Ecological Applications, 17(7), 2007, pp. 2087–2099

AMMONIA MODELING FOR ASSESSING POTENTIAL TOXICITY TO FISH SPECIES IN THE RIO GRANDE, 1989–2002

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Abstract. Increasing volumes of treated and untreated human sewage discharged into rivers around the world are likely to be leading to high aquatic concentrations of toxic, un-ionized ammonia (NH_3), with negative impacts on species and ecosystems. Tools and approaches are needed for assessing the dynamics of NH_3. This paper describes a modeling approach for first-order assessment of potential NH_3 toxicity in urban rivers. In this study daily dissolved NH_3 concentrations in the Rio Grande of central New Mexico, USA, at the city of Albuquerque's treated sewage outfall were modeled for 1989–2002. Data for ammonium (NH_4^+) concentrations in the sewage and data for discharge, temperature, and pH for both sewage effluent and the river were used. We used State of New Mexico acute and chronic NH_3-N concentration values (0.30 and 0.05 mg/L NH_3-N, respectively) and other reported standards as benchmarks for determining NH_3 toxicity in the river and for assessing potential impact on population dynamics for fish species. A critical species of concern is the Rio Grande silvery minnow (*Hybognathus amarus*), an endangered species in the river near Albuquerque. Results show that NH_3 concentrations matched or exceeded acute levels 13%, 3%, and 4% of the time in 1989, 1991, and 1992, respectively. Modeled NH_3 concentrations matched or exceeded chronic values 97%, 74%, 78%, and 11% of the time in 1989, 1991, 1992, and 1997, respectively. Exceedences ranged from 0% to 1% in later years after enhancements to the wastewater treatment plant. Modeled NH_3 concentrations may differ from actual concentrations because of NH_3 and NH_4^+ loss terms and additive terms such as mixing processes, volatilization, nitrification, sorbtion, and NH_4^+ uptake. We conclude that NH_3 toxicity must be considered seriously for its potential ecological impacts on the Rio Grande and as a mechanism contributing to the decline of the Rio Grande fish community in general and the Rio Grande silvery minnow specifically. Conclusions drawn for the Rio Grande suggest that NH_3 concentrations may be high in rivers around the world where alkaline pH values are prevalent and sewage treatment capabilities are poorly developed or absent.

Key words: ammonia; ammonium; endangered species; Hybognathus amarus; *long-term trends; New Mexico, USA; Rio Grande silvery minnow; sewage; wastewater; water quality.*

Introduction

Increasing volumes of treated and untreated human sewage discharged into rivers around the world may be leading to high aquatic concentrations of gaseous, dissolved, un-ionized ammonia (NH_3) in ecosystems in which alkaline pH values prevail. Ammonia is known to be toxic to numerous aquatic species across many taxa (USEPA 1999). Chronic effects of exposure to NH_3 in fish include impaired swimming, respiratory and hormonal dysfunction, growth of lesions, and damage to multiple organs. These chronic effects generally lead to decreased survival, growth, and reproduction. Ammonia toxicity can be lethal at higher levels (Thurston et al. 1986, USEPA 1999).

Manuscript received 31 July 2006; revised 7 February 2007; accepted 8 March 2007. Corresponding Editor: A. R. Townsend.

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Ammonia concentrations are widely regulated in surface waters throughout the United States (USEPA 1999). However, various workers have suggested that concentrations leading to chronic toxicity may be an order of magnitude lower than most regulatory limits (USEPA 1999, Dodds and Welch 2000, Buhl 2002). Ammonia dynamics in aqueous environments complicate the effort to assess levels of toxicity. In freshwater systems, total ammonia concentrations are composed of un-ionized ammonia (NH_3) and ammonium ion (NH_4^+) in an equilibrium that is mediated primarily by pH and temperature as described as follows:

$$NH_4^+ \leftrightarrow NH_3 + H^+ \qquad (1)$$

(pK_a for ammonia at 20° C is 1.710×10^{-5}).

Ionic strength also plays a role in NH_3 speciation, but its role is considered small, and in freshwater toxicity studies it is generally ignored (USEPA 1999). Ammonia is much more toxic than NH_4^+. However, NH_4^+ toxicity

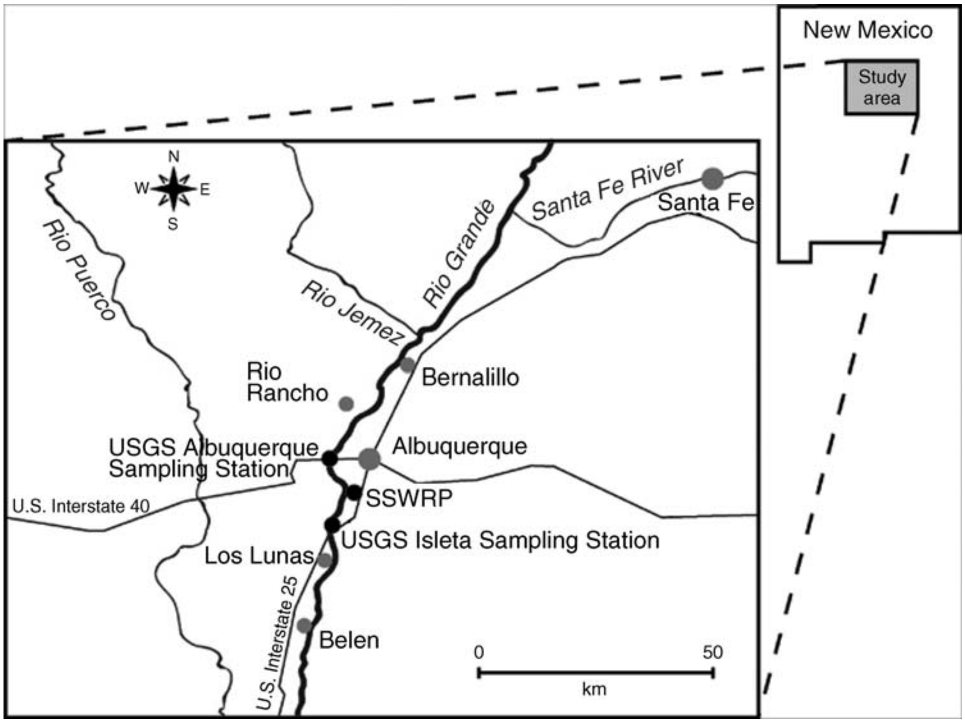

FIG. 1. Map of the study area around the city of Albuquerque, New Mexico, USA, including the Rio Grande, major tributaries, major cities, interstate highways, the South Side Water Reclamation Plant, and sampling locations.

is believed to contribute significantly to total NH_3 toxicity under conditions of low pH, when the NH_4^+ fraction of total ammonia is very high. In waters with pH values >7.5 un-ionized NH_3 concentrations are the predominant factor in NH_3 toxicity and NH_4^+ toxicity is generally ignored (USEPA 1999).

