Evaporation of Boric Acid from Sea Water[1]

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Abstract

Previous investigators have shown that the boron-chlorinity ratios of rain waters are many times greater than the boron-chlorinity ratio of sea water. The presence of boron in the atmosphere has been attributed to sea spray, volcanic activity, accumulation in dust, evaporation from plants, and industrial pollution. In this paper data are presented to demonstrate that boric acid in sea water has a vapor pressure at ordinary temperatures of the sea and, when sea water evaporates, boric acid occurs in the condensate of the water vapor. It is postulated that, while some of the boron in the atmosphere can be attributed to the sources mentioned above, most of the boric acid results from evaporation from the sea.

Introduction

SUGAWARA (1948), in his studies of the composition of rain water, noted the presence of boric acid and stressed the fact that the boron-chlorinity ratio was hundreds of times greater than the boron-chlorinity ratio of sea water. MUTO (1952) collected four different samples of water during a continuous three-day rain. His analyses showed that the chlorides decrease more rapidly than the boric acid content as the rain continued, and that the boron-chloride ratio was from 50 to 270 times greater than the boron-chlorinity ratio of sea water. MUTO (1953) examined the boron and chloride content of snow and obtained results similar to those on rain water.

Several theories have been advanced to explain the presence of boric acid in the atmosphere. TRUNINGER (1944) attributes the boron to the accumulation of fine dust; KALLE (1945) to volcanic activity and cyclic salts supplied by sea water; LANDERGREN (1945) to volcanism; and MUTO (1956) to industrial pollution of the atmosphere and to evaporation of boron compounds from plants. In support of this latter theory Muto showed that boron compounds are given off by some plants and that the rain waters over heavy vegetated areas have higher boron content than the rains and snows of high altitudes.

The authors of this paper postulate that much of the boron content of the atmosphere, and thus of rain and snow, results largely from the evaporation of boric acid from the sea. Experimental evidence is presented to substantiate this hypothesis.

SCHAFFGOTSCH (1859) demonstrated that some boric acid is removed with the water vapor when an aqueous solution of the acid is evaporated. TCHIJEWSKI (1884) stated that the loss of boric acid by evaporation of aqueous solutions is not proportional to the concentration of the boric acid in solution. LESCOEUR (1886, 1890) made vapor pressure studies of boric acid and its aqueous solutions. At 20° C boric acid had a vapor pressure of 2 mm and at 43.5° C, 5 mm. HEHNER (1891) stated that orthoboric acid would vaporize from its solution at 100° C, but WATSON (1893) maintained that it was the metaboric acid that vaporized. KONINGH (1897)

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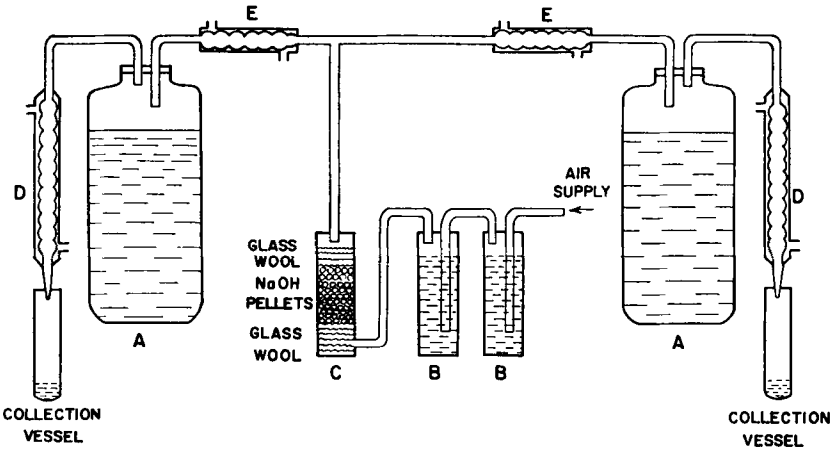

Fig. 1. Schematic cross section of the evaporators.
A. Polyethylene carboy of 50 liter capacity
B. Solution of NaOH
C. Glass wool and NaOH pellets
D. Cooling condensers
E. Warming condensers.

concluded that the evaporation of orthoboric acid noted by Schaffgotsch applied only to concentrated solutions and that dilute solutions could be evaporated without appreciable loss. This small loss can now be easily determined and is most pertinent to the present problem.

