

RELATIVE TOXICITY OF TWO AMMONIUM COMPOUNDS FOUND IN THE WASTE OF FERTILIZER PLANTS

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ABSTRACT

Bioassays of the two ammonium compounds namely ammonium chloride and ammonium sulphate were determined with particular reference to their safe permissible levels and their comparative toxicity to the freshwater barb, *Barbus ambassis*. The median tolerance limits (LC_{50}) were calculated for 24 and 48-h exposure of fish to various concentrations of the ammonium compounds. Using the 48-h LC_{50} values the safe concentrations for the two compounds were determined. The safe concentrations for ammonium chloride and ammonium sulphate were 29.49 ppm and 54.64 ppm respectively. There was a wide variation between the toxicities of the two compounds indicating that ammonium chloride is relatively more toxic than ammonium sulphate.

INTRODUCTION

Several ammonium compounds reach the aquatic environment through indiscriminate discharge of effluents from the fertilizer factories. Since the effect of these chemicals on fish life has not been clearly demonstrated, a series of experiments were conducted by employing the bioassay technique, to determine the toxicity of ammonium chloride and ammonium sulphate.

Ammonia is probably one of the most common pollutants discharged in the aquatic environment and its toxicity has been the subject of extensive laboratory and field investigations. Downing and Merckens (1953) and Llyod (1961) showed that the toxicity of an aqueous ammonia solution or of an aqueous ammonium salt solution depends mostly on the pH value of the water, because only the unionized molecule is toxic to fish. Llyod and Herberts (1969) and Merckens and Downing (1957) have also shown that the toxicity of ammonia is affected to some extent by temperature and dissolved oxygen and to a lesser extent by bicarbonate alkalinity and free carbon dioxide concentration of the water.

METHOD

Several exploratory experiments were conducted at first to ascertain a probable working range of these chemicals and detailed experiments were undertaken thereafter to evaluate the 48-h LC_{50} values of the two ammonium compounds. Fishes

were kept in the laboratory at room temperature for a fortnight. Eight to ten fishes measuring about 4.5 cm in length were used in each container. Replicate 96-h static bioassays were conducted in fresh water using five different concentrations and two controls were run simultaneously. Observations were made at 24, 48, 72 and 96 hours after the beginning of the test and the index of mortality was taken as the cessation of all movements by each fish.

Experiments were carried out at a controlled temperature of 28°C ($\pm 1^{\circ}\text{C}$) and pH 7.5. During the experiments, dissolved oxygen, pH, nitrite and nitrate were determined using the standard procedures of Strickland and Parsons (1969).

RESULTS

During the experiments no mortality was observed in the control tanks. This showed that there was no other toxic substance or any other condition causing the mortality of the fish excepting the toxicity of the chemicals introduced in the test tanks.

Temperature variations during the test were of the order of 1°C . Dissolved oxygen in all the tanks was above 5 mg/l and the pH varied from 7.5 to 7.6. The rate of mortality was maximum on the first and second day of the experiment. After 48 hours, the number of fishes in all the tanks remained almost constant. This may be because the turnover rate of ammonia is slow on the first two days. The nitrite and ni-

trate values on the first and second days were negligible, but there was a gradual increase in their concentrations on the third and fourth day. Maximum nitrite and nitrate concentrations recorded were 0.456 $\mu\text{g-at-N/l}$ and 1.1 $\mu\text{g-at-N/l}$ respectively. Both these values are within permissible limits.

In the experimental tanks, no mortality occurred within 96 hours test period at 400 ppm of ammonium sulphate and 150 ppm of ammonium chloride. However, concentrations higher than these were found to be toxic. The LC_{50} values were estimated by plotting the percentage mortality at 24-h and 48-h for each concentration and reading the estimated concentration lethal to 50% of the fish from the graph as shown in Figs. 1 and 2. The 48-h LC_{50} values for ammonium chloride was 295 ppm and the 48-h LC_{50} value for ammonium sulphate was 545 ppm. This shows that the fishes were more resistant to ammonium sulphate than to ammonium chloride.

For the estimation of safe concentrations for acute toxicity assays, some workers have come forward with certain formula and application factors to translate these experimental values into practical usable forms. The values of these application factors are assigned on the basis of experimental judgement (Sprague 1971). A number of application factors have been recommended recently by the U. S. National Technical Advisory Committee (1968). The recommendations for maximum levels ran-

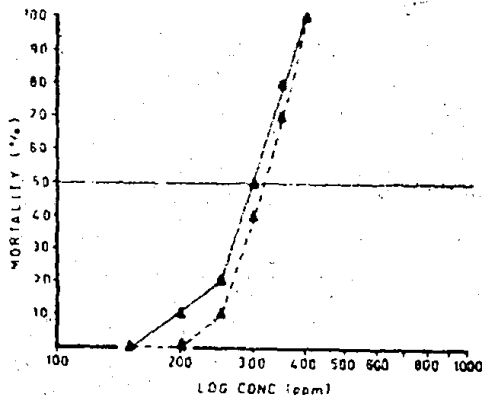


Fig. 1. Relationship between log concentration and percentage mortality for ammonium chloride, after a period of 24-h — ∇ — ∇ 48-h ... ∇ ... ∇ ,