The total nitrogen load added anthropogenically to global terrestrial and aquatic systems is well known to be increasing (Vitousek et al. 1997, Howarth et al. 2002). Increases in many rivers are positively correlated to increases in human population (Howarth et al. 1996, Caraco and Cole 1999). Point sources of nutrient inputs are significant sources for surface waters in urbanizing regions, and municipal wastewater is the primary point source of N in rivers of the United States (Mitsch et al. 2001). Ammonia concentrations are generally low (<0.01 mg/L) in well-treated sewage effluent such as that found in most parts of the United States, but they can be very high (>20 mg/L) at times when sewage treatment plants are malfunctioning or in parts of the world where sewage treatment is ineffective or nonexistent. Ammonium concentrations in sewage discharge in the United States are now widely monitored, although toxic, un-ionized ammonia (NH_3) generally is not. The dynamic reactions that take place when total ammonia in sewage discharge mixes with a receiving river and equilibrates between NH_4^+ and NH_3 complicate the effort to calculate the toxicity and both the spatial and temporal dimensions of the resulting NH_3 plume.

This paper quantifies the potential for NH_3 toxicity to be a water quality concern downstream of a major point source input of treated sewage effluent to the Rio Grande at Albuquerque, New Mexico, USA. A modeling approach is used to assess downstream NH_3 concentrations based upon discharge, pH, and temperature for the years from 1989 to 2002. Statistical methods are used to generate data for filling incomplete data sets. The same modeling and statistical approaches could be used for characterizing NH_3 toxicity in other rivers or could be used with minor modifications to characterize concentrations of other contaminants delivered to rivers from other point sources. In this study, calculated NH_3 calculations are used to assess potential toxicity to the Rio Grande silvery minnow (*Hybognathus amarus*), an endemic endangered fish.

METHODS

Study site

The Rio Grande flows ~3220 km from the mountains of Colorado, through arid and semiarid lands in New Mexico, along the border between Texas and Mexico, and on to its mouth in the Gulf of Mexico. The total catchment contributing runoff is ~470 000 km^2 (Revenga et al. 1998). In central New Mexico, the Rio Grande flows through the growing urban center around Albuquerque (Fig. 1), where municipal sewage from the city of Albuquerque's South Side Water Reclamation Plant (SSWRP) is the leading regional point source for

TABLE 1. Parameters included as input for the model.

Parameter	Unit	Medium	Data source	Temporal range of data
N-NH_4^+, (dissolved)	mg/L	sewage	SSWRP	1989, sporadic
				1991–1992 and 1996–1997, weekly
				1998–2002, daily
Discharge	m^3/s	sewage	SSWRP	1989–2002, daily
		river	USGS	1989–2002, daily
pH		sewage	SSWRP	1999–2002, daily
		river	USGS	1989–1997, sporadic
				1998–2002, monthly
Temperature	°C	sewage	SSWRP	1996–2002, daily
		river	USGS	1989–1996, daily
				1997–2002, monthly

Note: All time series data in the model begin on 7 November 1989, the first date for which South Side Water Reclamation Plant (SSWRP; Albuquerque, New Mexico, USA) data on N-NH_4^+ (dissolved) are available.

N to the river. A study of nutrient trends in the upper and middle Rio Grande from 1975 to 1999 showed decreases for many nutrient parameters across the region, but increases in dissolved nitrate concentrations and total N concentrations downstream of the SSWRP, the city's sole sewage outfall (Passell et al. 2005). These increases are positively correlated with increasing population in the region (Passell et al. 2005).

Nitrogen inputs to the Rio Grande represent only one of many important anthropogenic impacts to the river. Since Spanish colonization of the basin in the 1500s, the natural hydrology, water quality, and ecology of the river have been altered in many ways. Dams and reservoirs impound flow, jetty jacks impair lateral movement of flood waters and organic matter to the flood plain, and levees completely obstruct lateral movement. Floodplain land uses, species compositions, fire regimes, and other ecosystem processes have changed in both space and time. In addition, river beds are aggrading in some reaches and degrading in others. Large withdrawals of surface water for agricultural irrigation have strongly affected Rio Grande ecology since the late 1800s, and large withdrawals of both surface and groundwater, now for agricultural, residential, and industrial uses, continue to have strong effects. Point and nonpoint pollution sources have increased at the same time that river discharge volumes have decreased. Finally, native species have been threatened and nonnative species have prospered (Crawford et al. 1996, USFWS 2002*a*, Passell et al. 2004).

The endemic Rio Grande silvery minnow (Cyprinidae: *Hybognathus amarus*) is currently listed as an endangered fish species by the State of New Mexico, the United States, and the Republic of Mexico (USFWS 1999). The silvery minnow is the last surviving endemic pelagic minnow of the family Cyprinidae in the main stem of the Rio Grande (USFWS 1999). Four other cyprinids have been extirpated from the main stem of the Rio Grande (Sublette et al. 1990). Presently, the silvery minnow has been reduced to ~5% of its historic range. The minnow currently survives only in the middle Rio Grande (MRG) of New Mexico near Albuquerque, and remaining populations have undergone precipitous declines (Dudley and Platania 2002, USFWS 2003). Hydrological changes throughout the Rio Grande (e.g., dams, changes in channel morphology, diversions, dessication) are frequently blamed for the decline of silvery minnow populations. Biological factors such as predation, competition with nonnative species, and changes to algal community structure and productivity also are suggested as contributing to silvery minnow declines. We suggest that water quality also has contributed to the precipitous decline, but the role that changes in water quality play in the decline of silvery minnow populations has been difficult to assess or quantify (USFWS 2003). A modeling approach is used to assess the potential for ammonia toxicity from a point source as one causal mechanism in fish decline.

Modeling

Dissolved un-ionized ammonia (NH_3-N) concentrations were calculated on a daily time step for the Rio Grande at the outfall of the SSWRP from 7 November 1989 through 31 December 2002. Daily concentrations were calculated using daily values for dissolved ammonium, discharge, pH, and temperature (Table 1). Calculations were made using a system dynamics modeling platform called Studio Expert 2001 (Powersim, Bergen, Norway); system dynamics modeling platforms are increasingly used for modeling water resource dynamics (Simonovic and Fahmy 1999, Guo and Liu 2001, Xu et al. 2002, Stave 2003, Tidwell et al. 2004). Our model output includes the results of daily stoichiometric equilibrium calculations for the concentration of dissolved NH_3-N in the river. These values are derived from measured concentrations of dissolved NH_4^+-N in the SSWRP discharge and the dynamics involved in the mixing of pH, temperature, and water volume between SSWRP effluent discharge and Rio Grande discharge. These data were collected by both the U.S. Geological Survey (USGS) and the SSWRP, using standard methods. The equilibrium calculation applied in this model for the calculation of ammonia species is

$$K_b = [(NH_4^+)(OH^-)]/(NH_3) \qquad (2)$$

in which K_b is the dissociation constant for NH_4^+ (NRC 1979).

