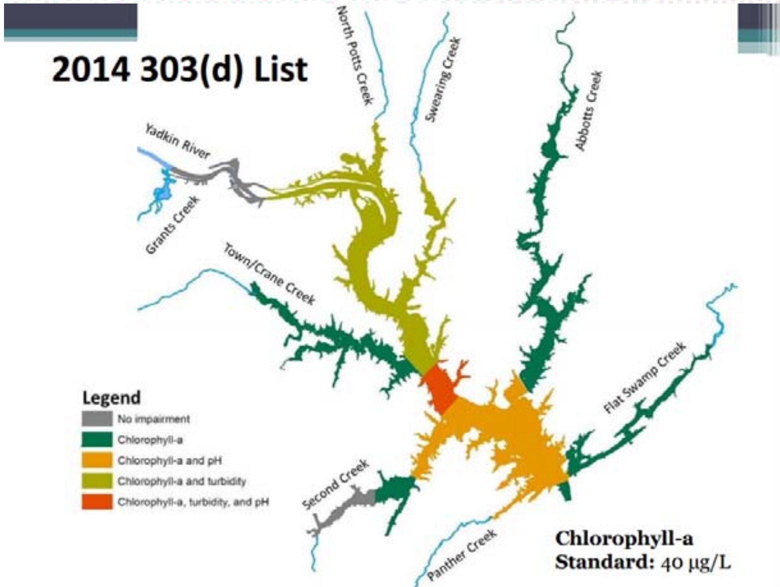


High Rock Lake – Summer 2016

Astrid Schnetzer

NCDP Scientific Advisory Council Meeting, May 2017

Solid Phase Adsorption Toxin Tracking - SPATT

A simple and sensitive *in situ* (monitoring) method that involves the passive adsorption of biotoxins onto porous synthetic resin filled sachets (SPATT bags) and their subsequent extraction and analysis (MacKenzie et al. , 2004 – Toxicon)

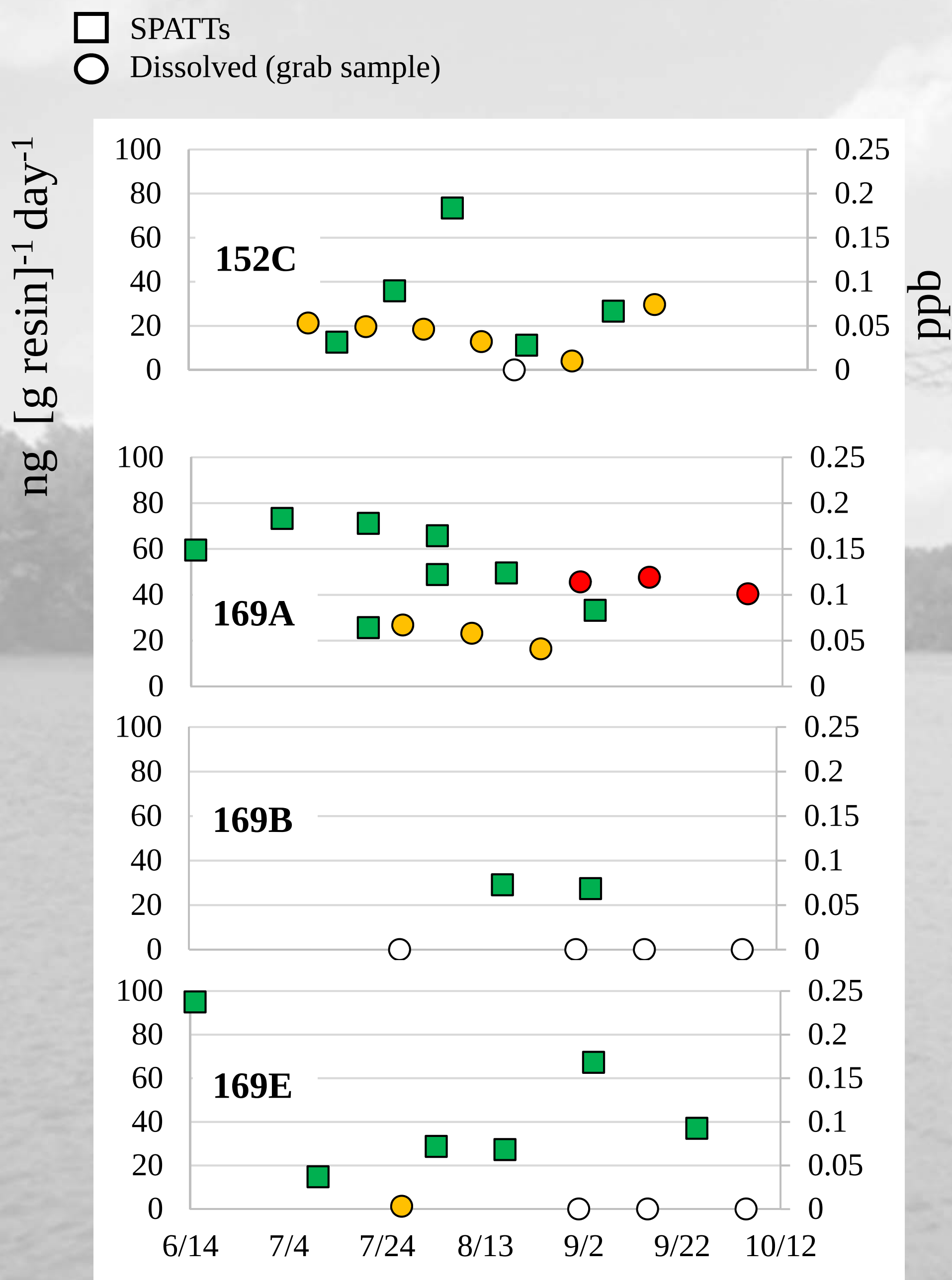
PROS

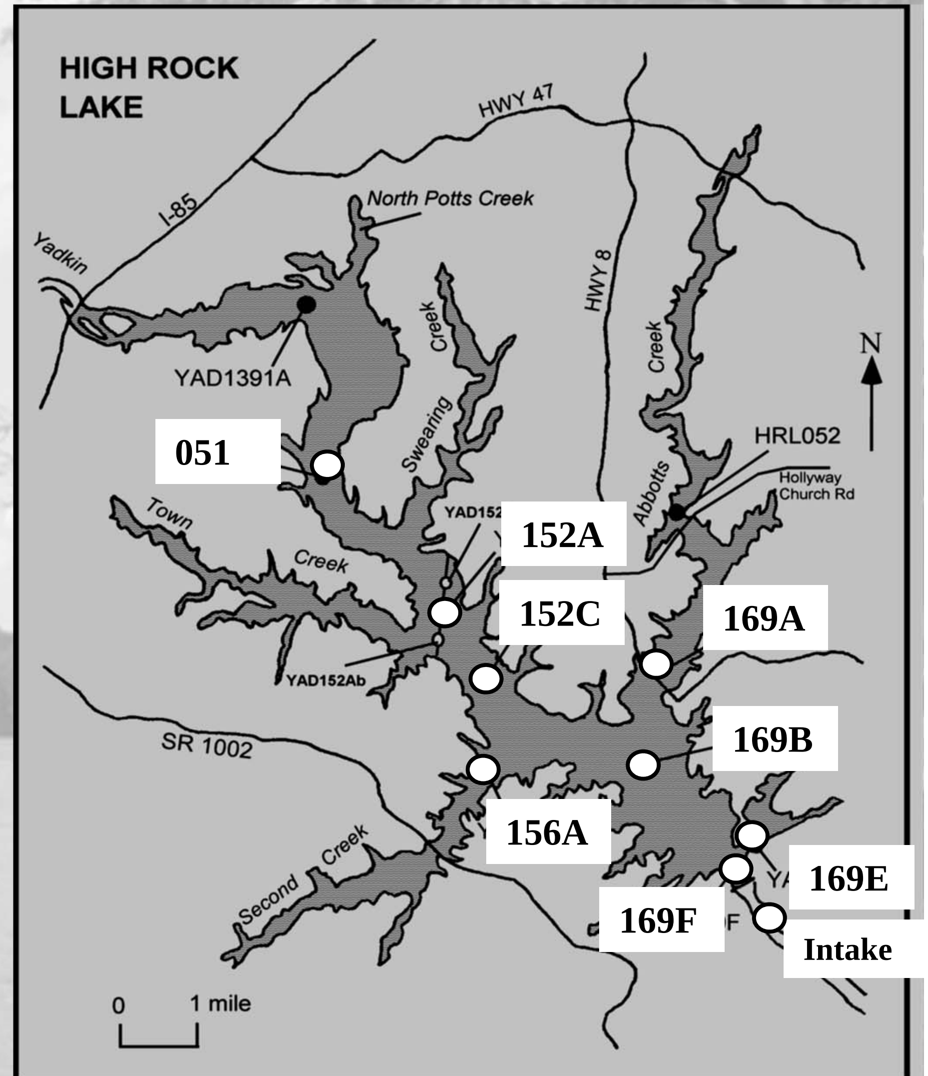
- Time-integrative signal
- Low detection limit
- Fresh to marine application
- Multiple toxin detection
- Easy to deploy and recover

CONS

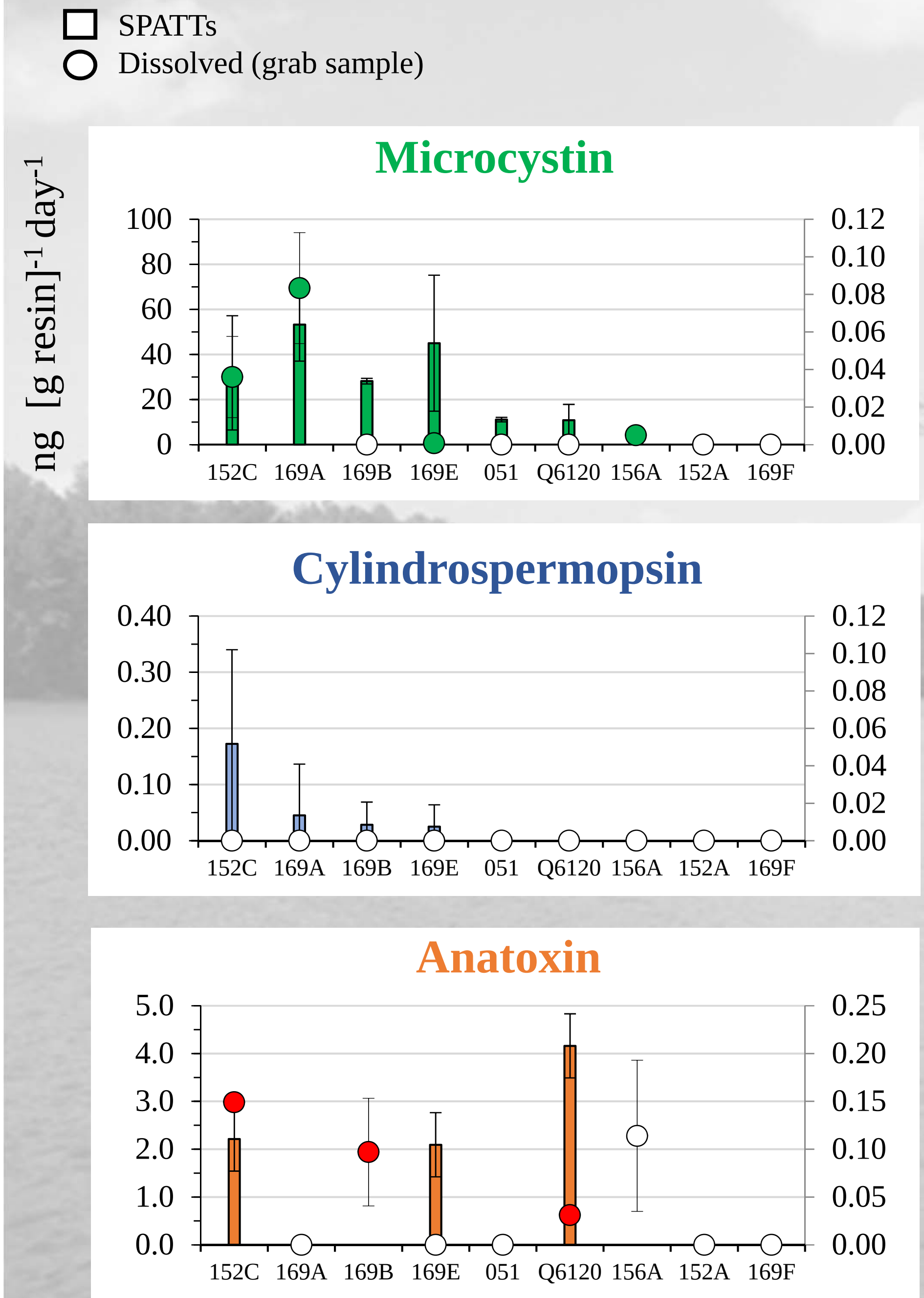
- Semi-quantitative
- No link to regulatory limit

