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Un-ionized Ammonia in Sediment Pore Water From the Upper Mississippi River

The toxicity of pore water (water occupying spaces between sediment particles) may have contributed to recent, widespread declines of the long fingernail clam (*Musculium transversum*) in the Upper Mississippi River, according to experts. Long fingernail clams are more sensitive to un-ionized ammonia (NH_3) than many other invertebrate and vertebrate species. The mean 96-h LC50 reported in the literature for long fingernail clams was 1,110 µg NH_3/L in acute toxicity tests. Researchers found that the growth of these clams was completely inhibited by exposure to 36 µg of NH_3/L for 6 weeks and hypothesized that elevated ammonia concentrations in pore water contributed to the decline of fingernail clam populations in the Illinois River in the 1950's. Recent unpublished studies by the U.S. Geological Survey have shown that surficial sediments are very enriched with nitrogen in the reach of the Upper Mississippi River where populations of long fingernail clams have declined.

Pore Water Sampled at Four Sites From February Through October

We examined temporal and spatial patterns of NH_3 in pore water and overlying surface water at four sites in Navigation Pool 8 on the Upper Mississippi River near La Crosse, Wisconsin, from February through October 1993. During each sampling period, three sediment cores (5.0 cm in diameter) were obtained at each site and sectioned into 0–4, 4–8, and 8-12 cm strata (depth below the sediment–water interface). Shortly after sectioning, each stratum was measured for temperature and pH. Composite samples of surface water were obtained from depths of 0.25, 0.50, and 0.75 times the maximum water depth at each site.

In the laboratory, sediments were centrifuged at 6,000 rpm for 20 min at 4°C, and pore water samples were decanted into 15-mL Vacutainers and preserved to pH <2 with 10% sulfuric acid. Samples were stored for a maximum of 4 days at 4°C ± 2°C until analyzed for total ammonia nitrogen on an autoanalyzer. Concentrations of NH_3 were calculated from total ammonia nitrogen, pH, and temperature. The accuracy and precision of our chemical determinations were verified by analysis of quality control samples, spiked water samples, triplicate subsamples, and replicate samples of pore water.

Variation in NH_3 Concentration

The NH_3 concentration in pore water differed significantly among sampling periods, with greatest concentrations in summer (Fig. 1*A*). At sites 1, 3, and 4, the maximum NH_3 concentrations were in late August, coinciding with maximum sediment temperature. NH_3 concentrations in pore water ranged from <1 to 20 µg/L in winter, and from 1 to 175 µg/L in summer. In winter, mean NH_3 concentrations were similar among sites, ranging from 2 to 10 µg/L.

The NH_3 concentration in pore water increased significantly with increasing sediment depth, with measured concentrations of 9 to 69 µg NH_3/L in the 8–12 cm stratum (Fig. 1*B*). Concentrations of NH_3 in pore water from the 0–4 cm stratum ranged from 2.5 to 63 µg/L, significantly less than those in pore water from the 4–8 cm and 8–12 cm strata.

Mean concentrations of NH_3 in surface water were always less than concentrations in sediment pore water (Fig. 1*B*). In summer, for example, NH_3 concentrations in pore water were 5 to 20 times those in overlying surface water. Concentrations of NH_3 in surface water, which ranged from 1.0 to 5.3 µg/L, were lowest in winter and highest in midsummer and late fall.

Higher Concentrations of NH_3 Likely During Warm Periods With Low Flow

Except for a brief period in late August, the measured concentrations of NH_3 in pore water from sites 1, 2, and 3 were less than concentrations known to adversely affect long fingernail clams. In 1975, dense populations of clams (2,500 to 5,200 clams/m^2) were observed at sites 1, 2, and 3. In the present study, densities of long fingernail clams at these sites were much lower (10 to 75 clams/m^2). For a 4-month period at site 4, concentrations of NH_3 in pore water from all sediment depths exceeded concentrations that inhibit growth of long fingernail clams in laboratory studies. However, these NH_3 concentrations did not seem to be acutely toxic to long fingernail clams, which were present at the site (130 clams/m^2).

The present study was conducted during a year of higher than normal flow and water levels. The declines of long fingernail clams in the Upper Mississippi River have occurred chiefly during low-flow periods associated with drought. The production of ammonia by microbial decomposition in the sediments is enhanced by high temperature and an abundant supply of biogenic matter, conditions associated with low-flow and drought that could cause episodic toxicity in the river sediment. We suspect that NH_3 concentrations in pore water during periods of low flow and high sediment temperature would be much greater than those measured in this study.

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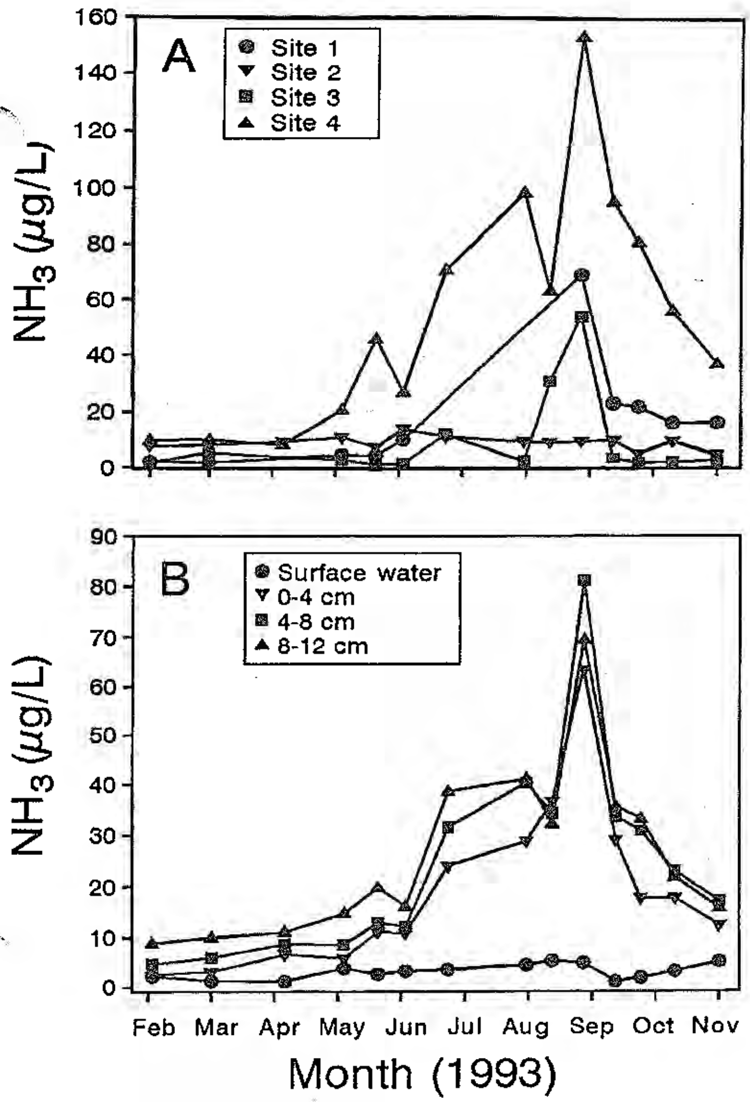

Fig. 1. (*A*) Temporal trends in mean un-ionized ammonia (NH_3) averaged over all sediment depths and (*B*) spatial trends in mean un-ionized ammonia (NH_3) concentrations in surface and pore water from three sediment depths below the sediment–water interface averaged over all sites in Pool 8, Upper Mississippi River.