The modeling effort was constrained by the availability of daily data for NH_4^+ concentrations in SSWRP effluent. These data were available from 7 November 1989 through 31 December 2002; however, they were collected sporadically at the beginning of the study period and daily toward the end (Table 1). Daily discharge data for both SSWRP effluent and the Rio Grande were available over the entire study period.

Ammonium concentrations in SSWRP effluent were measured using an automated analyzer (Bran+Luebbe, Tarrytown, New York, USA) and the phenate method, with a detection limit of 0.01 mg/L N. The same device and method were used for the entire study period. The method tests for total ammonia (NH_3-N plus NH_4^+-N). We assumed the reported value represented primarily NH_4^+-N because the sample was filtered before analysis and excess gaseous NH_3-N was lost to the atmosphere during filtration.

Daily SSWRP pH data were only available for a two-month period in 1997, a 10-month period in 1998 and 1999, and a three-year period from May 1999 through 2002 (Appendix A). These historic data show considerable variation and little sign of important trends and are normally distributed. Therefore, we generated pH data for the entire study period, 1 November 1989 through 31 December 2002, by sampling randomly from a normal distribution with a mean and standard deviation (SD) identical to the mean and SD for the historical data (Appendices A and B).

Daily Rio Grande pH data were collected sporadically across the entire study period at the USGS Albuquerque sampling station upstream of the SSWRP (Appendix A). There was a total of nine values for pH (from 1989 through 1997), and the distribution of these limited data was roughly normal. There was an average of 10 values per year from 1998 to 2002, with a declining trend in mean annual pH values from year to year. The data distributions for each year were roughly normal, and the distribution for all Rio Grande pH data taken together was normal. We generated Rio Grande pH data for years 1989–1997 by sampling from a normal distribution with a mean and SD identical to the mean and SD in the historic data (Appendices A and B). For the years 1998–2002, we generated data for each year by sampling normal distributions with means and SDs identical to those for the historic annual data (Appendix B).

Ammonia concentrations are sensitive to small changes in pH. Since we were generating daily pH values for both the SSWRP and the Rio Grande, we wanted to be sure that no single set of values generated probabilistically would have a large influence on our final calculations. Therefore, we generated 60 different sets of daily SSWRP pH values for the study period and 60 different sets of Rio Grande pH values for the study period. When we performed our final calculations, we ran the model 60 different times, with a different set of SSWRP pH values and a different set of Rio Grande pH values in each run. We then aggregated and reported the results.

Daily temperature data for the SSWRP effluent were available from 1996 to 2002 (Appendix A). Annual variation in the data was consistent, and there was no long-term trend. We used historic data from 7 November 1996 through 31 December 2002 to provide data in the study period from 7 November 1989 to 31 December 1995. We then used the actual historic data from 1 January 1996 through 31 December 2002 to complete the record (Appendix A).

Daily temperature data for the Rio Grande were available from 1989 through May 1993, and then two or three data values weekly were available through September 1996. Monthly data were available starting in October 1996 and continued through 2002 (Appendix A). Seasonal variation in all these data was consistent, and there was no long-term trend. The data through September 1996 were collected randomly at different times throughout the day. We applied locally weighted scatterplot smoothing (LOWESS) with a 0.5 tension (SYSTAT 9.0; SYSTAT, Evanston, Illinois, USA) to serve two purposes: (1) to reduce variation in the data collected through September 1996 that could have been caused by data being collected at different times during the day; (2) to generate daily data for the data gaps that occur in the record after October 1996 (Appendix A). The standard error between the historic values and the data generated by LOWESS was $\sim$0.02°C. The distribution of the errors was slightly skewed with a minimum of -0.4°C and a maximum of $\sim$5.6°C, with two standard deviations of $\pm$1.8°C.

The SSWRP effluent in the model is assumed to discharge into the river and then instantaneously mix with flow in the Rio Grande. Rapid and complete mixing is also assumed for pH and water temperature between SSWRP effluent and the Rio Grande. Further discussion of the mixing issue occurs below. Ammonium concentrations in the SSWRP effluent are likewise assumed to mix instantaneously with discharge in the Rio Grande. The resulting discharge, pH, water temperature, and NH_4^+ and NH_3 concentration data are based on instantaneous mixing of the two water sources.

Results

Modeled daily values for dissolved NH_3-N concentrations in the Rio Grande after mixing with the SSWRP outfall and averaged across 60 runs of the model are shown in Fig. 2. Annual mean NH_3-N concentrations modeled for each year in the study period are shown in Fig. 3, and summary statistics by year for modeled NH_3-N concentrations are shown in Appendix C.

Gaps in the daily values in Fig. 2 reflect gaps in NH_4^+-N data for SSWRP effluent. The upper dotted line in