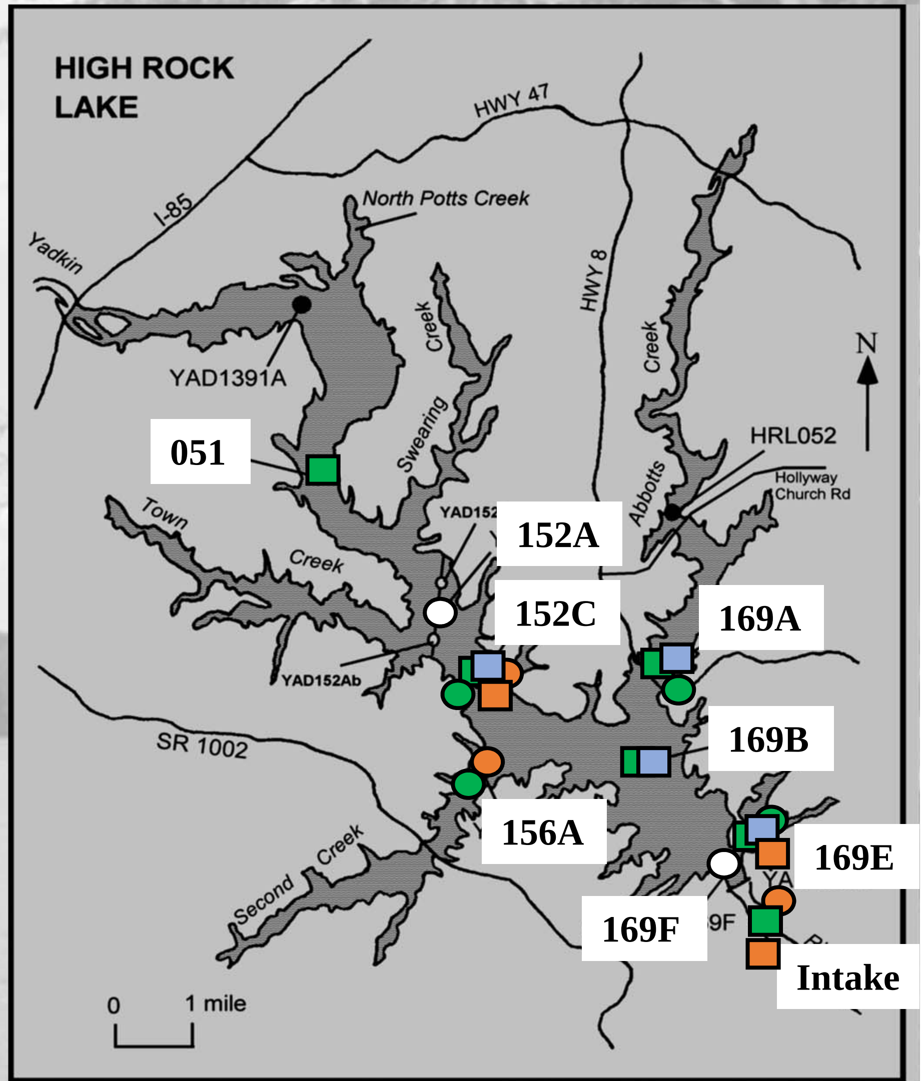
Microcystin





Drinking Water (10-day)		
	Infants/Pre-school	School-age/ Adults
Microcystin	0.3	1.6





Drinking Water (10-day)		
	Infants/Pre-school	School-age/ Adults
Microcystin	**0.3**	**1.6**
Cylindrospermopsin	**0.7**	**3**

So far…

- **Microcystin**, **cylindrospermopsin** and **anatoxin** were detected at varying stations and at multiple times based on SPATT sampling

- Potential multi-toxin exposure over several weeks at low concentrations

- Traditional grab samples allowed for detection
    - at ~25% of the time for **microcystin** (ldl 0.1 ug/L)
    - never for **cylindrospermopsin** (ldl 0.04 ug/L)
    - tbd for **anatoxin**

- Ranges for dissolved **microcystin** and **cylindrospermopsin** remain below drinking water and/or recreational thresholds

- Traditional grab samples analyzed for intracellular toxins did not yield detectable levels (problem of patchiness)

- Exposure risk based on food web accumulation is unknown at this time

North Carolina Nutrient Science Advisory Council

May 18, 2017

Follow-Ups on DO and pH from March 2017 SAC Meeting

NC’s DO Criteria for Class C Waters

- “…not less than a daily average of 5.0 mg/l with a minimum instantaneous value of not less than 4.0 mg/l; swamp waters, lake coves, or backwaters, and lake bottom waters may have lower values if caused by natural conditions.”
- March 2017 SAC meeting: Recommendation of additional narrative language
  - Natural conditions.
  - When/where does DO criterion apply

Strawman Language

- "For reservoir waters that exhibit thermal stratification, the dissolved oxygen criteria only apply to the epilimnetic waters."
- "In practice, dissolved oxygen criteria in [High Rock Lake] will be assessed using surface samples."
- "For epilimnetic waters, natural conditions that might lower DO concentrations include meteorological or hydrologic events that cause sudden destratification or loss of light in the photic zone."
- "Other natural conditions may also be considered."

Summary of pH Discussion to Date

- Existing pH criteria:
  - “pH: shall be normal for the waters in the area, which range between 6.0 and 9.0”
  - Narrative standard?
- Proposal of site-specific interpretation
  - “e.g., pH: shall be normal for the waters in the area, which range between 6.5 and 9.5
- Precedents from other states.
- SAC discussion from March 2017: Support/questions/concerns on modification of pH criteria

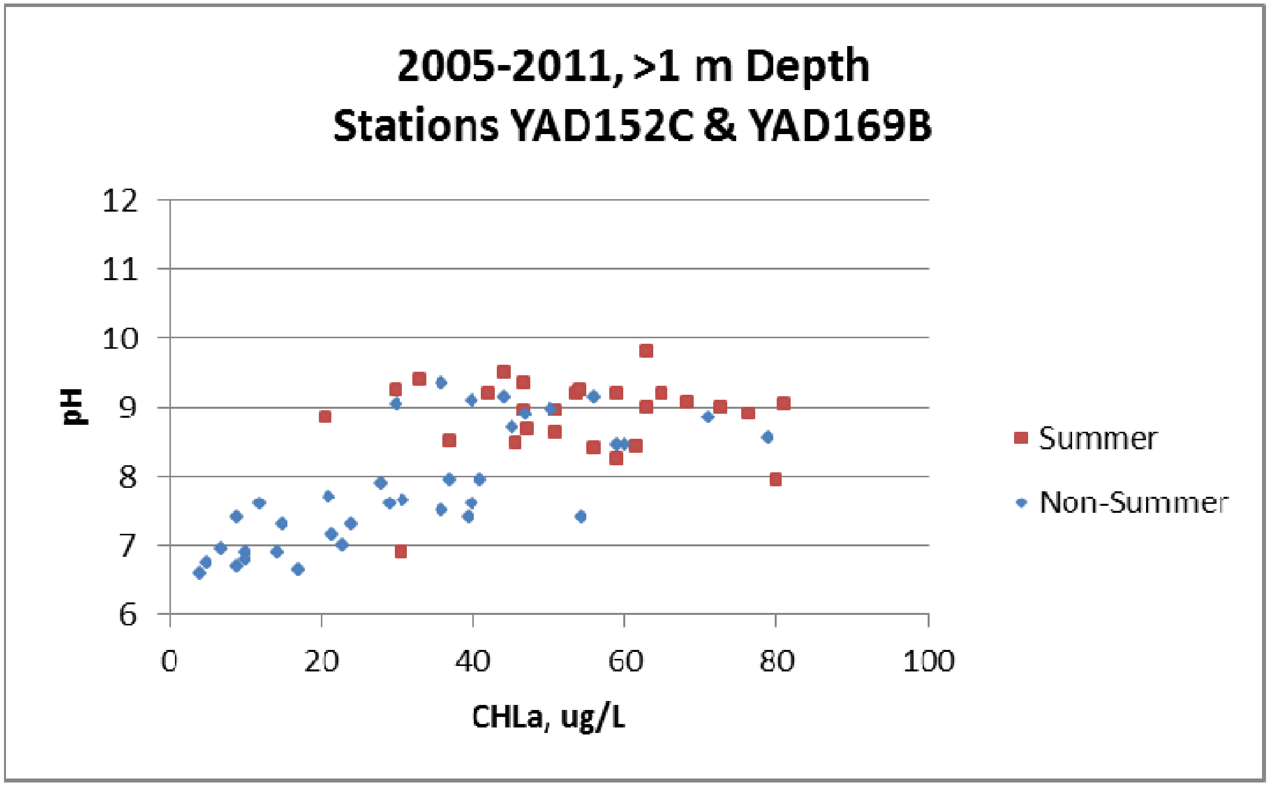
Technical Bases of pH Proposal

- Literature review: Values of up to 9.5 not inherently harmful to warm/coolwater fisheries
- Low ammonium in HRL
- Excellent status of HRL fishery

"Chronic exposure to pH values above 10.0 are harmful to all species studied, while salmonid and some other species are harmed at values above 9.0." EIFAC (1969)

HRL might meet CHLa criteria and still be 303(d)-listed for nutrients via pH?

- Summer pH not strongly correlated to CHLa



Examples of (paraphrased) discussion points from March 2017 SAC Meeting

- "What about joint effects of multiple stressors."
- "HRL has a high diel variability in pH."
- "As long as ammonium is low, it's fine."
- "If HRL met 9.5 (assessed as a 90th percentile), would there be deleterious effects at the high end of the distribution?"
- "Would some sort of averaging/aggregation show that existing pH criterion is attainable."

