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Water Chemistry Assessment of The Shenandoah Valley Sinkhole Ponds in Virginia

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INTRODUCTION

Low solubility, siliciclastic rocks of the Antietam Formation make up the underlying geology of the mountains and ridges of the Big Levels region in the Blue Ridge Physiographic Province of the Shenandoah Valley of Virginia (Werner, 1966; Bartholomew, 1977). Alluvial deposits of this rock lie over top of dolomitic limestone formations at the base of the mountains, creating a fan up to five kilometers wide and thirty meters deep (Hewitt et al., 1917; Whittecar & Duffy, 1992). The sinkhole ponds found in this region were created by the collapse of pockets in this limestone. The alluvium is covered by thin soils of medium water retention and moderate permeability of the Monogahelia and Sherando sandy loam types (Hockman, 1979). Although the hydrology of the fan has not been studied extensively, it is apparent that the ponds fill by water travelling down from the upper elevations through the alluvium and acidic soils. Few of the ponds are stream fed or fill fully by surface water runoff alone. Some maintain constant pool levels during dry seasons due to springs within the basins, while others rise and fall dramatically in pool depth (Buhlmann et al., 1999). Many ponds dry completely on an annual basis.

Headwater streams that originate from catchment basins with low solubility siliciclastic bedrock geology are particularly susceptible to acid rain impacts due to low carbonate buffer availability (Bricker & Rice, 1989). Rainfall in western Virginia averages pH 4.3 to 4.5 (NADP database), or between one-half and one pH unit lower than pre-industrial age precipitation (Drever, 1988; Schindler, 1988). In most surface waters, carbonate provided by minerals such as calcite neutralizes most of the anthropogenic acidity. However, those waters that do not contain much carbonate are reduced by acid rain in pH and acid neutralizing capacity (ANC). Burger et al. (1998) established that approximately 6 % of chronically acid trout streams in Virginia originate in watersheds with low solubility siliciclastic rock. Because the geology of the alluvial fan in which the sinkhole ponds are located provides little buffering capacity, biologists became concerned that similar water chemistry might be found here and that this could pose a risk to the state endangered tiger salamander (*Ambystoma tigrinum*) and other pond inhabitants.

This two-year study was initiated in 1995 to develop a database of chemical solutes and concentrations for many of the ponds and to provide information on both seasonal and episodic variations in chemical composition. These data would then be available for use in the habitat assessment for the unique flora and fauna that are dependent on the sinkhole ponds system.

MATERIALS AND METHODS

The Shenandoah Valley Sinkhole Ponds (SVSP) system is located south of Stuart's Draft and Sherando, Virginia, in the Pedlar Ranger District of the George Washington National Forest. There are three complexes of ponds. The one most extensively studied is within an area known as Maple Flats in the vicinity of Canada Run (78°59' 00" W; 37° 58' 25" N). There are also ponds to the east near Orebank Run (Sherando Complex) and to the west near Love's Run (Love's Run Complex). To date, 36 ponds have been surveyed and these are numbered for this report by the name/number system of Buhlmann at al. (1999). A detailed map of the study locations may be found in their paper.

We collected water samples from the ponds in acid-washed HDPE bottles, which were stored at 4° C, and returned to the laboratory for analysis. We collected samples at least one m from the shoreline and 0.3 m below

Table 1. Summary of laboratory analysis methodology, methods and equipment used for the various chemical analyses.

	Instrumentation	Technique summary
pH	Orion 811 M with Orion glass combination electrode (Ross) MDL No 8102	pH recorded for samples in open beakers ≤ 0.01 units/min., electrodes calibrated twice daily with pH 4.01 and 7.00 buffer.
ANC	Orion 811 M with Orion glass combination electrode (Ross) MDL No 8102 and 10 mL glass microburet	Two end point (pH 4.50 and 4.20) titration with standardized 0.005 M HCl. Analysis run in duplicate. (APHA, 1995, method 2320)
chloride, sulfate, nitrate	Dionex 4500I ion chromatograph with AS4A column and AS4G column, AMMS suppressor	Injector volume: 50mL eluant: 1.8 mM Na_2HCO_3, 2mL min^{-1} analysis time = 10 min per sample. Run in triplicate. (± 2% RSD) (APHA, 1995, method 4110)
calcium magnesium	Varian spectr AA-30 atomic absorption spectrophotometer with Ca/Mg lamp	Atomic absorption analysis at 422.7 nm (Ca) and 285.2 nm (Mg) (APHA, 1995, method 3111D).
potassium, sodium	Varian spectr AA-30 atomic absorption spectrophotometer	Flame emission analysis at 766.5 nm (K) and 589 nm (Na) (APHA, 1995, method 3500-K and 3500-Na D).
aluminum	Varian spectr AA-30 with GTA-96 graphite tube analyzer	Graphite furnace analysis of total Al (APHA, 1995, method 3113)

the surface. Leaves, twigs, and other large foreign objects were excluded from collection bottles at the collection site. In the laboratory, water samples were filtered with 0.45 Fm polycarbonate filters prior to analysis. Fractions of the samples were made as 5% high purity nitric acid for metal analysis without delay after collection. We obtained samples from sinkhole ponds 2, 4, 11, 12, 13, 16, 17, 18, 21, Spring Pond, and the two manmade ponds known as Maple Flats South and Maple Flats North monthly for two years beginning in September, 1995. Each sample was collected near each mid-month at least two days following episodic precipitation events. Some ponds could not be sampled due to absence of water in dry periods or the inability to gain access due to storm events. We placed ISCO automatic water sample collectors for short periods at ponds 2, 13, 17, and 21 during spring 1997 to monitor episodic events. In addition to the twelve ponds monitored regularly, fourteen other ponds were sampled at least once. Ponds that were not sampled were either dry during the project period, were on private property, or were otherwise inaccessible.

The parameters monitored including pH (laboratory, 25°C), acid neutralizing capacity (ANC), total aluminum (Al_T), calcium (Ca_T), magnesium (Mg_T), sodium (Na_T), potassium (K_T), chloride (Cl^-), nitrate (NO_3^-) and sulfate (SO_4^{2-}) with samples filtered through a 0.45 Fm polycarbonate membrane. Analytical protocols and methods used for this work are described in Table 1. In addition to the above parameters, the Ca/H ratio was calculated by dividing the concentration of calcium by the concentration of hydronium with both ions expressed in units of acid-base microequivalents per liter (μeq/L).