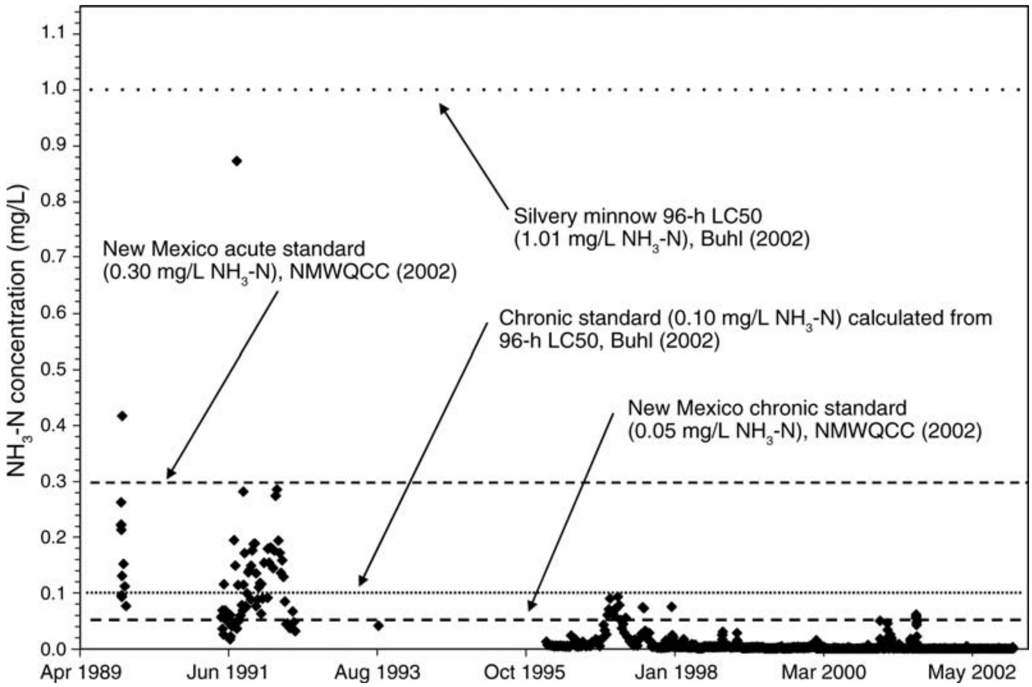

FIG. 2. Average daily NH_3-N concentration, 1989–2002, from 60 runs of the model. New Mexico standards (NMWQCC, New Mexico Water Quality Control Commission) are for warm-water fisheries at pH 8.0 and 25°C. The abbreviation "96-h LC50" refers to the lethal concentration at which half the number of fish would be expected to die in 96-h laboratory tests.

Fig. 2 (1.01 mg/L) indicates the approximate 96-h LC50 (the lethal concentration at which half the number of fish would be expected to die in 96-h laboratory tests) for the Rio Grande silvery minnow as determined by Buhl (2002). No modeled NH_3-N concentrations exceeded this value. The lower dotted line in Fig. 2 (0.10 mg/L) indicates the approximate NH_3-N concentration with chronic negative impacts on the silvery minnow, based on the 96-h LC50 concentration by Buhl (2002) and following guidelines for establishing chronic criteria derived from LC50 data described in USEPA (1999) and by the State of New Mexico (NMWQCC 2002). This value was exceeded by modeled NH_3-N concentrations on numerous dates in 1989, 1991, and 1992, and it was exceeded briefly in 1996 and 1997. These acute and chronic values, and all others reported in this paper, will assume NH_3-N concentrations at pH 8.0 and a temperature of 25°C, unless otherwise noted.

The upper dashed line and the lower dashed line in Fig. 2 show the acute criterion and the chronic criterion, respectively, established by the State of New Mexico for NH_3-N concentrations for warm-water fisheries (NMWQCC 2002). The acute NH_3-N standard was exceeded on two days, and the chronic standard was exceeded frequently in 1989, 1991, and 1992 and during brief periods in 1997 and 2001.

Table 2 shows NH_3-N concentration exceedences for each year averaged over 60 runs of the model for the four different acute or chronic criteria. Table 2A shows the mean number of days from 60 runs of the model on which NH_3-N concentrations were equal to or greater than 0.30 mg/L, the State of New Mexico's acute value. Ammonia nitrogen concentrations matched or exceeded that value on 13%, 3%, and 4% of the days for which data were available in the years 1989, 1991, and 1992, respectively. Only one data value for NH_4^+-N concentration in SSWRP effluent was available in 1993, and no data were available in 1994 and 1995. After 1996, no modeled NH_3-N values exceeded the state's acute criterion.

Table 2B shows the mean number of days from 60 runs of the model on which NH_3-N concentrations were equal to or greater than 0.10 mg/L. This is the chronic criterion established for the Rio Grande silvery minnow based on the 96-h LC50 concentration established by Buhl (2002) and following guidelines for establishing species-specific chronic criteria reported by the USEPA

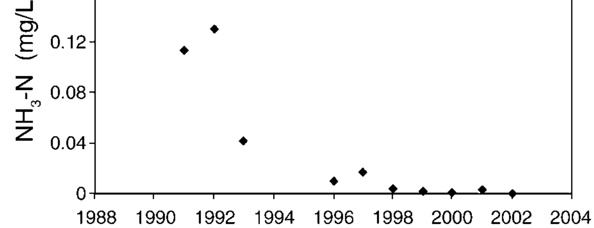

FIG. 3. Annual mean NH_3 concentrations, 1999–2002.

TABLE 2. Mean number of exceedences (ME) for NH_3-N for each year over 60 runs of the model of concentrations equal to or greater than (A) 0.30 mg/L, the New Mexico acute standard for warm water fisheries; (B) 0.10 mg/L, a chronic criterion calculated from the 96-h LC50 concentration from Buhl (2002); (C) 0.05 mg/L, the New Mexico chronic standard for warm-water fisheries; and (D) 0.001 mg/L, the possible low-end chronic value for Rio Grande silvery minnows and other aquatic species (USEPA 1999, Buhl 2002).

Year	ME	Median	Range	SD	±2 SD	*N*	Percent exceedence
A) Concentration ≥0.30 mg/L							
1989	1.40	1.5	0–3	0.86	0.22	11	13
1990	···	···	···	···	···	···	···
1991	1.55	2.0	1–3	0.60	0.15	47	3
1992	0.90	1.0	0–3	0.77	0.20	22	4
1993	0	0	0	0	0	1	0
1994	···	···	···	···	···	···	···
1995	···	···	···	···	···	···	···
1996	0	0	0	0	0	45	0
1997	0	0	0	0	0	108	0
1998	0	0	0	0	0	364	0
1999	0	0	0	0	0	365	0
2000	0	0	0	0	0	365	0
2001	0	0	0	0	0	365	0
2002	0	0	0	0	0	365	0
B) Concentration ≥0.10 mg/L							
1989	8.27	8	6–10	0.95	0.25	11	75
1990	···	···	···	···	···	···	···
1991	18.50	19	14–23	2.27	0.59	47	39
1992	12.50	13	10–15	1.15	0.30	22	57
1993	0	0	0	0	0	1	0
1994	···	···	···	···	···	···	···
1995	···	···	···	···	···	···	···
1996	0.02	0	0–1	0.13	0.03	45	0.04
1997	1.63	1	0–5	1.13	0.29	108	1.5
1998	0	0	0	0	0	364	0
1999	0	0	0	0	0	365	0
2000	0	0	0	0	0	365	0
2001	0	0	0	0	0	365	0
2002	0	0	0	0	0	365	0
C) Concentration ≥0.05 mg/L							
1989	10.7	11	7–11	0.93	0.24	11	97
1990	···	···	···	···	···	···	···
1991	34.9	35	29–40	2.22	0.57	47	74
1992	17.1	17	14–20	1.24	0.32	22	78
1993	0	0	0	0	0	1	0
1994	···	···	···	···	···	···	···
1995	···	···	···	···	···	···	···
1996	0.4	0	0–1	0.5	0.13	45	1
1997	11.4	11	8–14	1.44	0.37	108	11
1998	0.2	0	0–1	0	0	364	0.1
1999	0.0	0	0	0	0	365	0
2000	0.0	0	0	0	0	365	0
2001	3.6	4	0–7	1	0.37	365	1
2002	0.0	0	0	0	0	365	0
D) Concentration ≥0.001 mg/L							
1989	11	11	0	0	0	11	100
1990	···	···	···	···	···	···	···
1991	47	47	0	0	0	47	100
1992	22	22	0	0	0	22	100
1993	1	1	0	0	0	1	100
1994	···	···	···	···	···	···	···
1995	···	···	···	···	···	···	···
1996	45	45	0	0	0	45	100
1997	108	108	0	0	0	108	100
1998	362	362	359–364	1.1	0.28	364	99.5
1999	339	339	329–346	3.27	0.85	365	93
2000	141	142	132–150	3.64	0.94	365	39
2001	201	201	191–208	3.75	0.97	365	55
2002	69	70	59–80	4.48	1.16	365	19