A Summary of Some Effects of pH on Freshwater Fish and Other Aquatic Organisms

pH	Known effects
11.5–12.0....	Some caddis flies (Trichoptera) survive but emergence reduced.
11.0–11.5....	Rapidly lethal to all species of fish.
10.5–11.0....	Rapidly lethal to salmonids. The upper limit is lethal to carp (Cyprinus carpio), goldfish (Carassius auratus), and pike. Lethal to some stoneflies (Plecoptera) and dragonflies (Odonata). Caddis fly emergence reduced.
10.0–10.5....	Withstood by salmonids for short periods but eventually lethal. Exceeds tolerance of bluegills (Lepomis macrochirus) and probably goldfish. Some typical stoneflies and mayflies (Ephemera) survive with reduced emergence.
9.5–10.0....	Lethal to salmonids over a prolonged period of time and no viable fishery for coldwater species. Reduces populations of warmwater fish and may be harmful to development stages. Causes reduced emergence of some stoneflies.
9.0–9.5.....	Likely to be harmful to salmonids and perch (Perca) if present for a considerable length of time and no viable fishery for coldwater species. Reduced populations of warmwater fish. Carp avoid these levels.
8.5–9.0.....	Approaches tolerance limit of some salmonids, whitefish (Coregonus), catfish (Ictaluridae), and perch. Avoided by goldfish. No apparent effects on invertebrates.
8.0–8.5.....	Motility of carp sperm reduced. Partial mortality of burbot (Lota lota) eggs.
7.0–8.0....	Full fish production. No known harmful effects on adult or immature fish, but 7.0 is near low limit for Gammarus reproduction and perhaps for some other crustaceans.

Source: USEPA (1973). Table incorporates information presented by Alabaster and Lloyd (1980).

Tables reproduced in Robertson-Bryan (2004)

Limiting pH Values Minimum	Maximum	Remarks	Reference
3.3	10.7	Trout survived without adverse effects	1467
3.6	---	Tench survived two weeks but carp died	1302
3.6	10.5	96-hour TL_m range for bluegill sunfish	2034
3.8	10.0	Fish eggs could be hatched, but abnormal young were produced of extreme pH's	1468
4.0	10.0	The most resistant fish can tolerate such extreme pH values indefinitely after acclimatization	1460
4.0	10.1	Limits for the most resistant species	361
4.0	10.4	Limits for bluegill sunfish with HCl and NaOH	3606
4.1	8.5	Range tolerated by speckled trout in nature	1467
4.1	9.5	Range tolerated by trout	862
4.3	---	Carp died in 5 days	1303
4.4	8.7	Toxic limits for trout	3609
4.5	8–9	Trout eggs and larvae develop normally	1636
4.6	9.5	Toxic limits for perch	3609
4.6	---	Tench died in two days	2977
4.8	---	Lower limit for trout	1304
4.8	---	Illness and early death for carp	2977
4.8	9.2	Toxic limits for fish	1305
5.0	---	Toxic limit for sticklebacks	2941
5.0	9.0	Tolerable range for most fish	361, 2409, 3609
---	8.7	Upper limit for good fishing water	717
5.4	---	Lower limit for carp and tench	1306
---	9.2	Upper limit for trout and perch	2977
5.5	---	Lower limit for general fish protection	1307
5.4	11.4	Fish avoided waters beyond these limits	1046
6.0	11.0	Fish did not avoid waters in this range	1046
6.0	7.2	Optimum range for fish eggs	1468
6.5	8.4	Range tolerated by most fresh-water fish	1466

For other aquatic organisms, ranges were reported as follows:

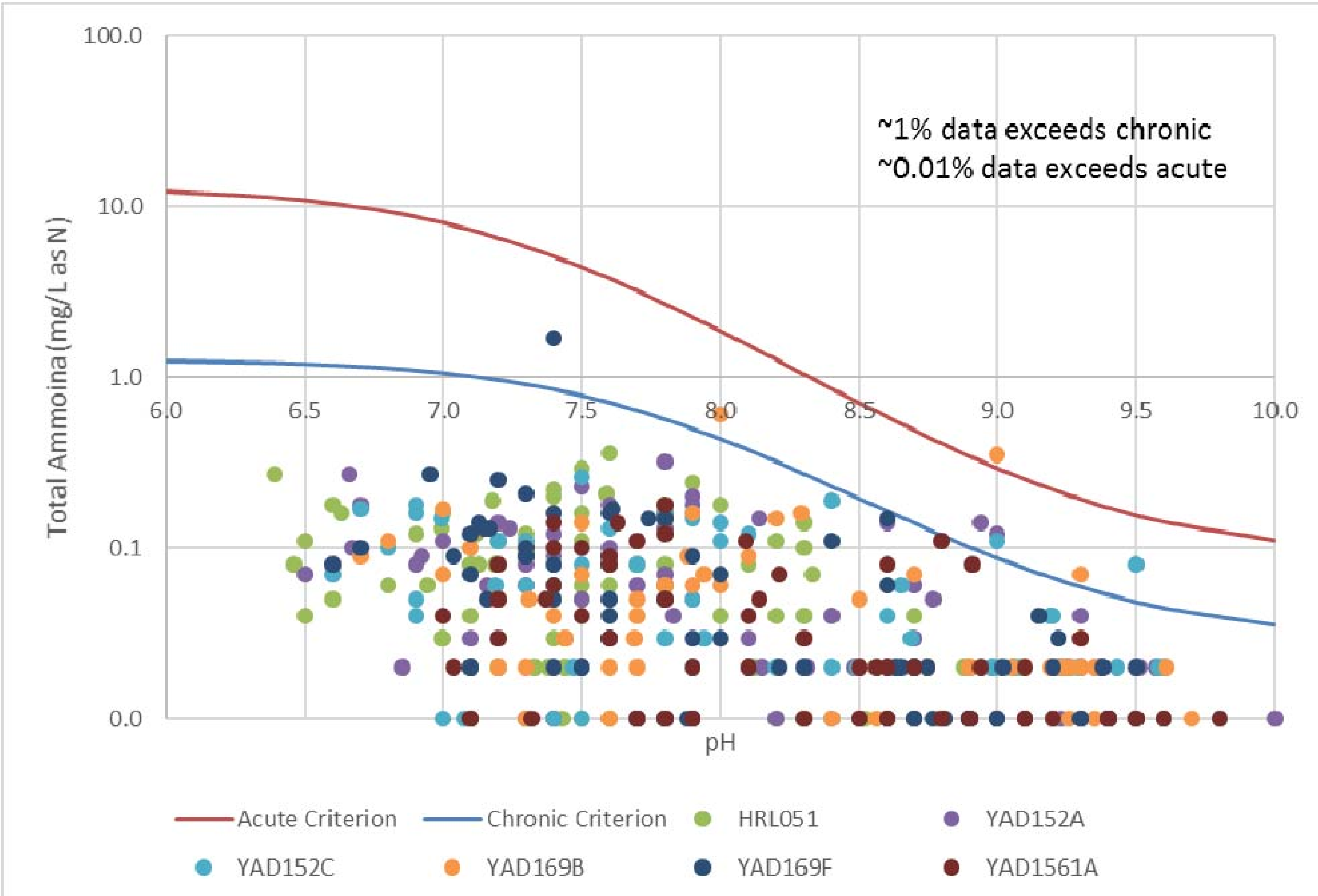
1.0	---	Mosquito larvae destroyed at this value	1308
2.5	---	Tolerated by *Chlamydomonas, Fragilaria, Asterionella, Aphanizomenon*	2168
3.3	4.7	Mosquito larvae thrived in this range	1309
4.0	---	Toxic for *Paramecium, Volvox, Asplanchna*	2977
7.5	8.4	Good range for plankton production	1021
---	8.5	Algae are destroyed above this value	

Source: McKee and Wolf (1963).

Diel impacts of pH variability?

- See Robertson-Bryan (2004) literature review
  - "If no acute mortality occurs, no chronic effects would be expected because of physiological acclimation…"
  - "…the ending pH is more important in determining mortality than the magnitude and rate of initial pH change.
  - "Available data regarding pH values tolerated by macroinvertebrates suggest that, like fish, they can rapidly adapt to changes in ambient pH levels *within their natural pH range* [emphasis added]."
- Overall, confirms that salmonids would be more sensitive to high pH variability with in the pH range of HRL.

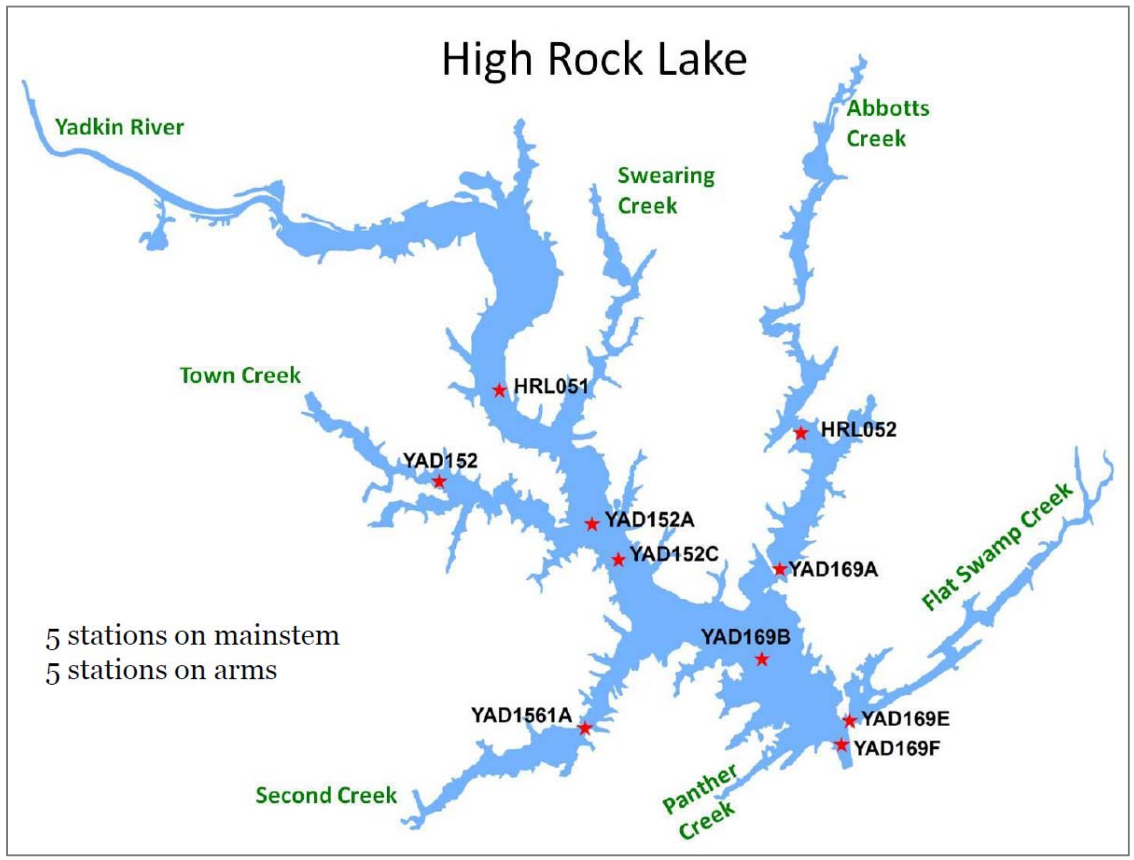
Follow Up: Lack of pH-Related Ammonium Toxicity in HRL (2005-2016)



Need to resolve with DEQ analysis of May 2017

Method for Evaluating Effects of pH Data Spatial Aggregation

- Calculated annual 90% percentile pH from 2005-2016 data
- Vertical aggregation
  - Surface sample only
  - ≤3 meters
  - Entire water column
- Spatial aggregation
  - Individual stations
  - Lower vs. upper reservoir
  - Entire reservoir