Table 2. Water quality parameters for two-year average values. Results are reported as mean ± one standard deviation (number of samples). Standard deviations are not reported for ponds sampled fewer than four times.

Pond No.	pH (s.u.)	ANC (μeq/L)	Al_T (ppb)	Ca/H
2	5.43 ± 0.23 (21)	13.4 ±10.26 (20)	62 ± 51 (19)	5.66 ± 4.65 (22)
3	5.08	2.7	209	2.93
4	4.67 ± 0.23 (19)	-26.4 ± 16.0 (19)	95 ± 60 (18)	1.10 ±0.77 (20)
5	4.98	10.0	73	1.16
6	4.58	-30.4	90	0.52
7	4.86	-14.3	88	1.34
8	4.76 ± 0.33 (4)	-28.0 ± 37.0 (4)	129 ± 50 (4)	1.68 ± 1.80 (4)
9	4.74	-28.0	122	1.29
10	5.20 ± 0.18 (4)	-6.1 ± 11.8 (4)	115 ± 83 (4)	6.12 ± 4.40 (4)
11	5.43 ± 0.25 (28)	14.9 ± 20.8 (28)	40 ± 34 (27)	3.91 ± 2.42 (28)
12	5.38 ± 0.39 (23)	9.4 ± 9.4 (23)	36 ± 45 (22)	3.74 ± 3.67 (23)
13	5.39 ± 0.25 (31)	8.9 ± 10.8 (28)	59 ± 67 (27)	4.85 ± 3.50 (28)
14	5.00	-18.3	97	1.19
15	5.28	-9.6	135	2.27
16	5.26 ± 0.22 (25)	17.5 ± 6.5 (28)	77 ± 77 (23)	3.63 ± 3.11 (25)
17	5.29 ± 0.29 (25)	1.8 ± 8.5 (23)	53 ± 43 (22)	3.31 ± 2.70 (23)
18	4.89 ± 0.30 (22)	-9.7 ± 22.9 (22)	146 ± 135 (21)	1.70 ± 0.82 (22)
21	5.18 ± 0.33 (24)	2.0 ± 16.9 (24)	50 ± 40 (23)	1.96 ± 2.10 (24)
23	4.94	8.7	63	1.21
24	4.78	-26.0	90	1.58
25	4.85	-24.2	52	1.38
26	4.98	-1.1	135	2.36
27	5.19	-8.1	36	1.83
28	4.93	-13.7	99	1.57
Spring	5.17 ± 0.31 (25)	6.7 ± 11.2 (24)	36 ± 24 (23)	3.22 ± 3.38 (25)
MFS	6.00 ± 0.33 (25)	22.2 ± 12.0 25)	38 ± 46 (24)	35.35 ± 31.30 (25)
MFN	5.94 ± 0.27 (25)	18.7 ± 10.0 (25)	23 ± 18 (24)	25.35 ± 19.33 (25)
Mills	5.68	67.1	39	33.98

Table 3. Base cations two-year average values. Numbers as in Table 2. Standard deviations are not reported for ponds sampled fewer than four times.

Pond No.	Na (μeq/L)	K (μeq/L)	Mg (μeq/L)	Ca (μeq/L)
2	19.3 ± 4.8 (20)	17.4 ± 5.7 (20)	24.9 ± 6.1 (20)	21.1 ±6.3 (20)
3	21.0 (1)	15.3 (1)	28.8 (1)	24.4 (1)
4	19.3 (2)	16.4 (2)	20.5 (2)	17.4 (2)
5	21.0 ± 8.2 (19)	18.7 ± 9.8 (19)	19.2 ± 6.4 (19)	21.4 ± 5.6 (19)
6	14.8 (1)	8.1 (1)	15.7 (1)	13.7 (1)
7	16.7 (1)	12.9 (1)	14.3 (1)	18.5 (1)
8	20.9 ± 1.8 (4)	21.8 ± 13.8 (4)	16.9 ± 4.7 (4)	19.4 ± 7.5 (4)
9	23.7 (2)	21.6 (2)	27.9 (2)	23.0 (2)
10	22.2 ± 5.6 (4)	15.2 ±17.3 (4)	27.5 ±12.4 (4)	34.7 ± 22.0 (4)
11	19.4 ± 5.0 (29)	13.8 ± 4.5 (28)	15.8 ± 3.0 (28)	12.8 ± 4.5 (28)
12	20.4 ± 7.4 (23)	12.2 ± 4.3 (23)	15.0 ± 2.4 (23)	10.8 ± 4.0 (23)
13	20.4 ± 6.4 (28)	19.7 ± 9.1 (28)	22.9 ± 4.6 (28)	17.8 ± 5.0 (28)
14	24.3 (1)	22.8 (1)	11.9 (1)	11.9 (1)
15	20.1 (2)	9.8 (2)	33.5 (2)	40.7 (2)
16	22.4 ± 6.0 (24)	16.2 ± 6.0 (24)	24.8 ± 4.8 (24)	18.1 ± 7.9 (24)
17	21.6 ± 4.2 (23)	19.2 ± 7.3 (23)	22.4 ± 4.0 (23)	16.7 ± 5.7 (23)
18	25.9 ± 8.6 (22)	15.4 ± 10.3(21)	31.1 ± 19.7(22)	23.9 ± 18.1 (22)
21	23.5 ± 6.1 (24)	17.7 ± 8.0 (24)	14.1 ± 3.4 (24)	9.2 ± 4.0 (24)
23	21.4 (2)	16.2 (2)	25.7 (2)	13.6 (2)
24	22.1 (1)	16.8 (1)	21.7 (1)	9.6 (1)
25	20.0 (2)	25.6 (2)	22.2 (2)	19.8 (2)
26	26.8 (1)	34.9 (1)	48.2 (1)	24.7 (1)
27	10.0 (2)	11.5 (2)	16.7 (2)	12.0 (2)
28	14.6 (1)	22.9 (1)	22.2 (1)	18.5 (1)
Spring	20.2 ± 6.1 (24)	18.2 ± 7.2 (24)	16.6 ± 6.9 (24)	17.3 ± 10.3 (24)
MFS	18.6 ± 3.3 (25)	16.0 ± 4.3 (25)	19.9 ± 3.5 (25)	26.0 ± 6.3 (25)
MFN	18.8 ± 3.1 (25)	15.7 ± 3.7 (25)	20.5 ± 4.0 (25)	23.7 ± 5.1 (25)
Mills	19.3 (1)	9.6 (1)	27.9 (1)	71.0 (1)

Table 4. Acid anions two-year average values. Numbers as in Table 2. Standard deviations are not reported for ponds sampled fewer than four times. RCO_2H is calculated from the summation of ANC_{obs} and concentrations of base cations less the strong acid anions concentrations. It is a measure of dissolved organic acids. NC indicates "not calculated" due to excessive sulfate concentrations.

