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Diurnal Patterns of Ammonium and Un-ionized Ammonia in Streams Receiving Secondary Treatment Effluent

W. G. Crumpton* and T. M. Isenhart

Department of Botany, Iowa State University, Ames, Iowa 50011

Ammonia is a common pollutant of streams receiving domestic and industrial wastewater effluent. In aqueous solution, ammonium (NH_4^+) and un-ionized ammonia (NH_3) form a pH dependent equilibrium according to the relationship $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$. Although ammonium is relatively nontoxic, un-ionized ammonia is toxic to a variety of aquatic organisms. Water quality criteria have been derived for un-ionized ammonia based on its toxicity to fish and aquatic invertebrates (USEPA 1984). These criteria are based on static toxicity tests, using fixed concentrations of ammonia. However, Thurston et al. (1981) demonstrated that, for the same total dose exposure, trout were significantly more susceptible to fluctuating concentrations of ammonia than to fixed concentrations.

The effects of fluctuating concentrations of ammonia could be especially significant in streams receiving sewage treatment effluent. Ammonia loads from sewage treatment facilities often display pronounced diurnal patterns, which may be imparted to receiving streams. In addition, diurnal patterns in stream pH and temperature could significantly affect ammonia speciation. The pH of most surface waters is controlled by equilibria between CO_2, HCO_3^-, and CO_3^{2-}. Photosynthetic consumption of CO_2 tends to increase pH during the day while respiratory production of CO_2 tends to decrease pH at night (Wetzel 1983). Diurnal patterns in pH due to photosynthesis and respiration could significantly affect ammonia speciation and thus un-ionized ammonia concentrations in poorly buffered or highly productive streams. This paper describes diurnal patterns in ammonium and un-ionized ammonia in a stream receiving secondary treatment effluent and illustrates the effects of effluent loads, pH, and temperature on un-ionized ammonia patterns.

MATERIALS AND METHODS

Until just north of Ames, Iowa, the South Skunk River meanders through a postglacial valley with pool and riffle areas over rock, sand, or mud bottom. From Ames south, the river follows a preglacial channel with a shifting sand

*Correspondence and reprint requests.

substrate (Jones 1975). The Ames municipal sewage treatment facility consists of standard rate trickling filters, and discharges secondary treatment effluent to the South Skunk River below Ames. A series of diel studies was conducted to determine patterns of ammonium and un-ionized ammonia below the Ames effluent discharge during periods of low flow in the summer of 1985. During each study, triplicate 20 ml samples were collected at middepth from a series of sites below the effluent discharge at approximately 3 hour intervals and preserved for analyses of ammonium as described by Crumpton et al. (1987). Stream temperature (+0.1 oC), pH (+0.01 pH), and dissolved oxygen (+0.05 mg O2 L-1) were measured in the field using portable meters. Stream velocity and discharge were determined using a Pygmy Gurley meter.

Orion model 95-12 gas-sensing ammonia probes were used to measure total ammonium-ammonia nitrogen based on ammonia in basified samples as described by Crumpton et al. (1987). In-stream concentrations of un-ionized ammonia were calculated according to the equation of Emerson et al. (1975), based on stream temperature, pH, and total ammonium-ammonia concentrations.

As part of a related study, gross primary production and community respiration were calculated based on diurnal changes in dissolved oxygen and temperature (Crumpton and Isenhart 1987).