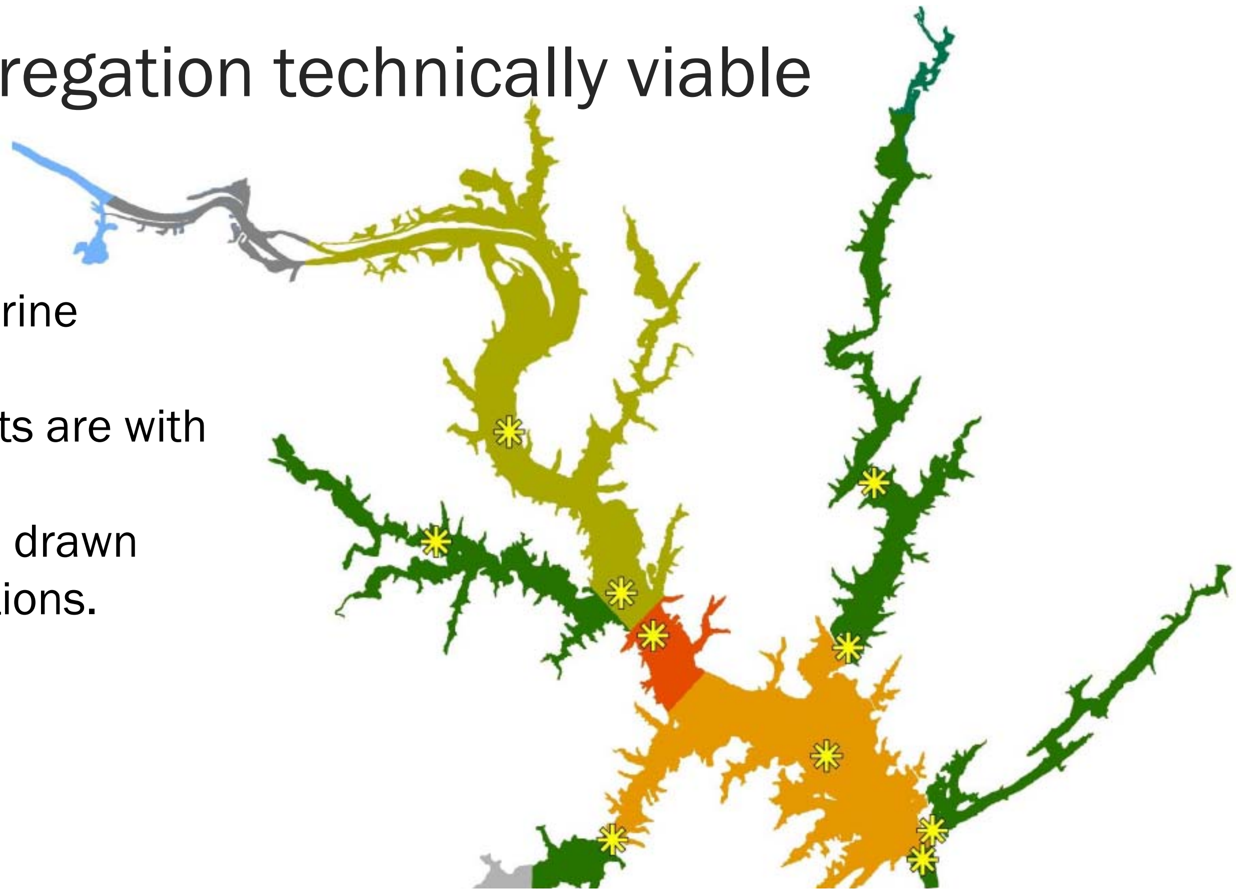


Values in 9.0 – 9.5 range persist regardless of aggregation

Year	Grouping1	90th percentile pH		
		≤0.5 m	≤3 m	All Depths
2005	Upper Lake	8.9	8.6	8.4
2006	Upper Lake	9.4	9.3	9.3
2008	Upper Lake	8.7	8.7	8.6
2009	Upper Lake	8.7	8.6	8.5
2011	Upper Lake	9.2	9.2	9.2
2016	Upper Lake	9.4	9.4	9.2
2005	Lower Lake	9.3	9.2	8.8
2006	Lower Lake	9.6	9.6	9.1
2008	Lower Lake	9.2	9.1	8.6
2009	Lower Lake	9.2	9.2	8.5
2011	Lower Lake	9.3	9.3	9.1
2016	Lower Lake	9.5	9.4	9.1

Thoughts on spatial aggregation of pH

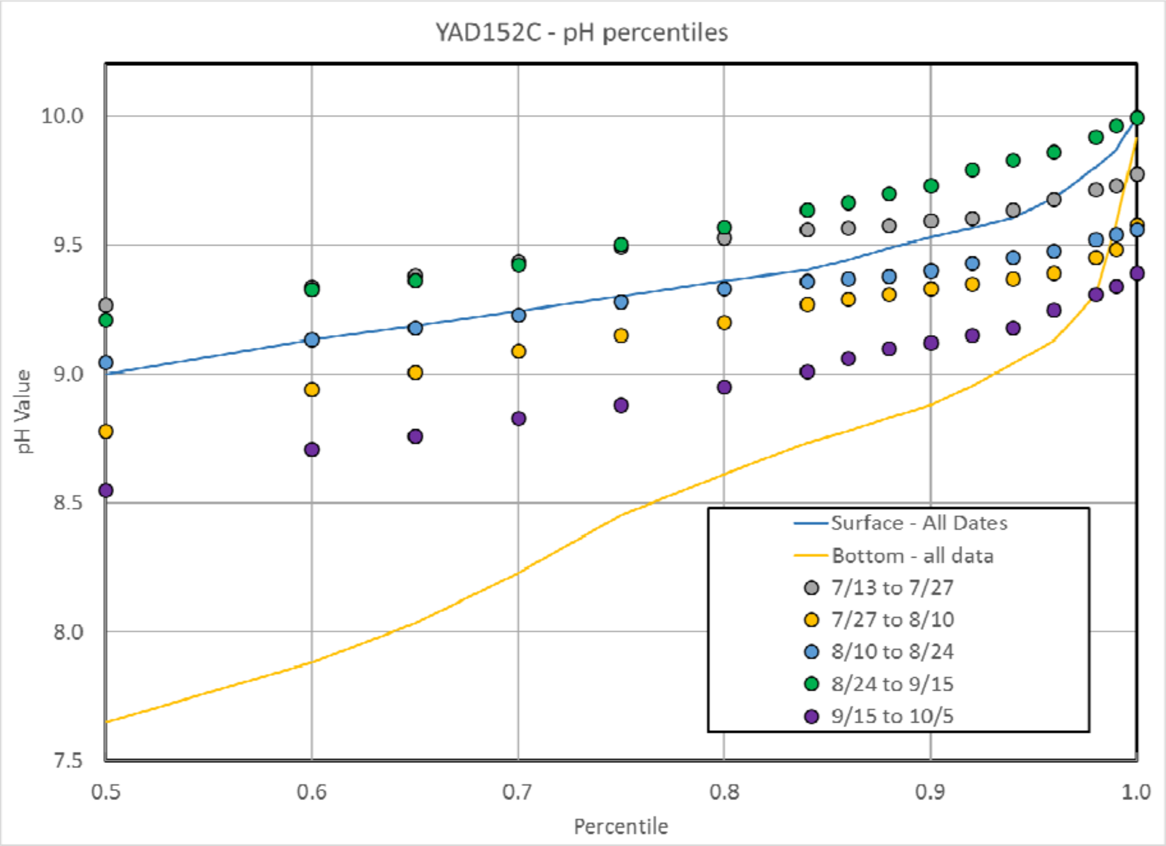
- Not recommended to aggregate entire water column—hypolimnetic waters not viable habitat.
- Simpler to use surface sample, consistent with DO.
- Horizontal aggregation technically viable



- e.g., Riverine & lacustrine segments
- Fish are mobile, effects are with longer-term exposure
- Avoid small segments drawn around individual stations.

Investigation into pH (temporal) distributions

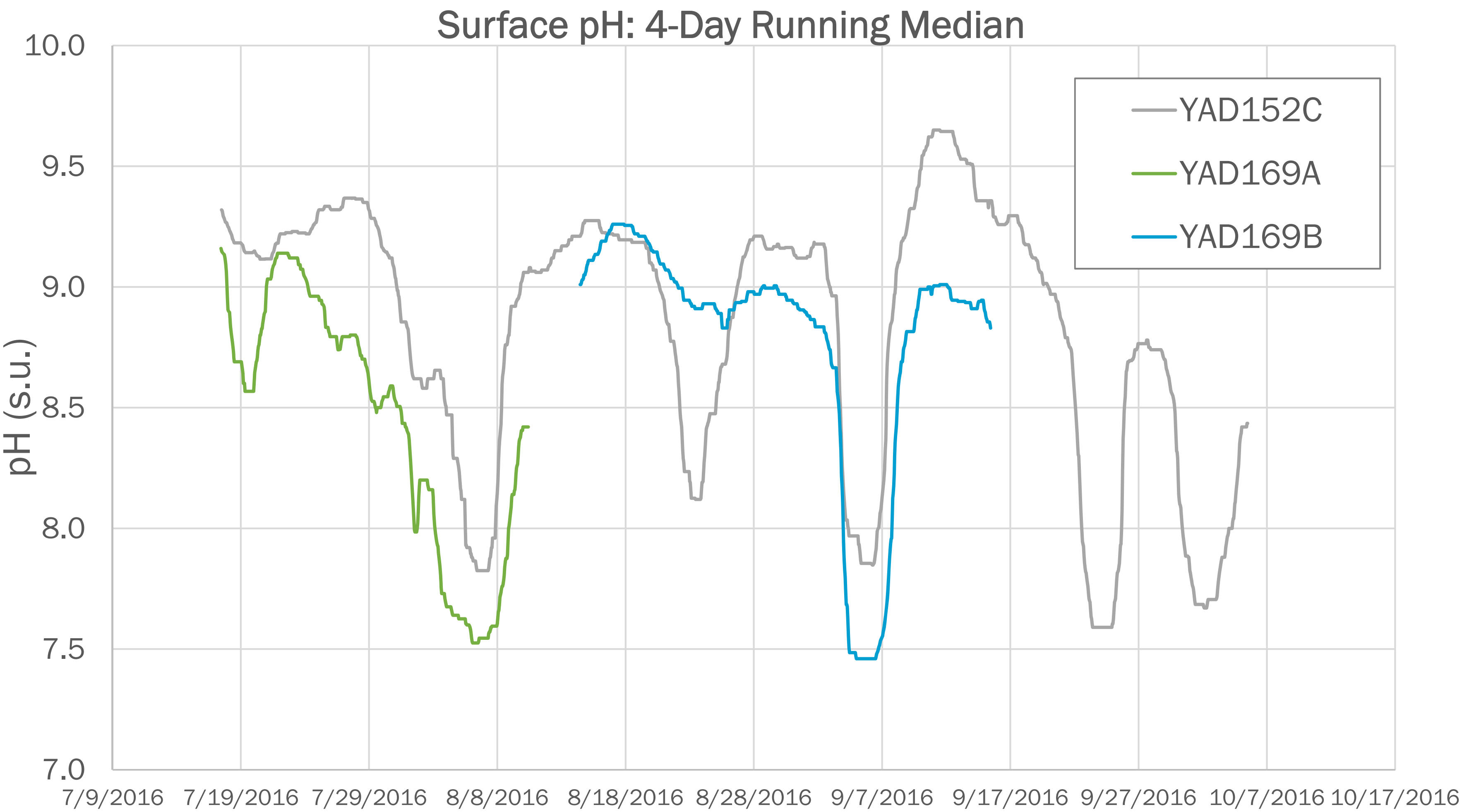
- See workbook on 2016 sonde data from M. Lebo
  - pH frequency distributions
  - Charts