Pond No.	Cl^- (μeq/L)	NO_3^- (μeq/L)	SO_4^{2-} (μeq/L)	RCO_2H (μeq/L)
2	19.2 ± 2.7 (19)	1.8 ± 2.7 (19)	18.0 ± 5.0 (19)	30.3
3	22.8	4.7	22.2	37.1
4	18.3	0.0	102.5	NC
5	19.8 ± 5.6 (18)	1.0 ± 1.0 (18)	32.1 ± 16.7 (18)	17.4
6	17.8	0.2	31.3	33.4
7	15.4	0.0	15.3	46.0
8	21.1 ± 14.7 (4)	0.6 ± 1.5 (6)	47.1 ± 50.1 (4)	76.3
9	42.1	4.2	16.8	61.1
10	36.7 ± 17.2 (4)	1.9 ± 1.1 (4)	25.1 ± 21.9 (4)	42.1
11	19.2 ± 7.5 (27)	0.9 ± 1.1 (27)	12.5 ± 7.5 (27)	14.3
12	17.7 ± 5.3 (22)	1.1 ± .5 (22)	11.7 ± 6.6 (22)	18.5
13	21.9 ± 7.0 (27)	1.1 ± 1.3 (27)	19.5 ± 13.8	29.4
14	29.0	1.9	100.3	NC
15	30.3	0.8	67.3	15.3
16	23.4 ± 3.8 (23)	1.2 ± 1.3 (23)	18.2 ± 11.0 (23)	21.2
17	20.9 ± 5.1 (22)	1.7 ± 2.3 (22)	34.1 ± 6.8 (22)	21.4
18	33.6 ± 28.0 (21)	0.5 ± 0.9 (21)	13.5 ± 10.3 (21)	58.4
21	19.5 ± 3.8 (23)	0.6 ± 0.9 (23)	15.9 ± 14.2 (23)	26.5
23	15.5	0.9	36.5	15.3
24	9.6	0.8	90	NC
25	17.4	1.0	54.2	39
26	26.4	0.8	45.4	63.1
27	15.3	0.4	73.4	NC
28	15.8	0.0	37.8	38.3
Spring	20.6 ± 7.0 (23)	0.7 ± 1.0 (23)	18.2 ± 13.3 (23)	26.1
MFS	17.7 ± 3.3 (24)	0.7 ± 0.9 (24)	31.2 ± 11.4 (24)	8.7
MFN	19.1 ± 3.8 (24)	0.4 ± 0.7 (24)	30.9 ± 9.5 (24)	9.6
Mills	25.3	2.9	14.3	18.2

RESULTS AND DISCUSSION

Tables 2, 3, and 4 show two year average values for the water quality parameters (WQPs) collected during this study. Standard deviation values were calculated for WQP's that were measured four or more times during the study period and are included to show the scatter in the data. Table 2 includes pH values. The sinkhole ponds are all acidic with $pH < 6$; many of the ponds (48%) were below pH 5.0. About 20% of the ponds did not exceed this value during the two year period of sampling. Several factors contribute to the acidity of these ponds. Rainfall in Virginia is monitored at Charlottesville and the Shenandoah National Park within 100 km of the Big Levels area as part of the network of monitoring stations for the National Acid Deposition Program (NADP web site: http://nadp.sws.uiuc.edu/nadpdata/). We averaged the values for pH and other WQPs from these two stations for the two year period of this study and provided these values in Table 5. The low pH 4.5 average indicates high acid loading from precipitation in the watershed of the sinkhole ponds system. As the atmospherically-derived water moves down through the acid soils and low solubility bedrock, it encounters little natural carbonate or other buffers available to neutralize the acidity before it enters the ponds. It is important also to note most of the ponds have collected a considerable load of organic matter. This decomposing material also provides some acidity from humic, fulvic acids, and other organic acids.

Acid neutralizing capacity (ANC) is an operationally defined parameter. It is the sum of titratable bases in a natural water sample (French & Downey, 1993). In many systems natural buffer present in water originates from the dissolution of carbonate bearing minerals such as calcite in the presence of CO_2 to form bicarbonate ion (HCO_3^-):

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^- \qquad (1)$$

Table 5. Annual average rainfall values for common water chemistry parameters. Sources is NADP (NRSP-3) NTN database and is the average of 1995-97 at Shenandaoh National Park (SNP) and Charlottesville Stations. All solutes are expressed in micro-equivalent per liter concentration units (μeq/L).

Parameters	Average Values
pH	4.5
Ca_T	2.7
Mg_T	1.6
Na_T	6.3
K_T	0.4
Cl^-	6.8
NO_3^-	14.2
SO_4^{2-}	30.9

Thus, the ANC titration gives results that may be interpreted as the bicarbonate acid-base equivalent. The charge balance expression for a natural water sample may be rearranged to give a useful mathematical expression to describe the relationship between major ionic solutes (Webb et al., 1989):

$$ANC\ (\mu eq/L) = \sum_{i}^{n} / Z_i / C_i - \sum_{j}^{m} / Z_i / A_i \qquad (2)$$

where: Z_i = charge of the ions, C_i = molar concentration of cations, and A_i = molar concentration of anions. The summation of cations and anions shows the contributions of individual solute ions:

$$\sum_{I}^{n} / Z_i / C_i = 2[Ca^{2+}] + 2[Mg^{2+}] = [Na^+] + [K^+] \qquad (3)$$

$$\sum_{j}^{m} / Z_i / A_i = [Cl^-] + [NO_3^-] + 2[SO_4^=] + [RCO_2H] \qquad (4)$$

Equations 3 and 4 show the summation of the concentrations of base cations and acid anions. ANC values for all the ponds are quite low as a result of a lack of base cations (Equation 3) and elevated levels of acid anions (Equation 4), with most being near zero or negative. The low values for base cations indicate a lack of mineral contribution to the pond water, which is an artifact of the insoluble bedrock geology. The high levels of sulfate are being deposited in the watershed by rainfall (Table 5) and this matches the elevated sulfate concentrations found in the ponds. Because sulfate concentration contributes in the negative direction to ANC (Equation 2), the importance of acid deposition on pond water quality is demonstrated. Finally, Table 4 shows high levels of organic acids which contribute to the low ANC; and a lack of nitrate contribution, even though it is a major component of rainfall. Nitrate is a nutrient and is consumed by growing plants (US EPA, 1994); thus concentrations are expected to be low (Galloway et al., 1984).