Note: The abbreviation "96-h LC50" refers to the lethal concentration at which half the number of fish would be expected to die in 96-h laboratory tests.

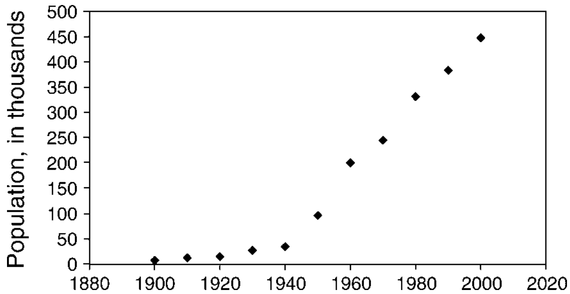

FIG. 4. Human population growth for the city of Albuquerque, 1900–2000 (Bartolino and Cole 2002).

(1999) and NMWQCC (2002). Ammonia nitrogen concentrations exceeded that value on 75%, 39%, and 57% of the days for which data were available in 1989, 1991, and 1992, respectively. Concentrations exceeded 0.10 mg/L on 0.04% and 1.5% of the days for which data were available in 1996 and 1997. After 1998, no modeled values exceeded 0.10 mg/L NH_3-N.

Table 2C shows the mean number of days from 60 runs of the model on which NH_3-N concentrations were equal to or greater than 0.05 mg/L, the chronic criterion established by the State of New Mexico for warm-water fisheries. Ammonia nitrogen concentrations exceeded that value on 97%, 74%, and 78% of the days for which data were available in 1989, 1991, and 1992, respectively. Ammonia nitrogen values exceeded 0.05 mg/L on 1%, 11%, 0.1%, and 1% of the days for which data were available in 1996, 1997, 1998, and 2001, respectively.

Table 2D shows the mean number of days from 60 runs of the model on which NH_3-N concentrations were equal to or greater than 0.001 mg/L. This value is a low-end chronic criterion proposed by the USEPA (1999) for preventing adverse effects on aquatic life. It is also proposed by Buhl (2002) as a possible chronic criterion for Rio Grande silvery minnow that accounts for the interacting effect of multiple waterborne toxicants. Ammonia nitrogen concentrations exceeded 0.001 mg/L on 100% of the days for which data were available through 1997. Exceedences decreased from 99.5% in 1998 to 19% in 2002.

DISCUSSION

The Rio Grande in the Albuquerque Reach

The human population in Albuquerque and surrounding areas grew steadily from 1940 to 2000 (Fig. 4; Passell et al. 2005). Population growth led to increases in the use of groundwater for residential and commercial purposes throughout the region. In Albuquerque and nearby municipalities, this water is carried through municipal drains to sewage treatment plants and then discharged to the Rio Grande. Albuquerque's SSWRP discharges to the river ~10 km below the USGS sampling station in central Albuquerque (Fig. 1).

The increase in Albuquerque's population is positively correlated to increases in effluent discharge from Albuquerque's SSWRP through about 1998 (Fig. 5a). Records from the SSWRP show that effluent discharge to the river increased from an annual average of ~1.5 m^3/s in 1977 (when data first become available) to a peak at ~2.4 m^3/s in 1996–1998. Effluent discharge then declines slightly to ~2.3 m^3/s in 2002, reflecting water conservation measures adopted in Albuquerque.

The USGS river discharge data for the Rio Grande at Albuquerque, 1977–2002, show large variation in annual averages (Fig. 5b). Application of Kendall's S test (Gilbert 1987, Helsel and Hirsch 2000) to those data indicates a nonsignificant trend of decreasing values ($S = -54$, $P = 0.23$). These results are heavily influenced by low discharge values for 1998–2002, which correspond to the onset of a regional, long-term drought believed to occur in a multidecadal pattern (Grissino-Mayer et al. 2002, Gray et al. 2003, Milne et al. 2003).

Annual discharge from the SSWRP to the Rio Grande makes the SSWRP one of the largest tributaries in the river's upper basin (MRGWA 1999, Passell et al. 2004). The SSWRP's role in mediating river water quality in the region is partly a function of the ratio between effluent discharge and the highly variable discharge in the Rio Grande. Fig. 5c shows that the ratio, expressed as a percentage, ranged from an average 2.2% in the high-water year of 1979 to an average of 16.6% in the low-water year of 2002. Kendall's S test

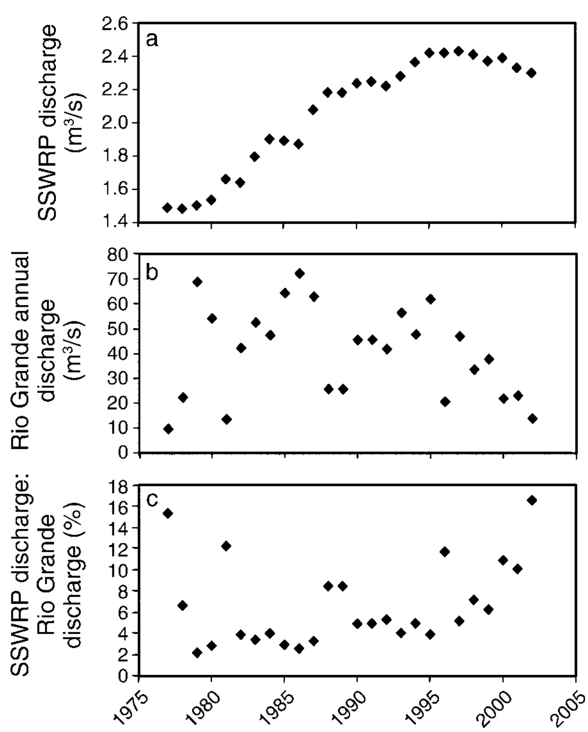

FIG. 5. (a) Albuquerque's South Side Water Reclamation Plant (SSWRP) discharge, (b) Rio Grande mean annual discharge at Albuquerque (10 km upstream of SSWRP), and (c) the ratio of SSWRP discharge to Rio Grande discharge expressed as a percentage.