RESULTS AND DISCUSSION

The South Skunk River is very productive, as are many of the small, low gradient streams in this heavily agricultural region. Under low flow conditions, these streams are broad and shallow, with high nutrient loads, low turbidity, and high light exposure. Although primary production of suspended algae is low, benthic algal production can be extremely high (Kortge 1984; Robertson 1986). The portion of the South Skunk River which we studied is devoid of aquatic macrophytes. During the current study, dissolved oxygen concentrations in the South Skunk River below the Ames effluent discharge ranged between lows of 30-50% of saturation at night and highs of 200-250% of saturation during the day. Rates of gross primary productivity ranged between 7.1 and 20.2 g C m-2 day-1 and rates of community respiration ranged between 12 and 21 g C m-2 day-1 (Crumpton and Isenhart 1987). These high rates of primary production and respiration were reflected by significant increases in pH during the day and decreases in pH at night (Figure 1). These rates of primary productivity are extremely high and roughly twice the peak summer rates reported for small agricultural streams in central Iowa in the absence of point source loads (Kortge 1984). These high rates may reflect stimulation of algal production by ammonium loads from the Ames sewage treatment plant. Bushong (1985) reported that ammonium stimulated periphyton production in the South Skunk River by 2-3 fold during several low flow periods.

Background levels of total ammonium-ammonia in the South Skunk River upstream from Ames are below 1 mg L-1 (Bushong 1985; Crumpton and Hersh 1987). However, effluent from the Ames sewage treatment plant dramatically

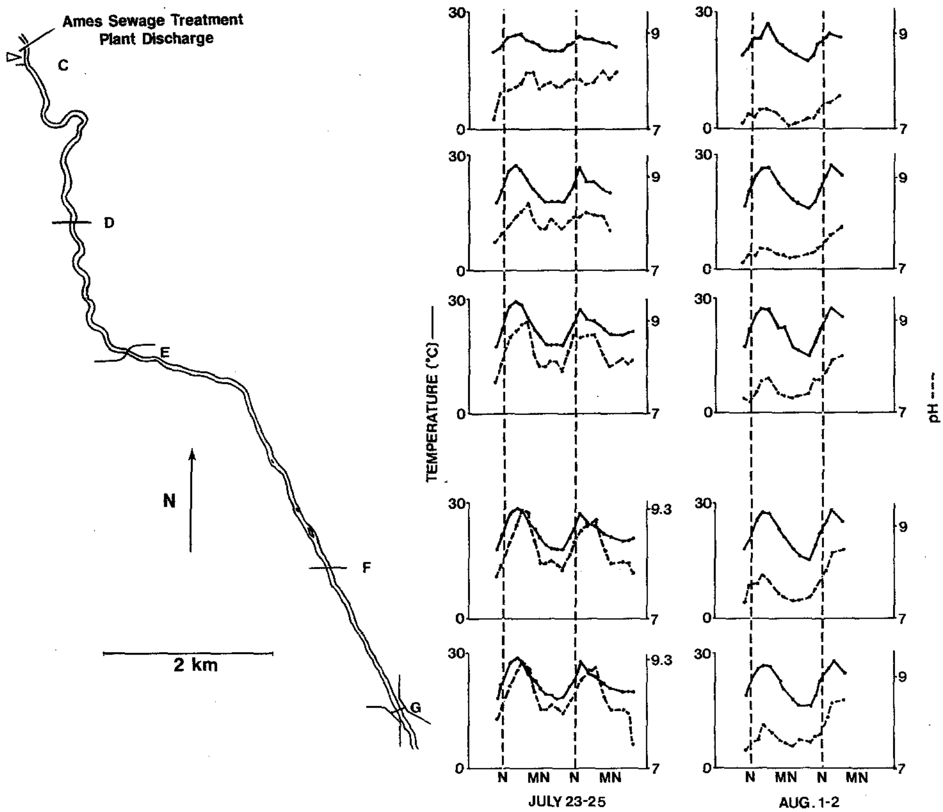

Figure 1. Temperature and pH at sites C-G on July 23-25 and August 1-2, 1985. N=noon, MN=midnight.

increases concentrations in the river during low flow periods (Crumpton and Hersh 1987). Effluent from the treatment plant displays diurnal patterns in discharge rate and total ammonium-ammonia concentration (Young et al. 1978; Crumpton and Hersh 1987). During this study, pronounced diurnal patterns in total ammonium-ammonia concentration were imparted to the river by effluent loads, and these patterns persisted as far downstream as we sampled, approximately 10.4 km (Figure 2). At the uppermost site, concentrations peaked about midday and then declined through the evening. Lowest concentrations were observed at early to mid-morning. Diurnal patterns persisted at the downstream sites but the peaks appeared later at each successive site, displaced by an amount reflecting stream travel time between sites. At the farthest site, peak concentrations of total ammonium-ammonia were displaced to after midnight (Figure 2).