The relationship between pH and ANC is depicted in Figure 1. As ANC decreases, pH also decreases. About 50% of the ponds have pH and ANC values below levels acceptable for aquatic biota for most surface waters (Baker & Christensen, 1991). The remainder of the ponds have ANC values that could be reduced further by continued acid deposition. As sulfate ion increases, ANC decreases (Equation 2). Sulfate retention catchment basins

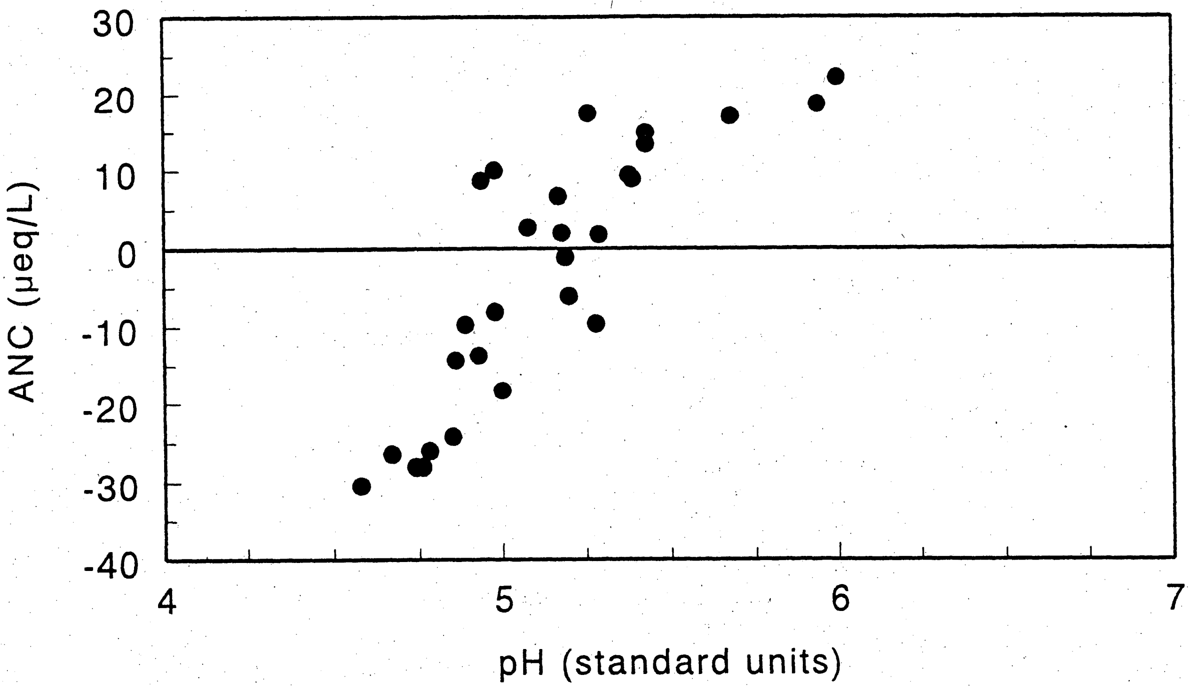

Fig. 1. Acid Neutralizing Capacity (ANC) observed for the ponds versus observed pH. Each data point represents the two-year average values for a single pond. The two points near pH 6 are for the manmade ponds: Maple Flats North and South, respectively, on Canada Run.

are probably not in equilibrium with atmospheric sulfate and continued deposition will ultimately exhaust the retention capacity (Bulger, 1998). Thus, even the ponds which have average pH > 5 will likely become more acidic.

Seasonal variation in pond water levels, the presence or absence of growing vegetation, and other factors are known to influence water chemistry in natural systems. *Ambystoma tigrinum* enters ponds from terrestrial burrows in winter to lay eggs, which hatch about a month later depending on temperature (Pague & Buhlmann, 1991). Larvae remain in the ponds several months, metamorphosing to sub-adults when the ephemeral ponds begin to dry. This period coincides with the lowest pH and ANC values for surface waters in Virginia. Figures 2, 3, and 4 shows the monthly pH, ANC and sulfate values found for three representative ponds. These three ponds were chosen for illustration for the following reasons: Pond 2 averages as one of the higher pH ponds and experiences dramatic fluctuations in pool level, Pond 18 is high in organic content, averages low in pH, and has less fluctuation in pool level, and Pond 21 is intermediate in pH with a relatively constant pool level. As pH and ANC values are generally low for the sinkhole ponds, little variation was observed due to seasonal cycling. Pond 2 increased slightly in pH and ANC values as it dried up in the summers of 1996 and 1997. High values were followed by lower values when the drying pool temporarily refilled due to summer storm events. In January 1996, a major snowstorm deposited up to two feet of snow in the Big Levels area. This snow was quite acidic (Downey, 1996, unpublished data) and when a warm front moved through in mid-January, a significant meltdown resulted. This caused a depression in pH and ANC, coupled with elevation of sulfate ion concentration. By the following month, values had returned to the pre-storm levels. This event suggested that episodic short term changes in water chemistry could be occurring that would not be observed by our monthly sampling protocols and that could adversely affect *A. tigrinum* and other aquatic biota. For this reason, several ponds were monitored with ISCO automatic sample collectors in the spring of 1997.