Acute vs. chronic impacts

- Acute impacts: These would occur at very high pH values (>10.5)
  - 2016 sonde data show no exceedances of 10.0
- Chronic impacts would be from prolonged exposure
  - Literature studies of high pH impacts vary in duration
  - Those cited in EPA Red/Gold books are 30+ days
  - We examined 4-day median pH (conservative)

4-Day Median pH Rarely Exceeded 9.5, briefly hit ~9.6 at one station



Conclusion

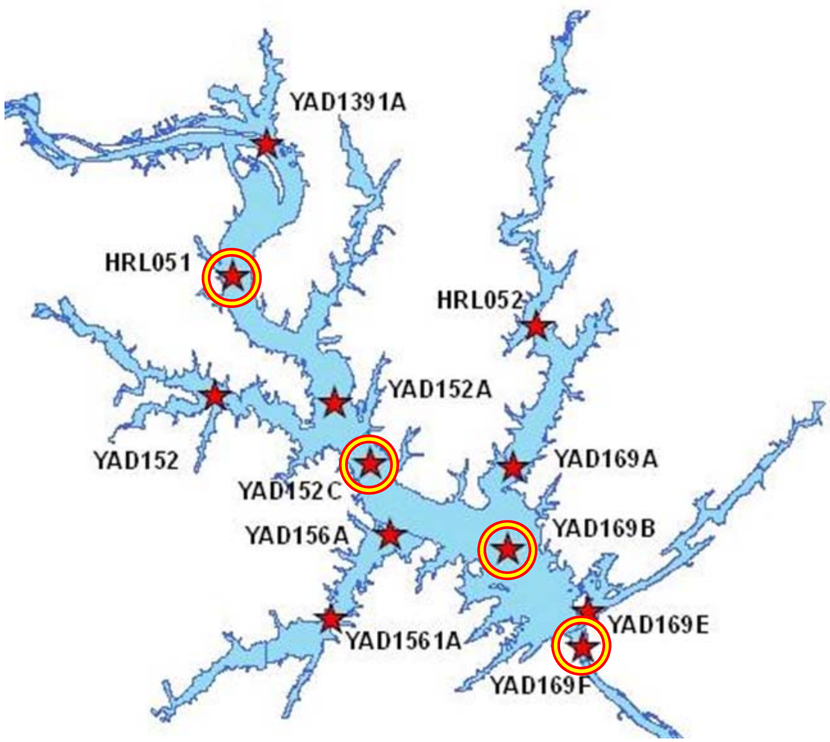
- Attainment of a theoretical pH criterion of 9.5--assessed using the state's existing methodology--would not be associated with common exceedances of 10.0 (short-duration) or 9.5 (prolonged exposure).

High Rock Lake "Turnover": Frequency and Spatial Extent

Division of Water Resources
NCDEQ

May 18, 2017
NCDP SAC Meeting

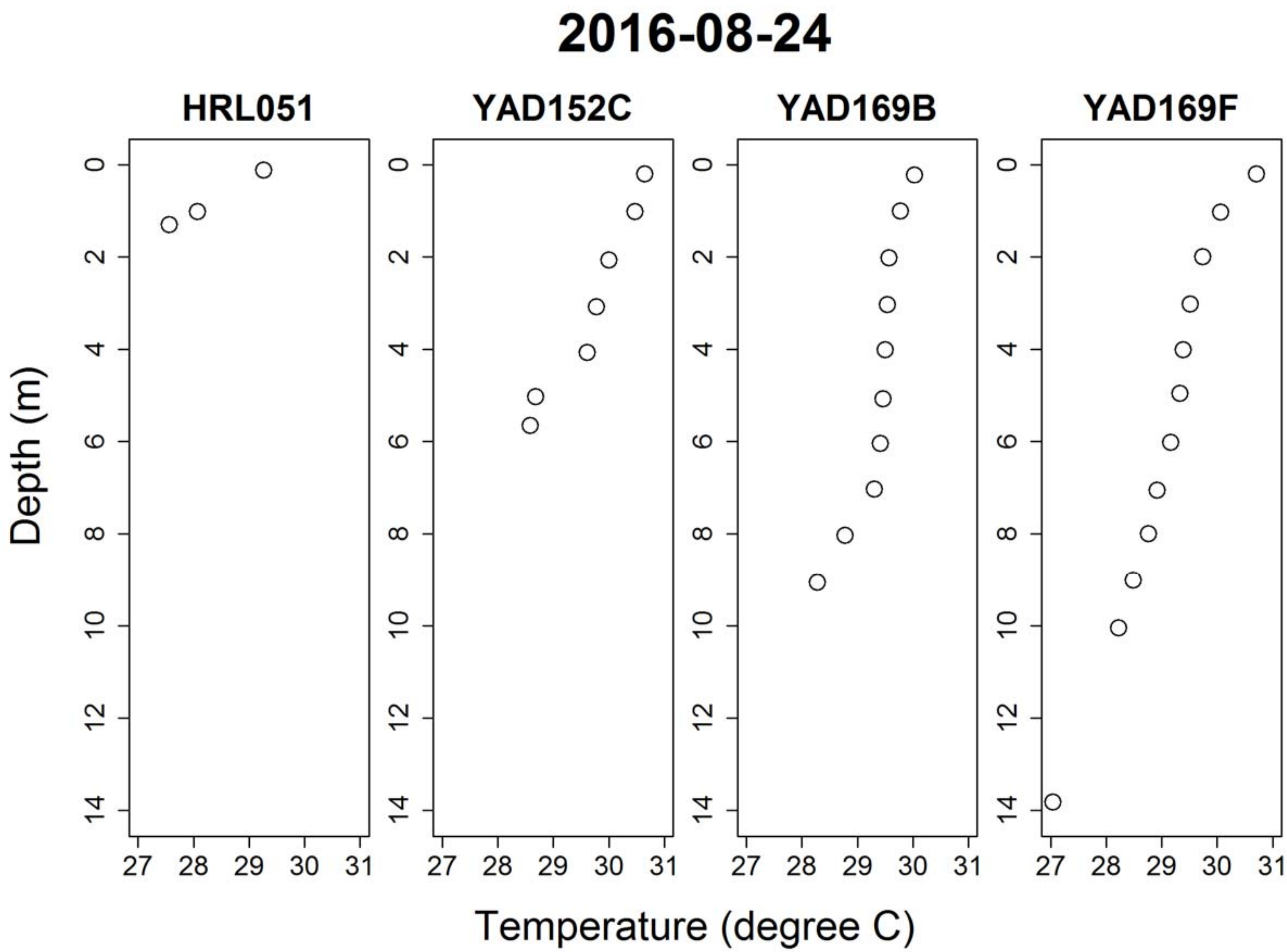
Available HRL Temperature Profiles



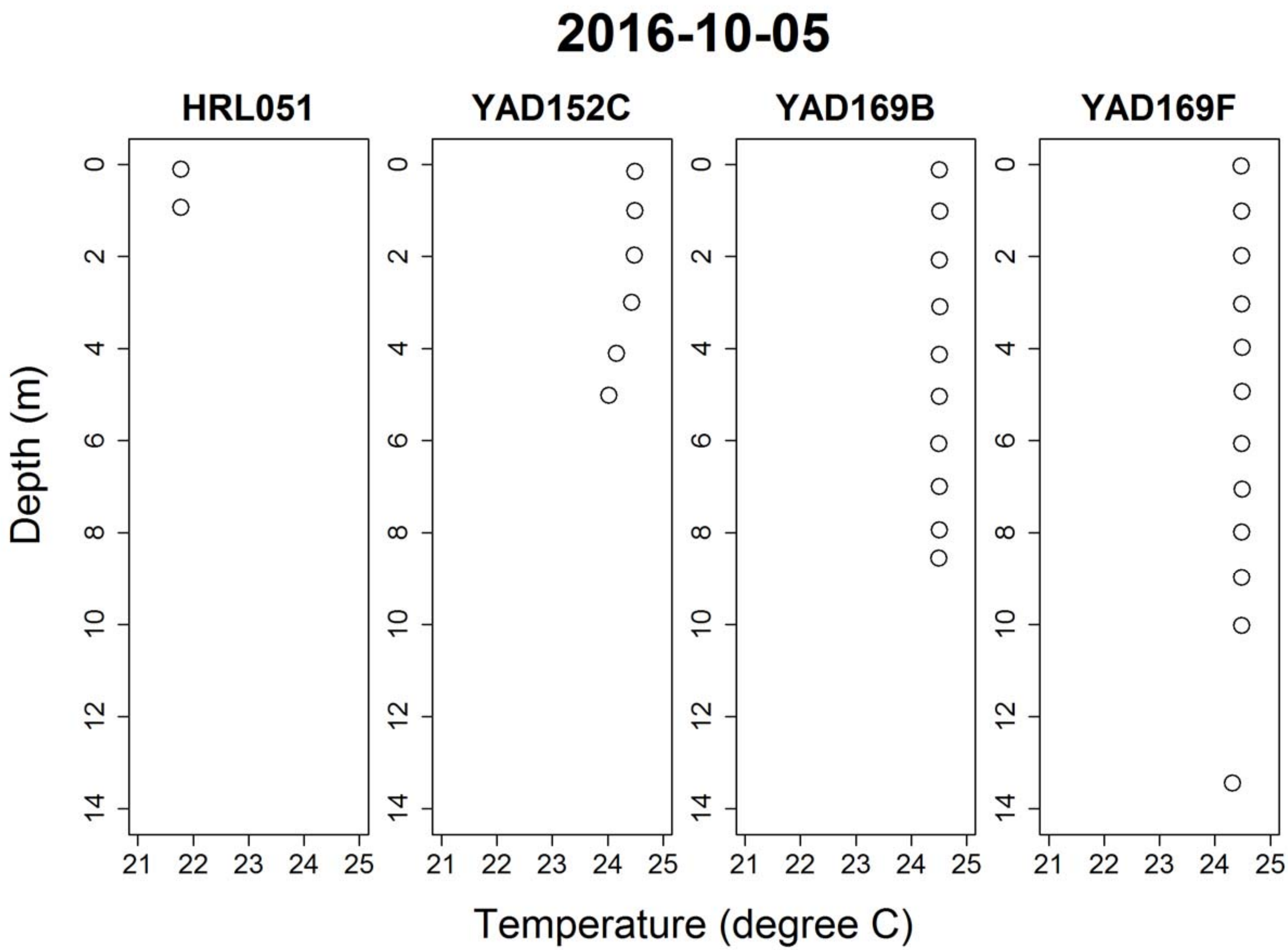
<u>Data from AMS (Ambient Monitoring System)</u>

- compiled from 1981 to 2016
  (High Rock Lake Data_1981_2016.xlsx)
- about 1000 temperature profiles available
- 4 stations used in this analysis:
  - HRL051 (79 profiles, max depth = ~3m)
  - YAD152C (113 profiles, max depth = ~8m)
  - YAD169B (111 profiles, max depth = ~13m)
  - YAD169F (107 profiles, max depth = ~16m)