Pronounced diurnal patterns in un-ionized ammonia were also observed (Figure 2). At the uppermost sites, un-ionized ammonia concentrations followed a pattern which was similar to that of total ammonium-ammonia. However,

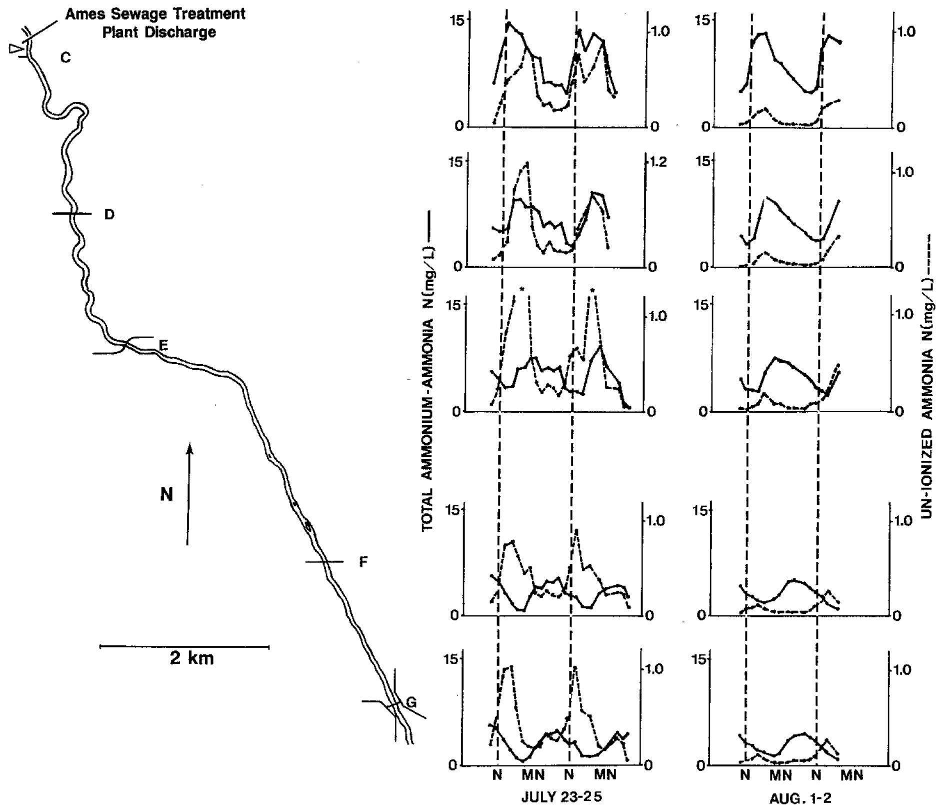

Figure 2. Total ammonium-ammonia and un-ionized ammonia at sites C-G on July 23-25 and August 1-2, 1985 (* off scale points, 2.2 and 1.4 mg/L). N=noon, MN=midnight.

un-ionized ammonia patterns at downstream sites did not mirror those of total ammonium-ammonia. Un-ionized ammonia concentrations peaked in mid-afternoon at all sites, regardless of total ammonium-ammonia concentrations. Despite the large fluctuations in total ammonium-ammonia concentration, un-ionized ammonia patterns were largely determined by the effects of pH and temperature on ammonia speciation, especially at downstream stations. Pronounced diurnal patterns in stream temperature and pH were observed at all sites, with daytime increases of 5-10 ^{o}C and 0.5-1.5 pH units (Figure 1). However, un-ionized ammonia concentrations calculated using the mean temperature for each site differ very little from results of calculations incorporating diurnal temperature patterns (Figure 3). Clearly pH had the most significant effect on patterns of un-ionized ammonia.