Figure 5 shows an episodic event recorded for Pond 2 that occurred in late February 1997. The pH was severely depressed from an acidic winter storm, yet the pond returned to pre-storm pH values within days. Additional events recorded for Ponds 13 and 21 (Figure 6) and Ponds 17 and 21 (Figure 7) demonstrated that when rainfall was of low pH and significant volume, pH depression followed by relatively rapid recovery. Figure 8 coincides with the data presented in Figure 7 and shows the sulfate increase that accompanies an acidic storm. It is not known whether the short term episodic events are detrimental to *A. tigrinum* or other aquatic life in the sinkhole

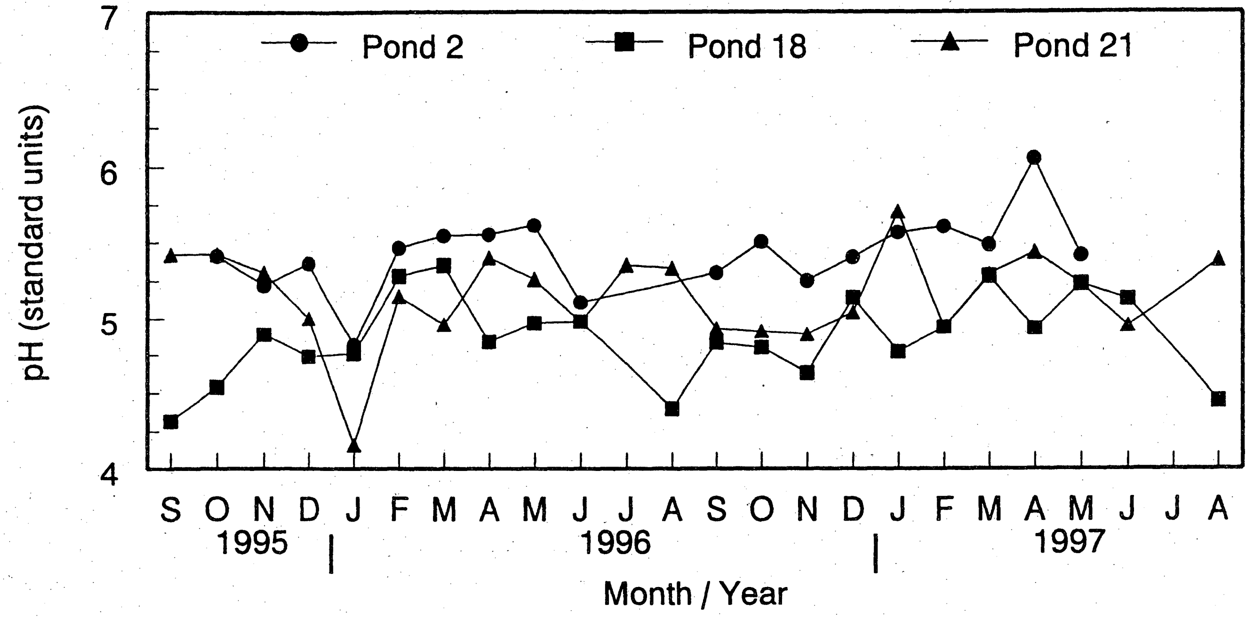

Fig. 2. Representative sinkhole ponds – pH versus month for a two-year period from September 1995 to August 1997. Data points are connected for clarity. Pond 2 was dry in July, August 1996, and June, July, August 1997.

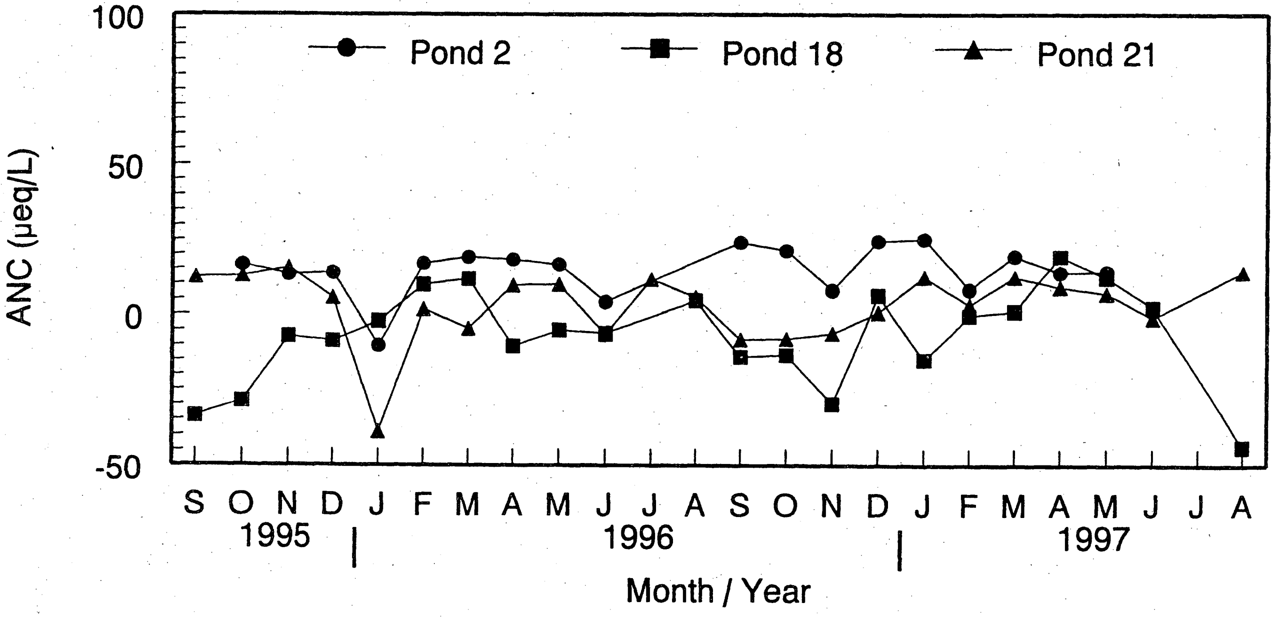

Fig. 3. Representative sinkhole ponds – ANC versus month for a two-year period from September 1995 to August 1997. Data points are connected for clarity. Dry periods for Pond 2 as in Fig. 2.