HRL Temperature Profile Example, Stratified

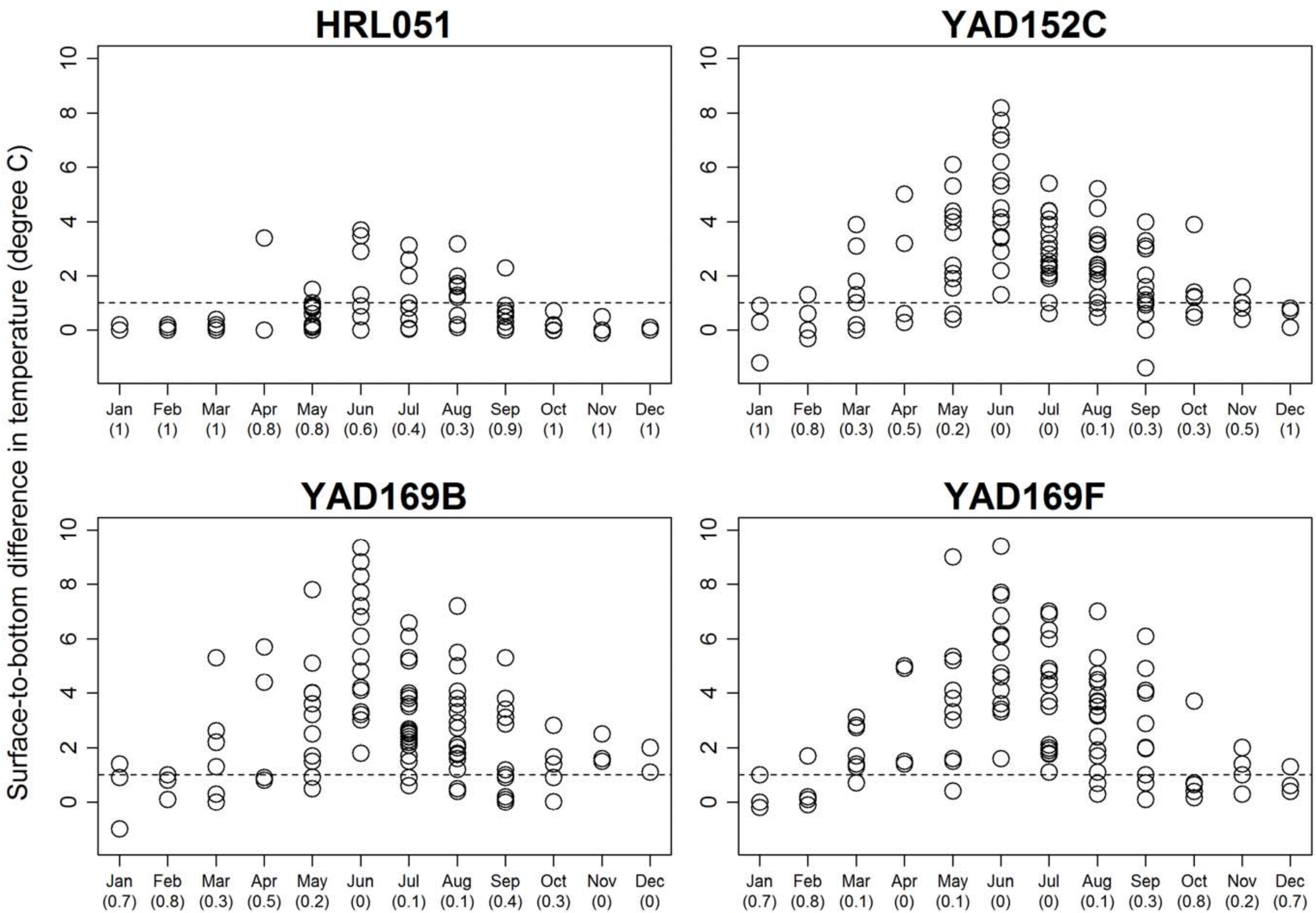


HRL Temperature Profile Example, Mixed



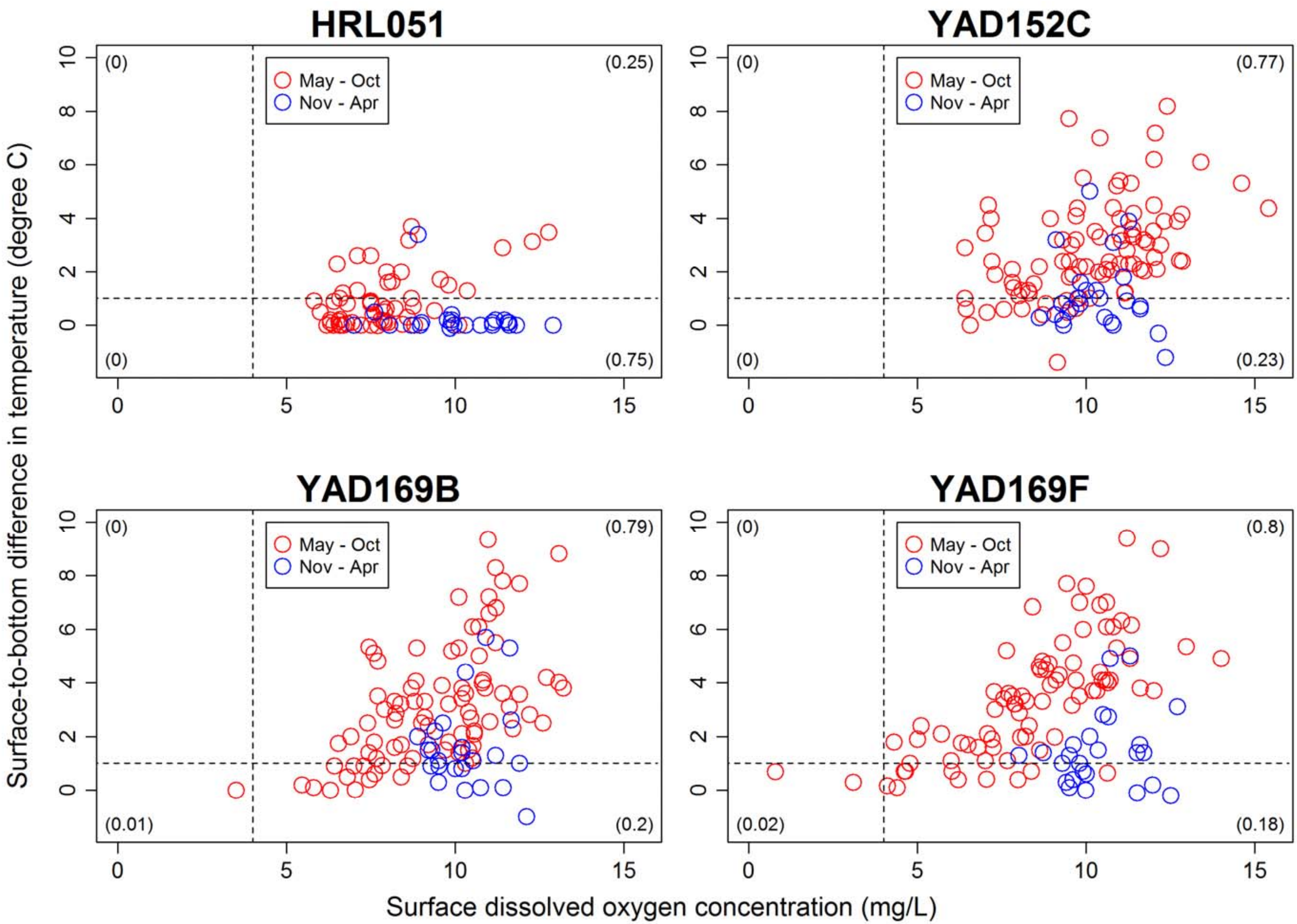
Surface-to-Bottom Difference in Temperature

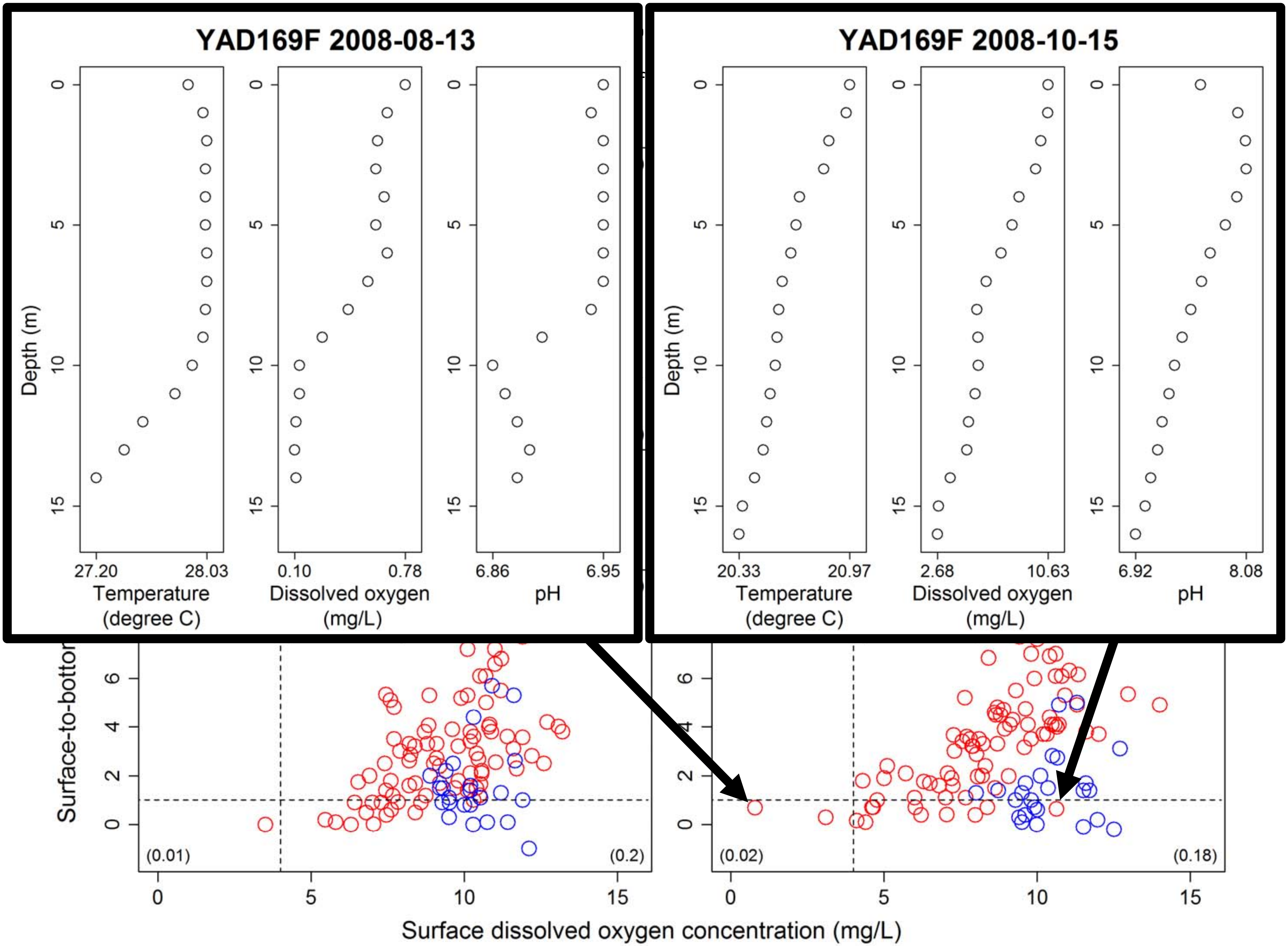
(numbers in parenthesis: fraction of monthly differences less than 1 degree C)



Temperature Difference vs Surface DO

(numbers in parenthesis: fraction of points belonging to each quadrant)