TABLE 3. Chronic and acute NH_3-N concentrations for different aquatic species.

Species	NH_3-N	pH	°C	Effect	Reference
Lethal effects on assorted species					
Lost River sucker†	0.39–0.64	8.0	20	LC50, 96-h	Saiki et al. (1999)
Shortnose sucker†	0.44–0.87	8.0	20	LC50, 96-h	Saiki et al. (1999)
Colorado pikeminnow†	0.72	···	···	LC50, 28-d	Fairchild et al. (2002)
Razorback sucker†	0.63	···	···	LC50, 28-d	Fairchild et al. (2002)
Rainbow trout	0.027	···	···	LC70, 73-d	de Solbe and Shurben (1989)
Lethal effects on Rio Grande silvery minnow and fathead minnow					
R.G. Silvery minnow†‡	1.13–1.19	7.9–8.4	25	LC50, 72-h	Buhl (2002)
R.G. Silvery minnow†‡	1.01–1.12	7.9–8.4	25	LC50, 96-h	Buhl (2002)
Fathead minnow	1.50	7.9–8.4	22	LC50, 96-h	Mayes et al. (1986)
Fathead minnow	1.85–3.44	7.8–8.2	12–22	LC50, 96-h	Thurston et al. (1986)
Fathead minnow	2.55	8.0–8.1	26	LC50, 96-h	Arthur et al. (1987)
Fathead minnow†	0.67	···	···	LC50, 28-d	Fairchild et al. (2002)
Influence of temperature on lethal effects					
Fathead minnow†	0.40	8.1	5.8	LC50, 96-h	Nimmo et al. (1989)
Fathead minnow†	0.94	7.8	19.8	LC50, 96-h	Nimmo et al. (1989)
Chronic effects on assorted species					
Fathead minnow	0.15–0.27	8.0	···	chronic	Thurston et al. (1986)
Rainbow trout	0.031	7.7	···	chronic	Thurston et al. (1984)
Rainbow trout†	0.05	7.5	···	chronic	Burkhalter and Kaya (1977)
Johnny darter	0.05	7.8–8.1	···	chronic	Nimmo et al. (1989)
Bluegill	0.11	7.78	···	chronic	Smith et al. (1984)
Channel catfish	0.32	7.95	···	chronic	Reinbold and Pescitelli (1982)
Green sunfish	0.40	7.9	···	chronic	McCormick et al. (1984)
Smallmouth bass	0.71	8.68	···	chronic	Broderius et al. (1985)

Note: The abbreviation "LC50" refers to the lethal concentration at which half the number of fish would be expected to die over various time periods, from 96-h laboratory tests to 73 d.
† Results for embryos, larvae, and/or juveniles.
‡ Results were the same for fathead minnow.

applied to the ratios from 1977 to 2002 reveal a significant increasing trend ($S = 107$, $P = 0.0146$). This result is due partly to increasing discharge from the SSWRP and partly to low flows in the river in 2000–2002.

If these low-flow years are the precursor to a longer drought, the importance of SSWRP discharge to Rio Grande water quality will continue to increase. Potential negative impacts from effluent discharge upon aquatic species will likely be exacerbated by continuing population growth and drought.

Ammonia toxicity

The effects of ammonia in wastewater treatment plant effluent on downstream ecological systems have been well studied (e.g., Tsai 1973, Birge et al. 1989, Crawford and Wangsness 1991, Goudreau et al. 1993, Kosmala et al. 1999, Vlaming et al. 2000, Dyer et al. 2003; and see Table 3). Table 3 shows the results of numerous laboratory tests on lethal and chronic ammonia toxicity to a variety of aquatic species. The LC50 concentrations for various species range from 0.39 mg/L over 96 h to 0.06 mg/L over 72 d. Chronic effects on various species, including embryos, larvae, juveniles, and adults, are 0.02–0.71 mg/L NH_3-N. Thurston et al. (1986) reported chronic concentrations for fathead minnows from 0.15 to 0.27 mg/L NH_3-N. Dodds and Welch (2000) suggest setting a regulatory chronic limit at 0.02 mg/L NH_3-N, but note that chronic effects may occur at concentrations as low as 0.005 mg/L. The USEPA (1999) reports that some data have indicated that NH_3-N can have adverse effects on aquatic life at concentrations as low as 0.001–0.006 mg/L.

Conclusions drawn from NH_3 toxicity levels produced by the model must be considered in the context of important model assumptions concerning: (1) downstream mixing dynamics of effluent and river water, (2) NH_4^+ uptake by biota, (3) NH_4^+ adsorption, (4) nitrification, (5) NH_3 volatilization, and (6) other NH_4^+ sources, all addressed below.

The model assumes instantaneous mixing and chemical equilibration between the river and the effluent discharge at the sewage treatment plant outfall. However, the Rio Grande near Albuquerque is a shallow, slow, braided stream during low flows. At those times complete mixing could be delayed for hundreds to thousands of meters with zones of higher and lower NH_3-N from one side of the river to the other. Also, NH_3 toxicity is well known to increase for some distance downstream of a sewage source, reach a peak, and then begin decreasing. This occurs because mixing occurs gradually, so temperature, pH, and equilibration rates change as a slug of water moves downstream (Lewis et al. 2002). More rapid mixing at higher discharge will speed equilibration and distribute concentrations, but also dilute N-NH_3 concentrations more rapidly. Fish behavior must also be considered since fish may simply avoid toxic areas. This strategy could lead to habitat fragmentation and species endangerment.

Biological uptake of NH_4^+ is a leading cause of NH_4^+ removal from aquatic environments, sometimes with very short uptake lengths and residence times, and is positively correlated with concentration (Mulholland et al. 2000, Peterson et al. 2001, Dodds et al. 2002). Ammonium adsorption to aquatic sediments is another important cause of ammonium removal (Rosenfeld 1979, Mackin and Aller 1984, Peterson et al. 2001). Nitrification is also an important term in NH_4^+ removal (Admiraal and Botermans 1989, Chesterikoff et al. 1992, Mulholland et al. 2000, Peterson et al. 2001). None of these processes, all of which would serve to lower ammonia toxicity levels in the Rio Grande, were included in the model.

