decrease is due to the reaction of the produced hydrogen ions with the bicarbonate to liberate carbon dioxide gas.

In some environments the nitrite ion is reduced by sulfide to ammonia; hence, no nitrite will be found where sulfides are present (Rider and Mellon, 1946, p. 969). In other sulfide environments oxidized forms of nitrogen do not occur. White (1957) believes that some of the water is connate; hence, these waters indicate an anaerobic environment brought about by the decomposition of organic matter in deeply buried sedimentary rocks. However, upon exposure to air in runoff channels, the reducing environment, which is characteristic of such waters, changes, and oxidized species such as nitrite, nitrate, and sulfate appear. The relationship between the presence of sulfide and the absence of nitrite is shown in tables 1 and 2.

W. L. Lamar (written communication, 1956) reported on the changes in nitrogen compounds and bicarbonate of water samples in storage. He showed that, where oxygen is available, there was a progressive loss of ammonia and of bicarbonate and a progressive increase of nitrite and (or) nitrate.

The results reported in this paper generally confirm the observations of Lamar. Any discrepancies were probably due to the different chemical histories of the waters sampled. Important variables in these histories are (a) release of pressure as water emerges, (b) reduction of temperature, and (c) exposure to oxygen, bacteria, and algae in runoff channels. In most cases the loss of ammonia is far greater than any observed gain in oxidized nitrogen.

A laboratory example of the loss of nitrogen in water containing ammonia is shown by a water sample collected at the Abbot quicksilver mine. This mine is in Lake County, 2 miles southwest of Wilbur Springs (fig. 3). The water was pumped from the mine and collected on March 27, 1957. A qualitative test in the field indicated nitrite was present at the time of collection. The ammonia, nitrite, and nitrate were determined both 3 weeks and 17 months after collection. The sample was stored in a stoppered gallon bottle one-third full. The following results, in parts per million, indicate that about 19 ppm of nitrogen was lost during storage.

	3 weeks		*17 months*	
	Amount of constituent	*Calculated as N*	*Amount of constituent*	*Calculated as N*
NH_4^{+1}	22	17	0.1	0.1
NO_2^{-1}	14	4.3	.0	.0
NO_3^{-1}	4	.9	13	2.9
Total	--------	22.2	--------	3.0

Some nitrogen is probably lost by the escape of ammonia gas. Hutchinson (1957, p. 850) states that at near-neutral pH values the ammonia is largely present as dissociated ammonium ions (NH_4^{+1}) with only a small part present as undissociated NH_4OH as follows: at pH 6.0 the ratio NH_4^{+1}/NH_4OH is about 3000:1, at pH 7.0 about 300:1, and at pH 8.0 about 30:1. At a pH of 9.5 the concentration of NH_4^{+1} and NH_4OH are approximately equal.

Assuming that these ratios apply to the conditions prevailing in the spring areas considered in the present paper, the loss due to the evolution of ammonia gas might be small at near-neutral pH values. In runoff channels downstream from the orifices of springs, however, the pH increases, as was observed in the runoff channels under study. The ratio NH_4^{+1}/NH_4OH decreases and the loss of ammonia gas may be appreciable. Another factor that may cause a large loss of nitrogen is organic activity utilizing the nitrogen present as nitrite and nitrate.

Analytical problems connected with determinations of nitrogen suggest that samples should be analyzed for nitrogen components as soon as possible after collection, preferably in the field. As this is usually difficult, especially with ammonia, the sample should be treated with chloroform or formaldehyde to inhibit bacterial action. Acidification of the sample to a pH of about 4 would tend to preserve the ammonia. For water having a pH greater than 6 this would seem especially desirable in order to inhibit loss of nitrogen as ammonia gas. A combination of an acid and an inhibitor of bacterial action, such as formaldehyde or chloroform, would probably prevent both the change of oxidation state of the nitrogen compounds and the loss due to evolution of ammonia gas. However, preservatives probably should not be relied upon to inhibit oxidation of the nitrogen for extended periods.

There is a need for definite knowledge of the changes undergone by the various forms of nitrogen in order to explain the unequal rise and fall in the quantity of ammonia versus nitrite and nitrate. The method of oxidation, whether biological and (or) chemical of the ammonia, and the source of oxygen, all need further investigation.

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