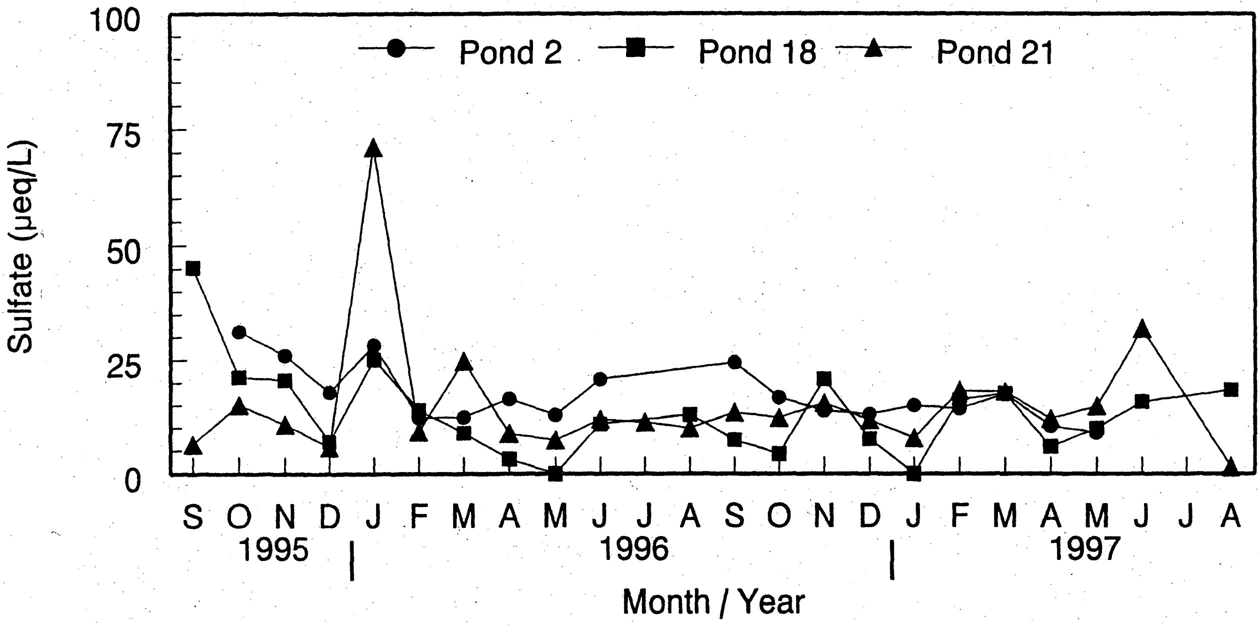

Fig. 4. Representative sinkhole ponds – Sulfate concentration versus month for a two-year period from September 1995 to August 1997. Data points are connected for clarity. Dry periods for Pond 2 as in Fig. 2.

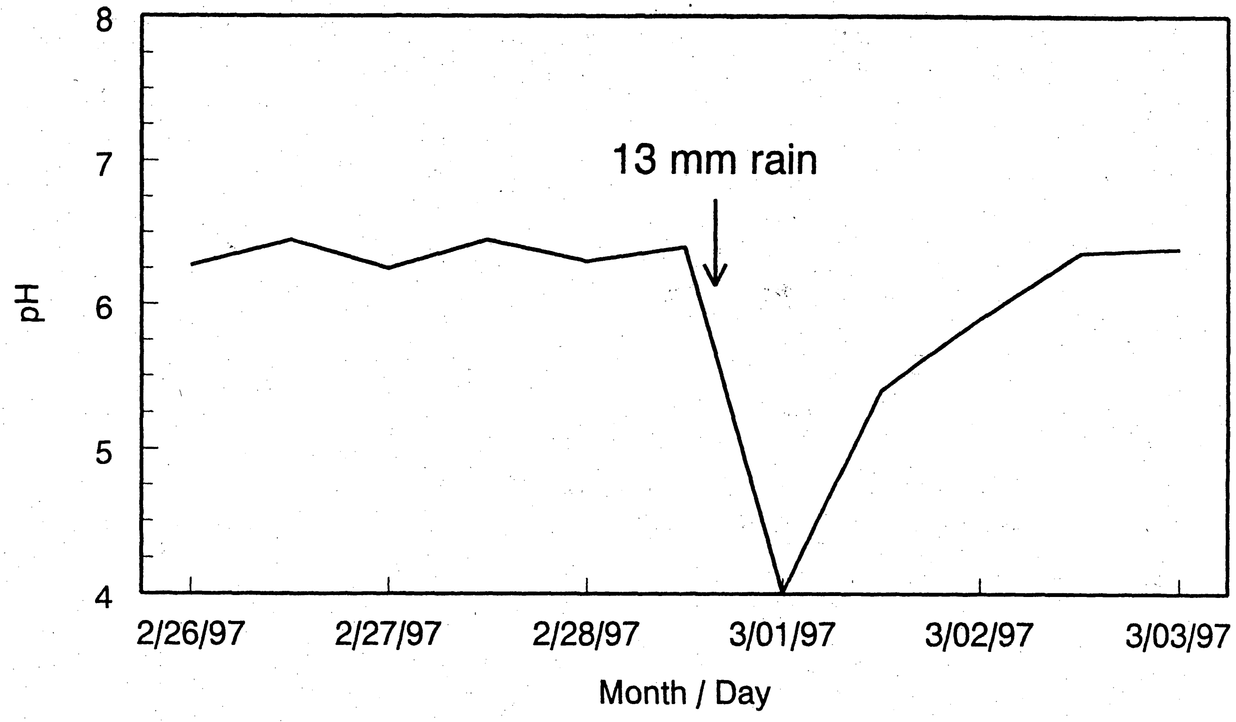

Fig. 5. Episodic event recorded for Pond 2. pH depression followed a 13 mm rain storm on February 28, 1997.