Few studies have addressed the volatilization of NH_3 from fresh waters. The rate of volatilization from water to air in the Rio Grande could be calculated using

$$(NH_3)_t = (NH_3)_0 e^{-K_2 t} \tag{3}$$

in which K_2 is the reaeration coefficient for NH_3. However, K_2 values for NH_3 are not known for the Rio Grande and are not readily available for other rivers. An estimate of NH_3 volatilization in the Rio Grande can be made using K_2 values for oxygen as a surrogate. The range for oxygen K_2 values in rivers of various sizes and hydrological characteristics ranges from 1 in high-order, low-gradient streams, to ~160 in low-order, high-gradient streams (Young and Huryn 1999, Jha et al. 2001, Hall and Tank 2003). We assume the K_2 value for the Rio Grande falls between 5 and 15. Using a K_2 value of 15 for NH_3 we estimate NH_3 concentrations will volatilize and be reduced by half over ~2 km, assuming a flow rate of 0.5 m/s. Using a K_2 value of 5, we estimate that NH_3 concentrations will be reduced by half over ~6 km. We estimate, therefore, that the range of distances over which half the concentration of NH_3 will volatilize from the Rio Grande is ~2–6 km.

We can also estimate the amount of time chronic NH_3 toxicity spanned that range of distances. Of the 81 days on which NH_3-N values in the Rio Grande are modeled from 1989 to 1992, NH_3-N values exceed 0.2 mg/L (2×0.10 mg/L, a chronic criterion drawn from Buhl [2002]) on eight days, or ~10% of the time. We estimate, then, that during 10% of the days from 1989 to 1992, chronic ammonia toxicity conditions (i.e., >0.10 mg/L NH_3-N) in the Rio Grande extended from 2 to 6 km downstream of the SSWRP.

Modeled NH_3 concentrations are calculated using outfall from the SSWRP, but don't include other sewage treatment plants from other upstream municipalities and villages contiguous to or nearby the Albuquerque area (Fig. 1). An upstream sewage treatment plant accident in the summer of 2000 spilled $\sim 4 \times 10^6$ L of untreated sewage directly into the river. Chlorine concentrations in the effluent were increased during the spill to reduce the public health risk (USFWS 2003). The spill itself would be expected to raise NH_3 toxicities downstream, and the presence of chlorine would further add to water toxicity (Buhl 2002).

A factor that increases the potential for NH_3 toxicity in the Rio Grande is the long-term trend of increasing pH at the USGS sampling station at Isleta, ~10 km below the SSWRP. Data at Isleta show pH increasing in a linear and statistically significant fashion ($P < 0.0005$), from an annual median of 7.9 in 1975 to an annual median of 8.1 in 1999 (Passell et al. 2004). The increase in pH is likely due to improved sewage treatment that discharges lower concentrations of dissolved organic carbon to the river, which results in lower microbial respiration and lower CO_2 concentrations. For example, at 25°C and pH of 7.9, 10 mg/L of NH_4^+-N will equilibrate to ~0.42 mg/L NH_3-N. At a pH of 8.1, the NH_3-N concentration increases to ~0.67 mg/L. Increasing pH values reflect improved water quality in the Rio Grande, but paradoxically increase ammonia toxicity.

The Colorado Department of Public Health and the Environment (CDPHE) has adopted a single removal rate for total ammonia ($NH_4^+ + NH_3$) in Colorado rivers that has been used in two surface water models of ammonia dynamics (Saunders et al. 1999, Lewis et al. 2002). The ammonia removal calculation is described by

$$(\text{total ammonia})_t = (\text{total ammonia})_0 e^{-K_t} \tag{4}$$

in which $-K$ is the rate of removal by all mechanisms for both NH_4^+ and NH_3. The rate constant adopted by the CDPHE after a review of numerous streams is 6.0 d^{-1}. Rates ranged from 0 to 13 d^{-1}. Rivers in the review that most resemble the Rio Grande include the Arkansas, Cache la Poudre, South Platte, and Yampa Rivers. Removal rates for these rivers are 10.7, 12.8, 9.5, and 7.9 d^{-1}, respectively, with a mean of 10.2 d^{-1}.

Using the rate of 10.2 d^{-1} and assuming river velocity of 0.5 m/s, total ammonia will be reduced by half over ~3 km. Using the lower rate of 6.0 d^{-1}, total ammonia is halved over ~5 km. The range of 3–5 km for the loss of half the total ammonia is similar to those found from calculations for NH_3 volatilization using Eq. 3.

Relationship between ammonia toxicity and other toxicants

Additional toxicants could act synergistically with NH_3 to raise toxicity. Buhl (2002) found chlorine was the most toxic agent by concentration among a list of toxicants found in the middle Rio Grande (96-h LC50 of 0.114 mg/L). Copper was second (96-h LC50 of 0.250 mg/L), and NH_3 was third. Buhl (2002) conducted laboratory tests to determine the toxicity of a mixture of aluminum, NH_3, arsenic, copper, and nitrate that replicated the mix of those toxicants in the Rio Grande near Albuquerque. Chlorine was excluded because the SSWRP dechlorinates its effluent before discharge, although it is still used at sewage treatment plants upstream. Buhl (2002) found that copper and un-ionized ammonia were the primary toxic components in the mixture, accounting for 93–98% of toxicity to both species. Copper contributed 49–62% and NH_3 contributed 36–50% of the mixture's toxicity to both species (Buhl 2002).

Buhl (2002) also found that the mixture of toxicants at Isleta produced a toxicity that was more toxic to both the silvery minnow and the fathead minnow than any of the five chemicals tested alone. Based on the mixture of toxicities and several different methods for establishing standards, Buhl (2002) estimates an appropriate chronic criterion for silvery minnow in the Rio Grande could be as low as 0.001 mg/L N-NH_3. This value matches the lowest concentration for NH_3-N leading to adverse effects on aquatic life suggested by the USEPA (1999), and it is similar to low-end chronic standards proposed by others (0.005 mg/L NH_3-N; Dodds and Welch 2000). Although individual toxicant concentrations in rivers are regulated, site-specific mixtures of toxicants are not. Buhl (2002) suggests that the synergistic effects of multiple toxicants in the Rio Grande may make site-specific acute and chronic values for the endangered silvery minnow more appropriate than national or statewide values.

Role of ammonia toxicity on the Rio Grande fish community

Buhl (2002) performed the only toxicity tests specific to the Rio Grande silvery minnow. He performed identical tests with the fathead minnow (*Pimephales promelas*), a species used extensively in other fish toxicity studies, and concluded that it is a suitable surrogate for the silvery minnow in toxicity studies. Buhl (2002) found that 96-h LC50 concentrations for larvae of the two species ranged from 1.01 to 1.12 mg/L NH_3-N in water simulating the present chemical and physical conditions of the Rio Grande near Albuquerque (Table 3). In other studies, the 96-h LC50 concentrations for the fathead minnow ranged up to 2.55 mg/L NH_3-N, and the LC50 concentrations over 7–28 d ranged from 0.28 to 0.67 mg/L.