Day to day variations in photosynthesis and pH peaks also significantly influenced patterns of un-ionized ammonia (Figure 2). Gross primary productivity and pH peaks on July 23 were comparable to those on July 24, and

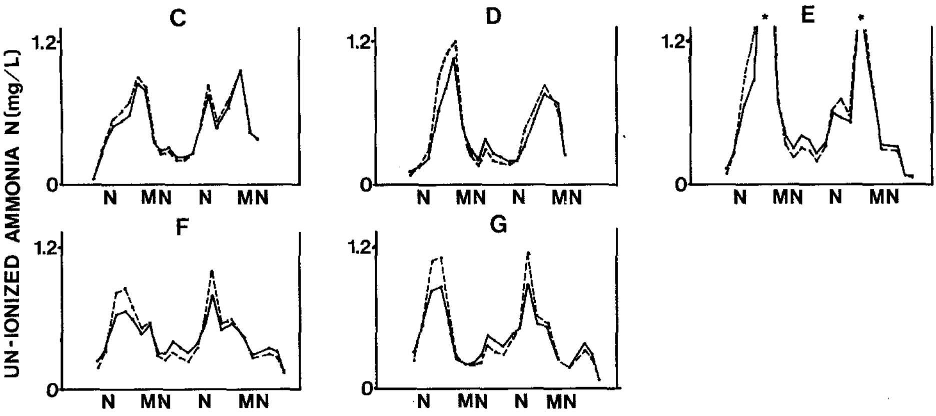

Figure 3. Un-ionized ammonia nitrogen at sites C-G on July 23-25 calculated using actual temperature (dashed line) and mean temperature (solid line) at each site (* off scale points, 2.2 and 1.4 mg/L). N=noon, MN=midnight.

un-ionized ammonia peaks were similar for these two days. On July 25, a major storm increased stream discharge more than an order of magnitude, to 5.3 m^3 sec^{-1}. The stream had returned to base flow (0.34 m^3 sec^{-1}) by August 1, but primary productivity and pH were still much lower than prior to the storm. Primary productivity and pH increased on August 2, but pH peaks were still about 0.5 unit lower than prior to storm flows. These patterns are reflected in the day-to-day variation in un-ionized ammonia concentrations within sites, despite similar temperatures and total ammonium-ammonia concentrations on all 4 days. Consistent with pH patterns, un-ionized ammonia concentrations were highest on July 23 and 24, lowest on August 1, and intermediate on August 2.

The combined effect of diurnal patterns in pH and total ammonium-ammonia concentration resulted in somewhat unexpected spatial patterns in un-ionized ammonia. Photosynthesis and pH peaks increased with distance downstream. In contrast, total ammonium-ammonia concentrations decreased with distance downstream. Total ammonium-ammonia peaks approximately coincided with pH maxima at the uppermost sites and with pH minima at the two farthest sites. Although total ammonium-ammonia concentrations were highest at the uppermost stations and peak concentrations coincided with pH peaks, pH maxima and therefore un-ionized ammonia concentrations were lower than at the middle site. Peak un-ionized ammonia concentrations at the two farthest sites were also lower than at the middle site. Although pH increased downstream, pH maxima at the farthest sites coincided with total ammonium-ammonia minima. As a result of these downstream trends, the middle site had the highest peak concentrations of un-ionized ammonia, not the sites closest to the effluent discharge.

Un-ionized ammonia concentrations can be greatly affected by diurnal loading patterns and by shifts in ammonia speciation due to diurnal patterns in temperature and pH. It is likely that many impacted streams will present diurnally fluctuating levels of toxicants, and of other stresses such as high temperature, high pH, and low dissolved oxygen. It is clear that algal photosynthesis can greatly affect patterns in pH and un-ionized ammonia, and these effects would be most significant in heavily impacted, highly productive streams. Although water quality criteria are normally based on static tests, fish may be much more susceptible to the diurnally fluctuating levels of toxicants expected in highly impacted streams (Thurston et al. 1981).

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