YAD169F 2008-08-13
Depth (m)
Temperature (degree C)
27.20
28.03
Dissolved oxygen (mg/L)
0.10
0.78
pH
6.86
6.95
YAD169F 2008-10-15
Depth (m)
Temperature (degree C)
20.33
20.97
Dissolved oxygen (mg/L)
2.68
10.63
pH
6.92
8.08
Surface-to-bottor
(0.01)
(0.2)
(0.02)
(0.18)
Surface dissolved oxygen concentration (mg/L)

PH CONSIDERATIONS IN HIGH ROCK LAKE

Division of Water Resources – Modeling and Assessment
NC Department of Environmental Quality

References

- Clifton Bell, 2016, Notes on pH as a Potential Nutrient Indicator for High Rock Lake. (**Bell, 2016**)
- Robertson – Bryan Inc., 2004. PH Requirements of Freshwater Aquatic Life. (**RBI, 2004**)
- Alabaster, J. S., and R. Lloyd. 1980. Water quality criteria for freshwater fish. European Inland Fisheries Advisory Commission Report (FAO). Buttersworth, London-Boston. 297 pp. (**A&L, 1980**)
- EIFAC (European Inland Fisheries Advisory Commission). 1969. Water quality criteria for European freshwater fish: Report on extreme pH values and inland fisheries. Prepared by EIFAC Working Party on Water Quality Criteria for European Freshwater Fish. Water Research. 3(8):593–611. (**EIFAC, 1969**)
- US Environmental Protection Agency (EPA), 2013. AQUATIC LIFE AMBIENT WATER QUALITY CRITERIA FOR AMMONIA – FRESHWATER. EPA-822-R-13-001 (**EPA, 2013**).
- Witschi, W.A., and C.D. Ziebel. 1979. Evaluation of pH shock on hatchery-reared rainbow trout. *Prog. Fish-Cult.* 41:3–5. (**Witschi and Ziebel, 1979**)
- …

Effects of high pH on fish

- Direct Lethal Impact
  - The pH of water affects the normal physiological functions of aquatic organisms, including the exchange of ions with the water and respiration (RBI, 2004)
  - destroy the gill and skin epithelium (EIFAC, 1969).
- Avoidance reaction (EIFAC, 1969)
- Ammonia: At high pH (and temperature) most ammonium in water is converted to toxic ammonia (NH_3), which can kill fish. The toxicity of NH_3 increases with an increase in pH value (EIFAC, 1969; EPA, 1999).
- Effects of Diurnal fluctuations and rapid pH changes (RBI, 2004)

pH Range	Effect on Aquatic Species		
	Bell, 2016	RBI, 2004	EPA, 1973 (A&L, 1980)
8.5-9.0	Unlikely to be harmful to fish, but indirect effects from chemical changes in the water may occur.	Not directly lethal to freshwater fish.	Approaches tolerance limits of some salmonids, whitefish, catfish, and perch. Avoided by goldfish. No apparent effects on invertebrates.
9.0-9.5	Likely to be harmful to salmonids and perch if present for a considerable length of time.	Partial mortality for bluegill sunfish (Lepomis macrochirus), rainbow trout (Oncorhynchus mykiss), brown trout (Salmo trutta), salmon, and perch.	(Bell, 2016)+ Reduced populations of warmwater fish, Carp avoid these levels.
9.5-10.0	Lethal to salmonids over a prolonged period of time, but can be withstood for short periods. May be harmful to development stages of some species.		(Bell, 2016) + Reduced populations of warmwater fish, causes reduced emergence of some stoneflies.

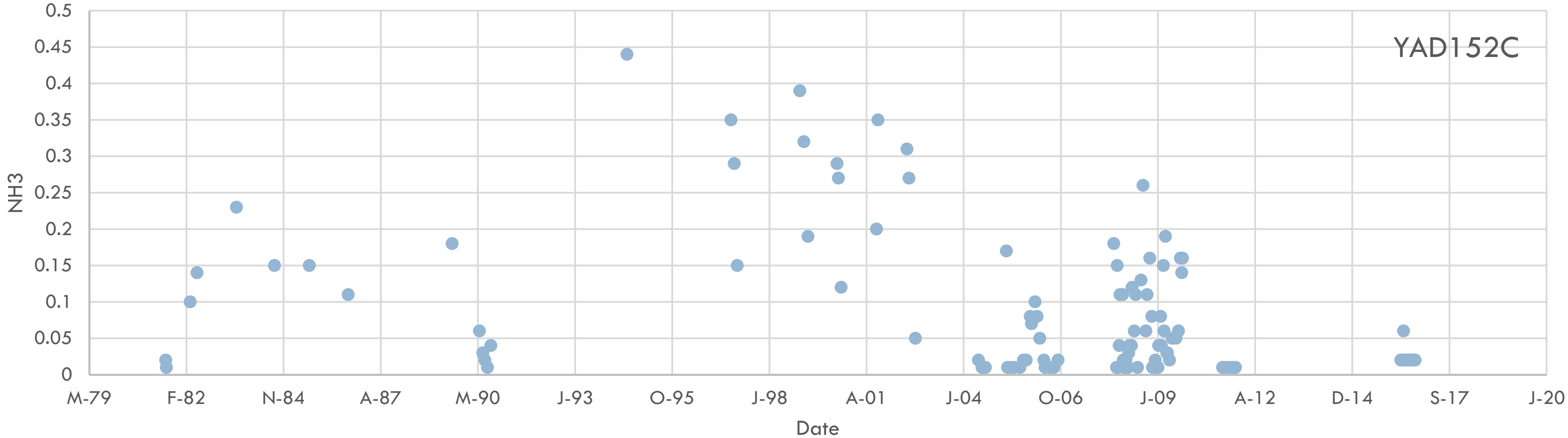
Uncertainties

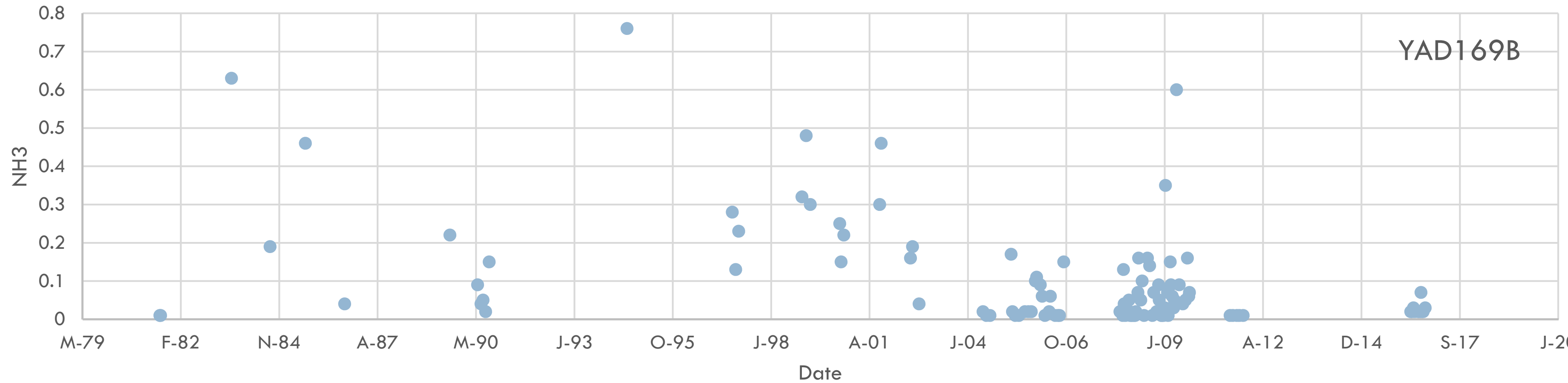
- High pH vs low pH
- Factors need to be considered
  - DO (*Wiebe (1931) found that bluegill sunfish showed distress, and some died, in water of pH value 9.6. and a dissolved oxygen of 5 ppm*)
  - Fish size, stage, etc.
  - High pH accompanied with high Temperature and supersaturation of dissolved gas not covered in the laboratory data
- Statistics used
  - 4-day median (Cairns and Scheier, 1958)
  - 1-day median lethal value (Jordan and Lloyd, 1964)
  - 3-20h (Sanborn, 1945)
  - Minimum lethal pH value (Brandt 1936) vs. Median lethal pH value for 10/15-day exposure (Jordan and Lloyd, 1964)
- *"(Lab) Control of pH values above 10.0 was within 0.05 unit of the intended value, but (lab) control was more difficult below l0.0, the values varying by ± 0.15 unit from the intended value in the range 9.5-10.0, and by ± 0.3 unit below a pH value of 9.5."* (Jordan and Lloyd, 1964).
  - Lab median vs. field median not directly comparable
  - Added uncertainties

ammonia toxicity (EPA Criteria)

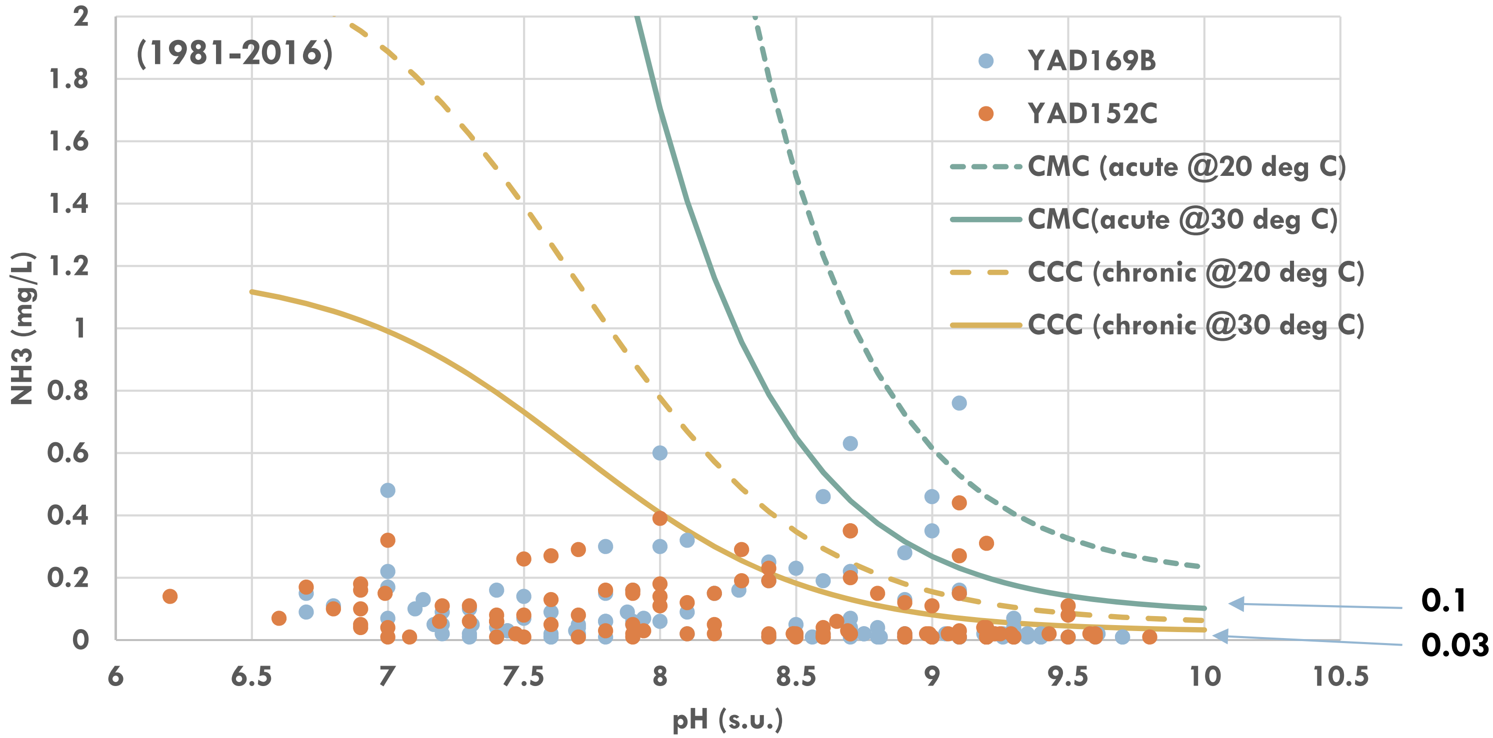
2013 Final Aquatic Life Criteria for Ammonia (Magnitude, Frequency, and Duration) (mg TAN/L) pH 7.0, T=20°C	
Acute (1-hour average)	17
Chronic (30-day rolling average)	1.9*
*Not to exceed 2.5 times the CCC as a 4-day average within the 30-days, i.e. 4.8 mg TAN/L at pH 7 and 20°C, more than once in three years on average.	
Criteria frequency: Not to be exceeded more than once in three years on average.	