No direct studies of chronic NH_3 toxicity for silvery minnows have been performed. Chronic values, however, can be estimated by alternative methods. The USEPA (1999) recommended a species mean chronic value (SMCV) of 0.17 mg/L NH_3-N for the fathead minnow. In a U.S. Fish and Wildlife Service (USFWS) Biological Opinion on the protection of the silvery minnow in the Rio Grande near Albuquerque, the USFWS adopted the USEPA SMCV for the fathead minnow as a chronic toxic value for the silvery minnow (USFWS 2003).

Another approach, documented by the State of New Mexico Water Quality Control Commission (NMWQCC), suggests that the chronic toxic concentration of a nonpersistent, non-bioaccumulating toxicant such as NH_3 should be set at 10% of the LC50 (NMWQCC 2002). If the low LC50 value of 1.01 mg/L NH_3-N from Buhl (2002) is used, the chronic value would be ~0.10 mg/L. Similarly, chronic criterion for the Tittabawasee River in Michigan for fathead minnow embryos and larvae was established at 0.095 mg/L NH_3-N (Alexander et al. 1986), and chronic criterion for fish species in the St. Vrain River in Colorado was 0.05 mg/L NH_3-N (Nimmo et al. 1989).

Table 2A–D shows the predictable result that the percentage of days in which modeled NH_3 values exceed acute and chronic criteria goes up as the criterion goes down. Of note are the exceedences that reached high levels for some years at the current New Mexico chronic criterion of 0.05 mg/L NH_3-N and reached 100% for all years through 1997 using the chronic criterion 0.001 mg/L NH_3-N proposed by the USEPA (1999) and others. Also notable is the dramatic decline in all exceedences starting in 1998.

Declines in NH_3 concentrations are due mostly to improvements to sewage treatment technologies. From 1975 to approximately 1990 Albuquerque's sewage treatment was split between trickling filters and activated sludge processes aimed mainly at nitrification. In the early 1990s trickling filters were phased out completely, improving overall nitrification rates. A US$42 million project from 1996 to 1998 added biological nutrient removal (BNR) nitrification/denitrification facilities that reached full operation over the following few years (D. Daily, *personal communication*).

Model results for exceedences of 0.1 mg/L in the years 1989, 1991, and 1992 show no clear trend, so it is impossible to infer what NH_3 concentrations might have been in years immediately prior to 1989. One of the greatest limitations of this study is the incomplete nature of the long-term NH_4^+ data record. It is possible that the very high NH_4^+ levels early in the study period represent periodic spikes in an otherwise consistent long-term record. However, high values during those three years suggest that years immediately preceding may have been similarly high. High exceedence percentages may have occurred throughout the 1980s or even earlier.

Improvements at the SSWRP resulted in a modeled, 2002 average NH_3-N concentration of 0.0004 mg/L (Appendix B), almost an order of magnitude lower than the lowest chronic values proposed. However, several factors could still contribute to a risk of NH_3 toxicity in the middle Rio Grande, including (1) increasing human populations upstream and downstream of Albuquerque; (2) storm drain runoff that for many locations drains directly to the river; (3) risk of accidental sewage spills all along the reach; and (4) synergistic effects of ammonia mixing with other toxicants.

Four other cyprinids are extinct or extirpated from the mainstem of the Rio Grande, with three disappearing in approximately the last 40 years. Extirpated species are the Rio Grande shiner (*Notropis jemezanus*), last collected between 1901 and 1950, and the speckled chub (*Extrarius aestivalis*), last collected in the 1960s (Sublette et al. 1990). Extinct species are the phantom shiner

(*Notropis orca*) and the bluntnose shiner (*Notropis simus simus*), last collected in 1964 and 1975, respectively (Sublette et al. 1990). All four have ecological requirements and reproductive habits similar to those of the silvery minnow.

It must be noted that loss and endangerment for all these species and the silvery minnow have multiple causes. A shortage of water in the river is considered the single most important limiting factor for the silvery minnow (USFWS 2001). Reproductive strategies, once well adapted to the Rio Grande, now expose these organisms to additional risk. Bouyant eggs and larvae can float in the current for hundreds of kilometers downstream before swimming laterally into low-velocity habitats (Platania and Altenbach 1998, USFWS 2001). The MRG, the last remaining silvery minnow habitat, is only ~160 km long and now terminates in Elephant Butte reservoir, where minnow eggs and larvae are believed to become prey for nonnative fish. Eggs and larvae can also be entrained in irrigation channels where survival may be low (USFWS 1999, 2001). Finally, three river-wide diversion dams between Cochiti and Elephant Butte reservoirs fragment fish habitat by making upstream migration of juveniles and adults impossible (USFWS 2002*b*).

Model results, however, suggest that NH_3 toxicity, both in the Albuquerque region and along the entire river, may have played some role in the disappearance of the four cyprinids and may have played some role in the current endangerment of the silvery minnow. Ammonia toxicity downstream of the SSWRP and other treatment plants in the MRG likely had direct negative effects on fish embryos, larvae, juveniles, or adults through chronic or acute toxicity. In addition to direct effects, NH_3 toxicity downstream of the SSWRP may have fragmented fish habitat in the Rio Grande by creating an NH_3 barrier through which migrating fish would not pass. Unfortunately, current and historic data on minnow populations in the study area are inadequate for assessing whether reduced NH_3 concentrations now are correlated with increased long-term populations. At a larger scale, the model results suggest that NH_3 toxicity may be having large impacts in river ecosystems around the world, especially in developing nations with limited sewage treatment capabilities.

Acknowledgments

We are grateful to Doug Daily, Steve Glass, Bob Hogrefe, and Abibi Jefera with the Water Reclamation Division, Albuquerque-Bernalillo County Water Utility Authority, for providing data, information, and valuable insight. Linda Beal of the U.S. Geological Survey graciously helped provide data. Joel Lusk of the USFWS in Albuquerque, Kevin Buhl of the USGS Columbia Environmental Research Center in Yankton, South Dakota, Laura Crossey in the Department of Earth and Planetary Sciences at the University of New Mexico (UNM), and Tom Turner of the Department of Biology at UNM all provided valuable information, insights, and other kinds of support. Two anonymous reviewers made helpful suggestions for improving the paper.

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APPENDIX A

Measured data and generated data for four variables used in the model (*Ecological Archives* A017-083-A1).

APPENDIX B

Means and standard deviations used in the generation of pH data (*Ecological Archives* A017-083-A2).

APPENDIX C

Summary statistics by year for modeled NH_3-N concentrations (*Ecological Archives* A017-083-A3).