In the well-known mannitol method for the determination of boric acid, the carbonates are first destroyed by acidification and the resulting carbon dioxide is expelled by boiling. In this process the analyst always employs a reflux condenser to prevent loss of boric acid. It has been recognized for many years that boric acid in aqueous solutions has a definite vapor pressure depending upon the temperature and concentration. As far as the present authors can ascertain, this knowledge has not been considered in investigations of the evaporation of sea water nor offered as an explanation for the presence of boric acid in rain and snow at atmospheric temperatures. RANKAMA and SAHAMA (1949) cite references to some geochemical studies which state that the boric acid is volatile at 100° C.

Experimental

Methods of Analysis. The improved mannitol method of GAST and THOMPSON (1958) was used in the determination of boric acid in sea water. The colorimetric method of PHILIPSON (1953), because of its sensitivity for determining traces of boric acid, was employed in the analysis of distillates and condensates, a Beckman DU spectrophotometer being used for the measurement of optical densities.

Distillation of Sea Water. 500 ml of sea water with a chlorinity of 16.22 ‰ and containing 3.753 mg/l of boron as boric acid was distilled, using a Hopkins head, until 100 ml of distillate was obtained. Distillates from samples of the same water, which had been acidified before distillation, were likewise collected and analyzed. Averaged results were as follows:

Sea water contained
3.7537 mg/l boric acid-boron
Distillate of untreated water,
0.1126 mg/l boric acid-boron
Distillate of acidified water,
0.1408 mg/l boric acid-boron

None of the distillates showed the slightest trace of chlorides.

Evaporation of Sea Water. Both the early literature cited above and the fact that some boric acid is removed from solution by distillation indicate that boric acid in solution has a definite vapor pressure at atmospheric temperatures. When sea water evaporates the water vapor should also include small quantities of boric acid. To demonstrate this the apparatus

shown in Fig. 1 was assembled. Two carboys of polyethylene were used (A). One carboy was filled with 50 liters of sea water having a chlorinity of 16 ‰, and the other with the same quantity of distilled water. Air was gently blown over the surfaces of the waters. No spray or bubbles formed. The air was first cleaned by passing through a concentrated solution of sodium hydroxide (B), passed over pellets of sodium hydroxide (C), to remove much of the water vapor, and then warmed in condensers (E). A common air supply, used simultaneously in both carboys, eliminated the possibility of variable contamination, should such a condition exist. The dried air entered the carboys at a temperature of 32° C, plus or minus 3° C. The waters in the carboy were kept at a temperature of 25° C. The air, after passing over the water surfaces, entered cooling condensers (D), to condense much of the water that had evaporated. Portions of 100 ml of condensates were collected and analyzed. In one series of experiments the temperature of the cooling condensers was 12° C, and in another series 0° C. The results are summarized as follows:

	Air Temp. °C	Water Temp. °C	Condenser Temp. °C	Boric Acid-Boron in Condensate µg/L
Distilled Water	32°	25°	12°	5.0
Sea Water	32°	25°	12°	60.0
Sea Water	32°	25°	0°	65.0

The condensate from the distilled water yielded the equivalent of 5 µg of boric acid-boron per liter. This result is considered as a blank determination.

Evaporation of Dilute Solutions of Boric Acid: Dilute solutions of 50 liters of boric acid were prepared by dissolving boric acid in distilled water. The concentrations of these solutions were 1.083 mg, 2.166 mg, and 3.249 mg boric acid-boron per liter, respectively. Dry air was passed over these solutions and the condensates were collected and analyzed as described above with the following results:

	Air Temp. °C	Water Temp. °C	Condenser Temp. °C	Boric Acid-Boron in Condensate µg/L
Solution, 1.083 mg B/L	32°	25°	12°	19.0
Solution, 2.166 mg B/L	32°	25°	12°	42.0
Solution, 3.249 mg B/L	32°	25°	12°	60.0
Solution, 3.249 mg B/L	32°	25°	0°	66.0

Graphical portrayal of the above results in-di cates that the concentration of boric acid evaporating is proportional to the boric acid in solution and confirms the observations of SCHAFFGOTSCH (1859).

Discussion of the results

In both series of experiments with sea water and the experiment with dilute solutions of boric acid, the boron content of the condensates at 0° C showed slightly higher concentrations than at 12° C, indicating a vapor pressure of boric acid at these lower temperatures. Thus, the boron content of the condensates is actually less than the boron that had evaporated from the sea water and the solutions.

The vapor pressure of boric acid is a function of the temperature and the salinity (boric acid concentration) of the sea water. The rate at which boric acid may evaporate or be 'steamed distilled' from the sea surface is directly proportional to the rate of evaporation. The concentration of boron in the rains or snows resulting from this evaporation is a function of the temperature of condensation and the temperature at time of precipitation.