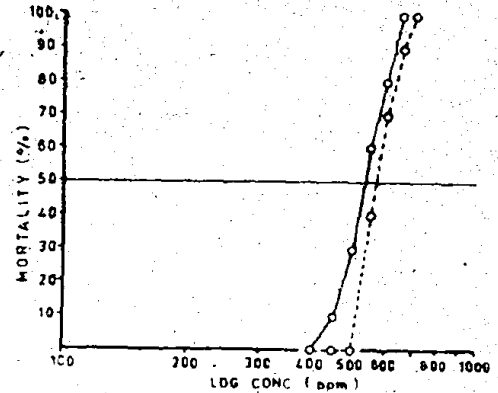


Fig. 2. Relationship between log concentration and percentage mortality for ammonium sulphate, after a period of 24-h — \circ — \circ —, 48-h ... \circ ... \circ ,

ge from 0.1 to 0.05 of the 48-h LC_{50} for all non-persistent pollutants. The median lethal concentrations (LC_{50}), fiducial limits, the threshold concentrations and the safe concentrations for both ammonium sulphate and ammonium chloride are presented in Table 1.

DISCUSSION

Numerous studies on the toxicity of ammonia to fish carried out earlier have yielded varying results. Several investigators have noted that the toxicity of ammonium salts such as the chloride and sulphate is considerably greater in alkaline tap-water than in distilled water. Ellis (1937) pointed out that the toxicity of ammonium compounds depends on the pH of the solution which increases with the increase in pH value. Therefore, it is essential to maintain a constant pH throughout the experiment, because the results on ammonia toxicity would be meaningless if the pH at which the experiments were conducted is not mentioned. Downing and Merckens (1955) determined that trout were more resistant to ammonia at pH 7 than 8. They found that ten times as much ammonium chloride had to be added to water of pH 7 to achieve a similar lethal effect found at pH 8.

The toxicity of solutions of ammonium compounds is attributed largely to the undissociated base probably because of its distinctive penetrative properties rather than to the ions present. The ammonium

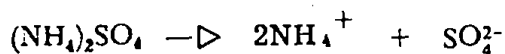
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Table 1: Results showing threshold concentrations, LC₅₀ values, fiducial and safe concentrations for the two Ammonium compounds.

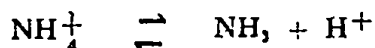
Name of the compound	Threshold concentration ppm	Mean 24-h LC ₅₀ value ppm	Fiducial limits ppm		Mean 48-h LC ₅₀ value ppm	Fiducial limits ppm		* Safe concentration ppm
			lower	upper		lower	upper	
Ammonium chloride	150.0	315.0	311.90	318.10	295.0	289.63	300.57	29.49
Ammonium sulphate	400.0	566.0	562.39	569.61	546.0	542.39	549.61	54.64

*Safe concentrations were calculated from the formula suggested by Turnbull, De Mann, and Weston (1954).

compounds in solution get ionised as follows:



At pH values higher than 7, ammonium ion undergoes dissociation as follows:-



The above reaction is pH dependent. It is the un-ionized form of ammonia (NH₃) which is responsible for fish mortality as the ionized form (NH₄⁺) is unable to pass the tissue barriers (Milne et al., 1958). However, it has not been established whether the ammonium ions have any pronounced influence upon chronic toxicity of solutions of ammonia and the ammonium salts. Furthermore, a high concentration of ammonium ions in the water which is not initially toxic, should be regarded as a potential hazard to fish life, if the pH is subjected to considerable fluctuations. Such changes may result either due to natural cause or due to intermittent addition of other pollutants of an alkaline nature (Dondoroff and Katz 1950).

Dissolved oxygen level is another important factor affecting the ammonia toxicity. The level of dissolved oxygen in all the test containers of the present experiments was maintained above 5 mg/l. Merkens and Downing (1957) reported that a decrease in dissolved oxygen increased the toxicity of un-ionized ammonia. Burrows (1964) stated that the effects of even low concentrations of un-ionized ammonia are real,

demonstrable and definitely detrimental to living organisms. Thus, from the available evidence it can be demonstrated that when un-ionized ammonia concentrations become dominant in rearing ponds, growth rate, physical stamina, and disease resistance are impaired (Burrows, 1964). He also observed that the exposure of chinook salmon fry to sublethal levels of ammonia produces considerable hyperplasia of the gill epithelium, with concomitant decreased resistance to bacterial gill disease.

A concentration of the non-ionic ammonia or ammonium base of 1.2 to 3 ppm (as NH₃) has been reported to be quite rapidly and uniformly toxic to relatively hardy species in solutions of varying pH and ammonium ion contents. Several investigators have reported that the lethal levels for many species are even lower. There is a very wide variation in the results of earlier investigators who have studied the toxicity of ammonium salts under different conditions. Further studies are evidently needed to establish more definitely the minimal lethal concentration of ammonia for various fish species under different sets of experimental conditions.

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