

SCIENTIFIC RESULTS OF THE KATMAI EXPEDITIONS OF THE  
NATIONAL GEOGRAPHIC SOCIETY.

---

VII. AMMONIA AND NITROUS NITROGEN IN THE  
RAIN WATER OF SOUTHWESTERN ALASKA.

J. W. SHIPLEY,

Chemist of the 1917 Expedition.

While engaged in the work of the 1917 Katmai Expedition of the National Geographic Society, directed by Dr. R. F. Griggs, opportunity was afforded for making observations on the ammonia and nitrite content in the rainfall of Katmai and adjacent districts. Determinations were made on the Bering Sea side of the peninsular axis, on the Pacific slope, and on Kodiak Island, 100 miles to the eastward. The most extended series of observations was made at our Base Camp on Kashvik Bay, during a very rainy period from August 19th to August 27th. This constitutes the major part of the work done and the results, together with those of Kodiak Island, are to be found in the accompanying Table. Kashvik Bay is on Shelikof Strait, about 25 miles due south of Katmai Volcano and the same distance southeast from the Valley of Ten Thousand Smokes.

The chemical reagents, brought with the expedition for determining ammonia and nitrites in the volcanic ash, were equally well adapted for measuring the same nitrogen bearing compounds in rain water. Ammonia was determined by color comparison with Nessler's reagent, using a standard solution of ammonium chloride. The nitrites were compared with a standard solution of sodium nitrite through Greiss's reagent, (a naphthylemine and sulphanilic acid). These solutions were prepared according to the A. P. H. A. Standard methods of Water Analysis. On returning from the expedition the standard solutions were compared with freshly prepared solutions of the same salts, using the reagents brought back from Alaska. The  $\text{NH}_4\text{Cl}$  proved to be unchanged, but the  $\text{NaNO}_2$  had decomposed 50%. A sample of the same nitrite solution, as taken on the expedition, but left in a dark cupboard in the laboratory, had also decomposed to the same degree. The solutions were

prepared May 16, 1917, and were compared on December 19th, seven months later. A comparison made on May 22, 1918, showed a further decomposition amounting to an additional 15%. Assuming that the decomposition followed the law of mass action, corrections were applied to the field determinations, and the results tabulated are the corrected observations.

The necessity for preparing distilled water was fortunately obviated by the almost total absence of either nitrous nitrogen

TABLE.

## AMMONIA AND NITROUS NITROGEN IN RAIN WATER OF SOUTHWESTERN ALASKA.

Place	Collection	Analysis	Parts Nitrogen per 100,000		Remarks
			NH <sub>3</sub>	NO <sub>2</sub>	
Base Camp Kashvik Bay	(1) Aug. 19	Aug. 22	trace	0.0008	Stood in covered aluminum pail.
	(2) Aug. 15-22	Aug. 22	0.03	0.001	In brass rain gauge for almost a week.
	(3) Aug. 19	Aug. 25	trace	0.0004	Same sample as (1).
	(4) Aug. 25	Aug. 25	trace	0.0003	Rain gauge $\frac{3}{4}$ " fall. N. E. storm.
	(5) Aug. 25	Aug. 25	trace	0.00035	Glass funnel and Nessler tube.
	(6) Aug. 25	Aug. 25	trace	0.00016	Later in day, rain gauge.
	(7) Aug. 25	Aug. 25	trace	0.00014	Same time as (6).
	(8) Aug. 26	Aug. 26	trace	0.00012	Funnel, in morning.
	(9) Aug. 26	Aug. 26	none	none	Funnel, in afternoon near end of rain.
	(10) Aug. 25-26	Aug. 26	0.0015	0.00016	Rain gauge, storm from over Shelikof Strait.
Kodiak	(11) Aug. 27	Aug. 27	none	0.0003	Funnel, $\frac{1}{4}$ " fall, no wind.
	(12) Aug. 27	Aug. 27	none	0.00018	Rain gauge, same as (11).
	(13) Sept. 15	Sept. 15	trace	0.00014	Off metal roof, N. E. Storm.
	(14) Sept. 15	Sept. 15	trace	0.00016	Collected in aluminum pail.

or ammonia nitrogen in the spring and creek waters of the district, and in water obtained from melting snow. At Kashvik Bay no coloration whatever was produced by Nessler's reagent in the water from the creek. On adding to 50 cubic centimeters of the creek water 0.05 cubic centimeters of the standard NH<sub>4</sub>Cl solution containing 0.00001 grams nitrogen per cubic centimeter, a distinct coloration was produced, and on diluting to half this concentration the solution was more strongly colored than an equal volume of creek water. A similar test, using the standard NaNO<sub>2</sub> solution proved the almost entire absence of nitrites in the water of the creek.

In addition to water collected in the rain gauge, use was made of an aluminum pail and glass funnels set in the mouth of 50 cubic centimeter Nessler tubes. The latter proved to be the most serviceable. The collections at Kashvik Bay were made over the tundra, not less than eight inches above the vegetation in the case of the funnels, and almost two feet in that of the rain gauge. The Nessler tubes were always rinsed with the first fallings. Excepting the rain gauge, collections were made to the windward of camp, and far enough removed to prevent the possibility of contamination from the occasional camp fire.