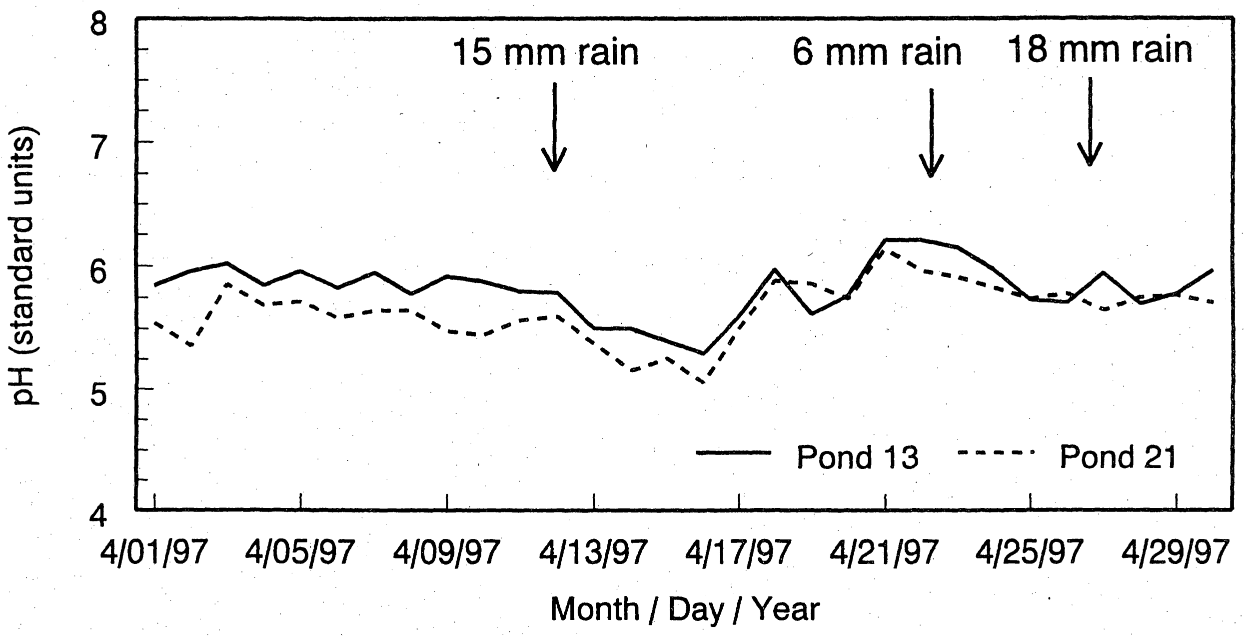

Fig. 6. Episodic events recorded for Ponds 13 (solid line) and Pond 21 (broken line) for three storms in April 1997 showing pH depression.

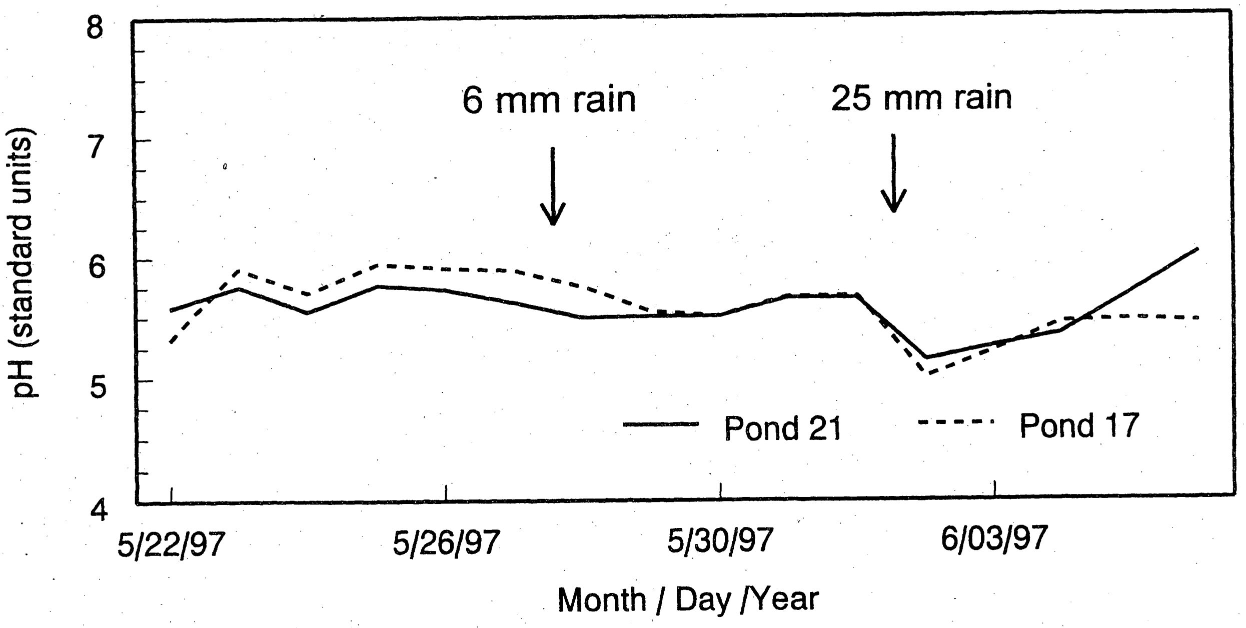

Fig. 7. pH values recorded for Pond 17 (broken line) and Pond 21 (solid line) for the period May 27 through June 6, 1997. The pH was depressed in both ponds after an acidic (< pH 5) storm event on June 1.

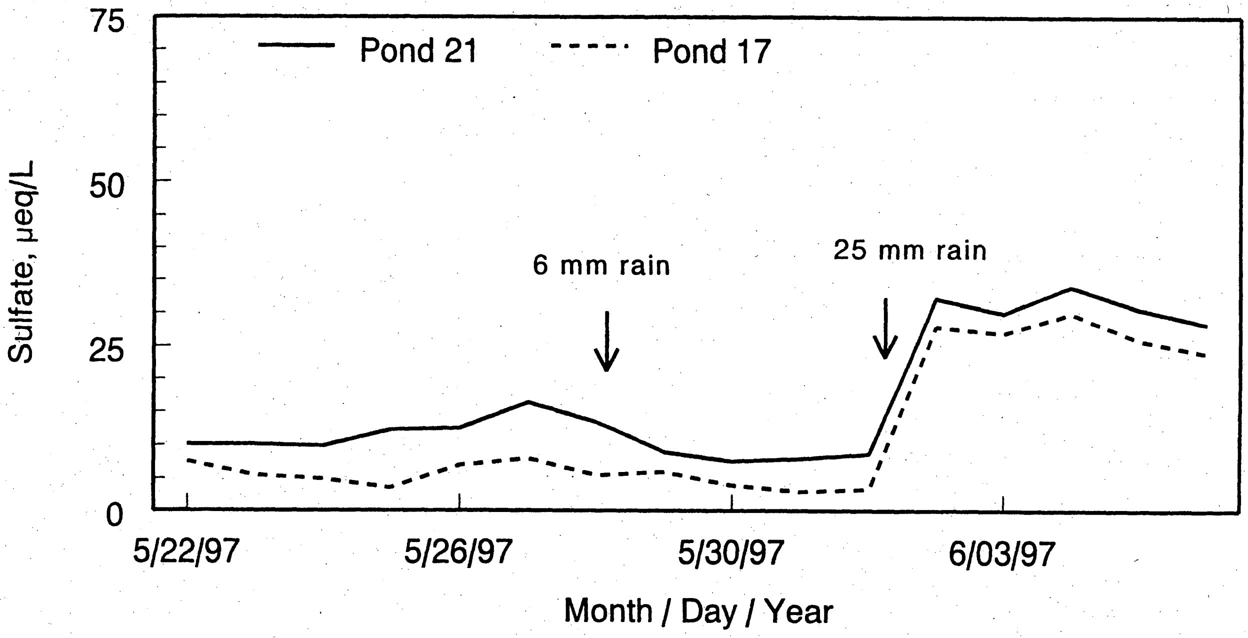

Fig. 8. Sulfate values recorded for Pond 17 (broken line) and Pond 21 (solid line) for the period May 27 through June 6, 1997. Sulfate ion concentration increased in both ponds after an acidic storm event on June 1.