In tropical regions, during periods of little rainfall, the evaporation of boric acid into the atmosphere would tend to give a boron-chlorinity ratio of the surface waters slightly lower than normal. In areas where water and air temperatures were considerably lower, the amount of boric acid entering the atmosphere would be less and thus lessen the effect on the boron-chlorinity ratios of the waters. These ratios might even be slightly higher than normal if cold waters were subjected to the influence of air and moisture coming from tropical or warmer regions.

In a recent paper, the authors (1958) cited data by the United States Geological Survey showing the boron content of several rivers of the Pacific Northwest. The waters of these rivers on the western slope of the Cascade mountains represent the drainage of rains falling in the region. These rains had their origin over the Pacific Ocean. The boron content of the river waters are comparable with the boron found in the condensates obtained from sea water in the above experiments.

MORDY (1957), in his report of the 3rd Annual Conference on Atmospheric Chemistry, cites the data of several investigators who reported on the analyses of the boron content of rain waters collected over northern Europe. These results are much lower than those reported by any of the Japanese investigators; however, all the data tend to support the hypothesis that much of the boron in the atmosphere and in rains and snows is the result of evaporation from sea water. Most of the rain falling over Japan had its origin in warmer regions of the Pacific Ocean. The origins of the rains mentioned by Mordy are more complicated, having come from the evaporation of colder sea water or from the evaporation of fresh water on land areas.

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REFERENCES

GAST, J. A., and THOMPSON, T. G., 1958: Determination of the alkalinity and the borate concentration of sea water. *Anal. Chem.*, **30**, No. 9, pp. 1549—51.

HEHNER, OTTO, 1891: Experiments on the estimation of boric acid. *Analyst*, **16**, p. 141.

KALLE, K., 1945: *Der Stoffhaushalt des Meers*. Leipzig, p. 97.

KONINGH, L. DE, 1897: Note on the volatility of boric acid; separation of boric acid from phosphoric acid; estimation of boric acid in foods. *J. Am. Chem. Soc.*, **19**, p. 385.

LANDERGREN, S., 1945: Contribution to the geochemistry of Boron (II). The distribution of boron in some Swedish sediments, rocks and iron ores. The boron cycle in the upper lithosphere. *Arkiv kemi mineral. geol.*, **19 A** No. 26.

LESCOEUR, H., 1886: Sur les relations de l'efflorescence et de la deliquescence des sels avec la tension maximum des solutions saturées. *Acad. sci., Paris Compt. rend.*, **103**, p. 1260.

— 1890: Recherches sur la dissociation des hydrates salins et des composes analogues. *Ann. chim. et phys.*, Ser. 6, 19, p. 43.

MORDY, W. A., 1957: Report of the 3rd annual conference on atmospheric chemistry. *Tellus*, **9**, pp. 127—134.

MUTO, SATORU, 1952: Geochemical studies of boron (III). Boron content of rain waters. *J. chem. soc. (Japan).*, Pure chem. sect., **73**, pp. 446—448.

— 1953: Geochemical studies of boron (VI). Comparison of chemical composition of rain and snow at Kiriu. *ibid.* **74**, pp. 420—423.

— 1956: Geochemical studies of boron (XI). The source of boron in rain water. *ibid.* **77**, pp. 1770—1773.

PHILIPSON, T., 1953: Boron in plant and soil, with special regard to Swedish agriculture. *Acta agr. scand.*, **3**, pp. 121—242.

RANKAMA, K., and SAHAMA, T. G., 1949: *Geochemistry*. Univ. Chicago Press, Chicago. 912 pp.

SCHAFFGOTSCH, F. G., 1859: Ueber die Bestimmung freier Borsäure und die Flüchtigkeit dieser Säure. *Ann. phys. und chem.*, **107**, p. 427.

SUGAWARA, K., 1948: Chemistry of precipitation (Rain and snow). *Kagaku* (Science, Japan) **18**, pp. 485—492.

TRUNINGER, E., 1944: The effect of boron as a trace element. *Ann. agr. Suisse*, **58**, pp. 1—36.

TCHIJEWSKI, PAUL, 1884: Recherches sur l'entraînement des substances solides par la vapeur d'eau et sur la combinaison de l'acide borique avec la vapeur d'eau. *Arch. sci. phys. et natur.*, Ser. 3, 12, p. 120.

WATSON, G., 1893: The volatility of pyrophosphoric acid. *Chem. news*, **68**, p. 199.