The two determinations made at Kodiak were during the progress of a heavy northeasterly storm, lasting the entire day. Sample (13) was collected about mid-day, while (14) represents all but the beginning of the rain. Due to the direction of the wind, no contamination from smoke was possible.

The first three determinations in the Table were made on samples standing for some time after collection. The high nitrite content of these three is probably associated with this long standing. The high ammonia content of (2) was the result of small twigs and pieces of bark, wind-driven into the exposed rain gauge during the previous week.

The almost entire absence of ammonia in the rainfall of southwestern Alaska is in striking contrast with that found at a similar latitude in Europe. The average of a number of observations in Scotland gave 0.61 parts of ammonia nitrogen per million on the seacoast, and 0.44 parts at inland country places, while Glasgow gave 7.49 parts per million. The highest observed at Kashvik Bay was 0.015, and in most cases there was but a mere trace if any. At the Experimental Station, Rothamsted, England, the average of ammonia nitrogen in rain water over a fifteen year period was 0.45 parts per million. Storer states that the average in regions where factories are absent is about 0.02 parts per million.

Nitrous nitrogen was positively present in every determination excepting (9). The presence of even the small quantity of nitrites represented by the Table, in the rain water of a region devoid of thunderstorms, is highly interesting. One might expect that all nitrites would be transformed into nitrates in the presence of such oxidizing agents of the atmosphere as ozone

and hydrogen peroxide. But instead, nitrites were found to the extent of 0.0035 parts per million of rain water at the beginning of a rainfall.

The rainfall of August 25th-26th shows a gradual falling off in nitrite content as the storm progressed, until towards the end none was observed. The content in the rain gauge throughout the storm is the average of that found at the beginning and at the end, as well as the average of all five samples collected in the funnels. It is also to be noted that the nitrite content had again risen to the maximum in a quarter inch rainfall the very next day, while the ammonia content still remained at a minimum.

One further peculiar circumstance was observed, in that, on standing for about four hours in the Nessler tubes, the reddish color produced in the samples of rain water faded out, while those in the standard solution of creek water retained their color.

The observations made on the Bering Sea side of the peninsular axis were quite irregular in the amount of ammonia and nitrite found. The determinations were carried out at Camp V in the Valley of Ten Thousand Smokes, just at the western entrance of Katmai Pass. When the wind blew from over the Valley, the ammonia and nitrite content was relatively high, while only traces were observed when the storm was blowing into the Valley. The rainfall, when the wind blew from over the Valley, also contained notable quantities of chloride and sulphate, and at times was so strongly acid as to make the eyeballs smart. Samples of rain water were collected close to fumaroles, so that the rain fell through ascending gases. Many of these gave so much ammonia that a heavy yellow precipitate formed with Nessler's reagent. The quantity of nitrous nitrogen was also greater than in an ordinary rainfall, and one fumarole in particular gave a deep red color, indicating the presence of considerable quantities of nitrites in the gaseous emanation. Quantitative comparisons were not made excepting in the cases when the storm was blowing into the Valley. Here, as already stated, the ammonia and nitrite content differed but little from that observed at Kashvik Bay.

Water from melted snow was used for the standard solutions. The drip from the snow bank was remarkably free from ammonia and nitrites, although these were being poured

forth from the millions of fumaroles in the immediate neighborhood. Air, laden with these products, was constantly in contact with the thin layer of ash above the snow, and the frequent rains must have carried them down into the snow beneath. Nevertheless, melted snow from the bank behind Camp V gave no positive test for either ammonia or nitrite during the whole month we were in the Valley. Rain Water collected above the snow bank, when the wind blew from over the Valley, gave considerable quantities of both. This freedom from ammonia and nitrites was also observed in water from a snow bank on Observation Mountain at the eastern entrance of Katmai Pass. Here the bank in question was covered by several feet of ash, and was highly discolored from the leaching due to frequent rains. This bank served as a source of water for the standard solutions used in the comparison cylinders at Camp IV. One possible explanation for the absence of these nitrogenous substances is the presence of organisms in the snow capable of utilizing the ammonia and nitrite content of rain water in their assimilative processes.

A sample of rain water collected by hanging an aluminum pail from the dead branch of a tree gave an unusually large content of ammonia. The only contamination apparent was the drip from a short section of this one small dry branch. Water, in which a few twigs broken from the same cottonwood tree were allowed to stand for a short time, gave a heavy yellow precipitate with Nessler's reagent, proving that the high result noted above came from ammonium or similar nitrogen compounds in the decaying wood. The soil must receive considerable additions of ammonium compounds washed down from decaying trees, and in this region, where the lack of nitrogenous material for plant growth is so marked, this source of nitrogen may have some little influence on the revegetation of the destroyed area.

Manitoba Agricultural College, Winnipeg.