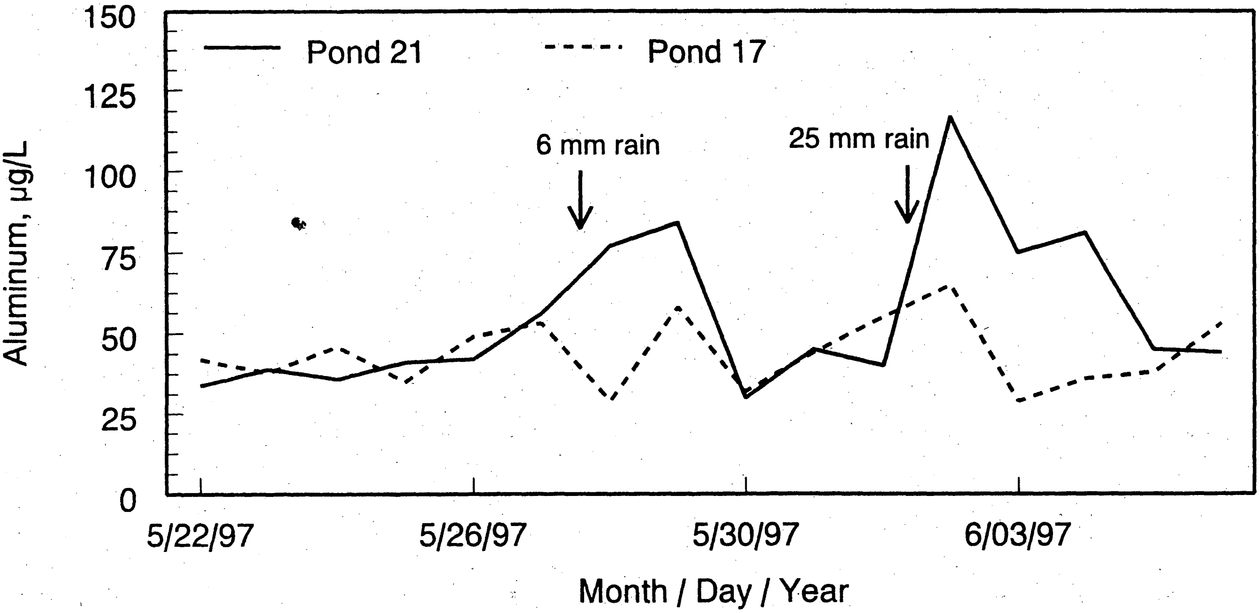

Fig. 9. Total aluminum values recorded for Pond 17 (broken line) and Pond 21 (solid line) for the period May 27 through June 6, 1997. Aluminum concentration increased in Pond 21, but did not signficantly change in Pond 17, after an acidic storm event on June 1.

ponds complex. Additional work is needed to integrate the knowledge of water chemistry to population density, individual behavior, reproductive success, and survivorship for *A. tigrinum*.

Table 2 includes the WQPs of aluminum and calculated calcium ion to hydronium ion ratio, Ca/H, which are important for the health of fisheries. Concentration of aluminum in natural water has been proven to be a major factor in the mortality of fish (Wood et al., 1988; McCahon et al., 1987). Aluminum dissolution from soils and minerals in a watershed increases as pH decreases (Cronan & Schofield, 1979). Calcium is beneficial as it inhibits aluminum binding by fish gills (Brown, 1982). The larger the Ca/H ratio, the better the survival rate even when toxic aluminum is elevated. Estimated values for no observed adverse effects on trout for these two WQPs are $Al_T < 100$ ppb and $Ca/H > 6$ (Menendez et al., 1996). It is not known if these values represent acceptable limits for *A. tigrinum*, but, if so, the two year average data in Table 2 suggest that Ca/H ratios in these ponds may be critically low. The low Ca/H ratio values confirm the lack of carbonate mineral dissolution (low calcium and high hydronium) contributing to water quality as described above. In most cases, the total aluminum is well below 150 ppb, although episodic events cause elevation in some ponds as shown in Fig. 9.

In the data sets of Tables 2, 3, and 4, the ponds MFS and MFN are the manmade wildlife ponds (South and North) on Canada Run which are situated in the middle of the Maple Flats sinkhole ponds complex. The pH and ANC values (Fig. 1) for these two ponds are significantly higher than for the sinkhole ponds. There is less organic acid, as Canada Run flows through these two ponds and flushes out organic matter. Other water quality parameters are also higher for these ponds than for the sinkhole ponds.

CONCLUSION

Water chemistry data collected for twenty-six natural sinkhole ponds and two man-made ponds for a two year period has revealed that all the natural ponds are chronically acidic with average values pH<6 and ANC< 20. About half the natural ponds were extremely acidic (pH<5, ANC< 0). Base cation and acid anion concentrations were also found to be low in all the ponds. Organic acids, atmospherically derived acid, and a lack of carbonate buffer from the acidic soils and bedrock geology of the system contribute to the poor water quality. Episodic precipitation events further decreased pH and other water quality parameters in these acidic ponds for short periods. The manmade ponds have slightly higher pH (pH 6) due to flushing from a tributary stream.

Although there are a number of species of plants and animals that are dependent on the ponds, this project was conducted primarily to provide data for assessing potential impacts from water chemistry on *A. tigrinum*. The low pH and poor water quality is a concern that could affect reproductive success and other aspects of the life cycle of the tiger salamander. Whiteman et al. (1995) indicated that *A. tigrinum* can tolerate relatively low pH values. They found embryo survival of > 70% at pH 4.5 and above, although they suggested sublethal effects could reduce hatchling survival. They also found an adult pH discrimination ability to ponds of higher pH. It is interesting to speculate that the higher pH of the two manmade ponds may be attractive to spawning adult salamanders from the nearby acidic sinkhole ponds. However, as these two ponds support predatory fish populations that could consume emigrating adult salamanders (Buhlmann et al., 1999), more study is needed to determine if they actually a pose a threat. It is not unreasonable to suggest their removal if such is the case.

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