NH3 in High Rock Lake





ammonia toxicity (Unionid Mussels Present and Salmon Absent)



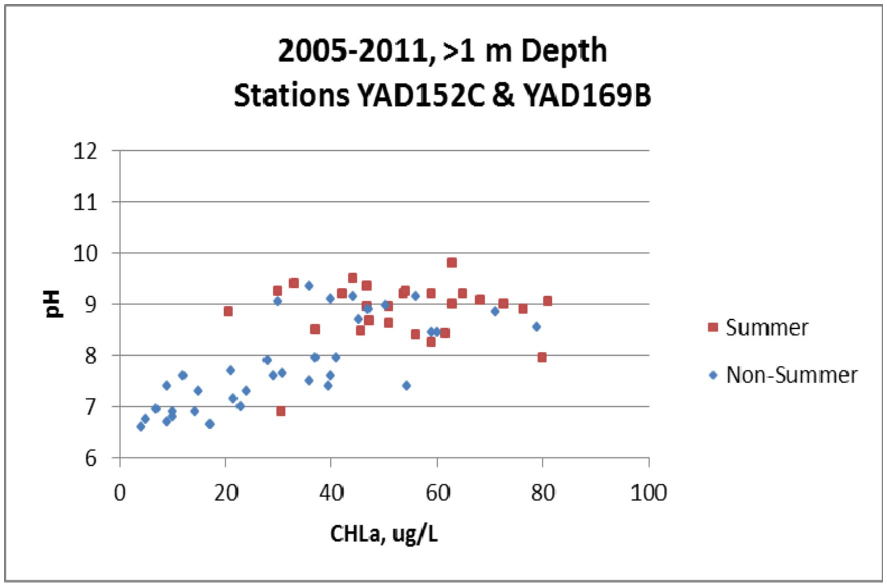
	Median Temp (°C)*	CMC Exceedance	CCC Exceedance	Total Samples
YAD152C	30.0	3 (3%)	14 (12%)	113
YAD169B	29.9	4 (4%)	13 (12%)	110

* 2016 surface continuous data

Diurnal and Rapid pH change

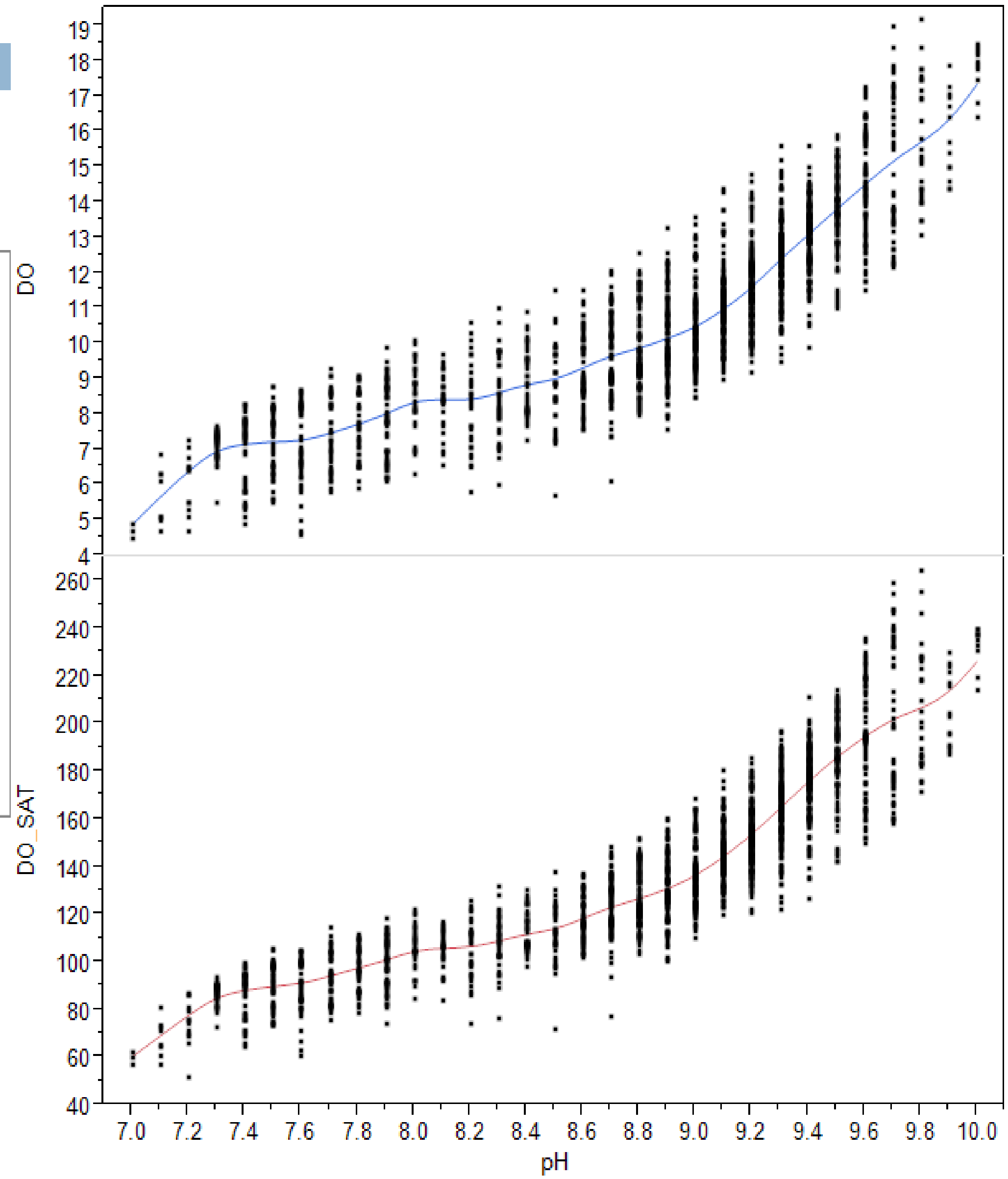
- The fish species studied tolerated rapid pH changes of 1.3 to 3.5 units when these changes occurred within the physiological-tolerance pH range. When the pH changed to a value that approached the species' normal upper tolerance level (i.e., 9.0) or exceeded their upper tolerance limit (9.5 and 10.0), mortality occurred (Witschi and Ziebell 1979).
- Unless diurnal fluctuations result in ambient pH falling below 6 or being elevated above 9, they generally have no adverse impact on aquatic life (RBI, 2004).
- Diurnal pH change in HRL (up to 2.7) while diurnal range in most lakes are within 2.0 s.u. (RBI, 2004)

High pH in HRL



(Bell, 2016)

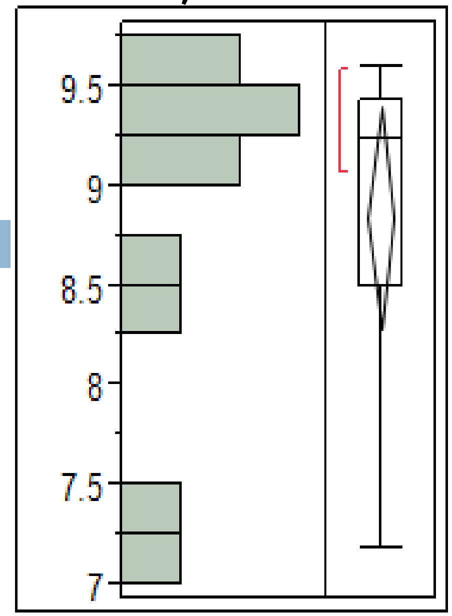
YAD152C (2016 Continuous Data)

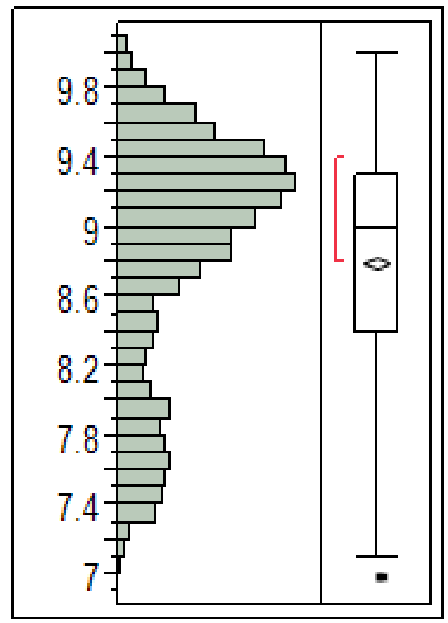


Considerations for pH criteria

- 10% or more of samples can be higher than criteria before an impairment is determined.
- Criteria is assessed with ambient monitoring data which has a much smaller sample size and often smaller range than continuous data.
- **Multi-stressor:** "*Where high pH is caused by aquatic plant photosynthesis, high water temperatures and supersaturation of dissolved gasses may also occur and may contribute to physiological effects experienced by aquatic organisms, making it difficult to correlate mortality with laboratory data on pH alone.*" *(RBI, 2004)*
- Other uses (is fishery the most sensitive use in High Rock Lake) ? Downstream?

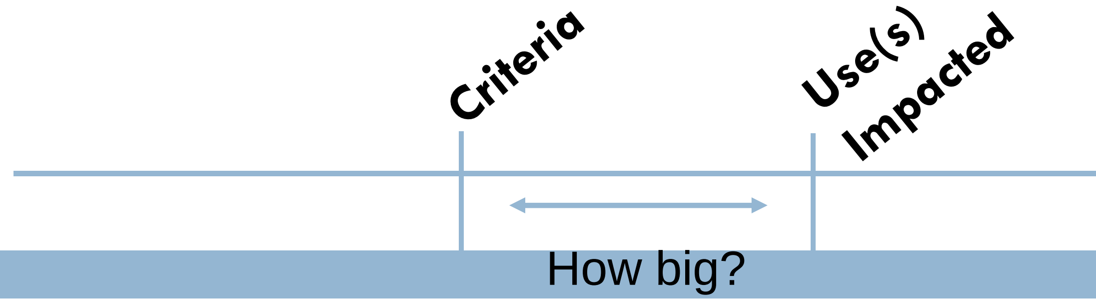
N=11, max =9.6





N=2013, max =10

9.0 - 9.5?



- Criteria exceeded = Use(s) Impacted
- Criteria attained = Use(s) protected

What are Water Quality Standards?

"Water quality standards are state regulations or rules that serve to ***protect*** *the lakes, rivers, streams, and other surface waters of the state from the deleterious effects of pollution. Surface waters are* ***protected*** *based on their designated "best uses" as defined in the surface water classifications established in Title 15A of the North Carolina Administrative Code (NCAC) subchapter 02B."*

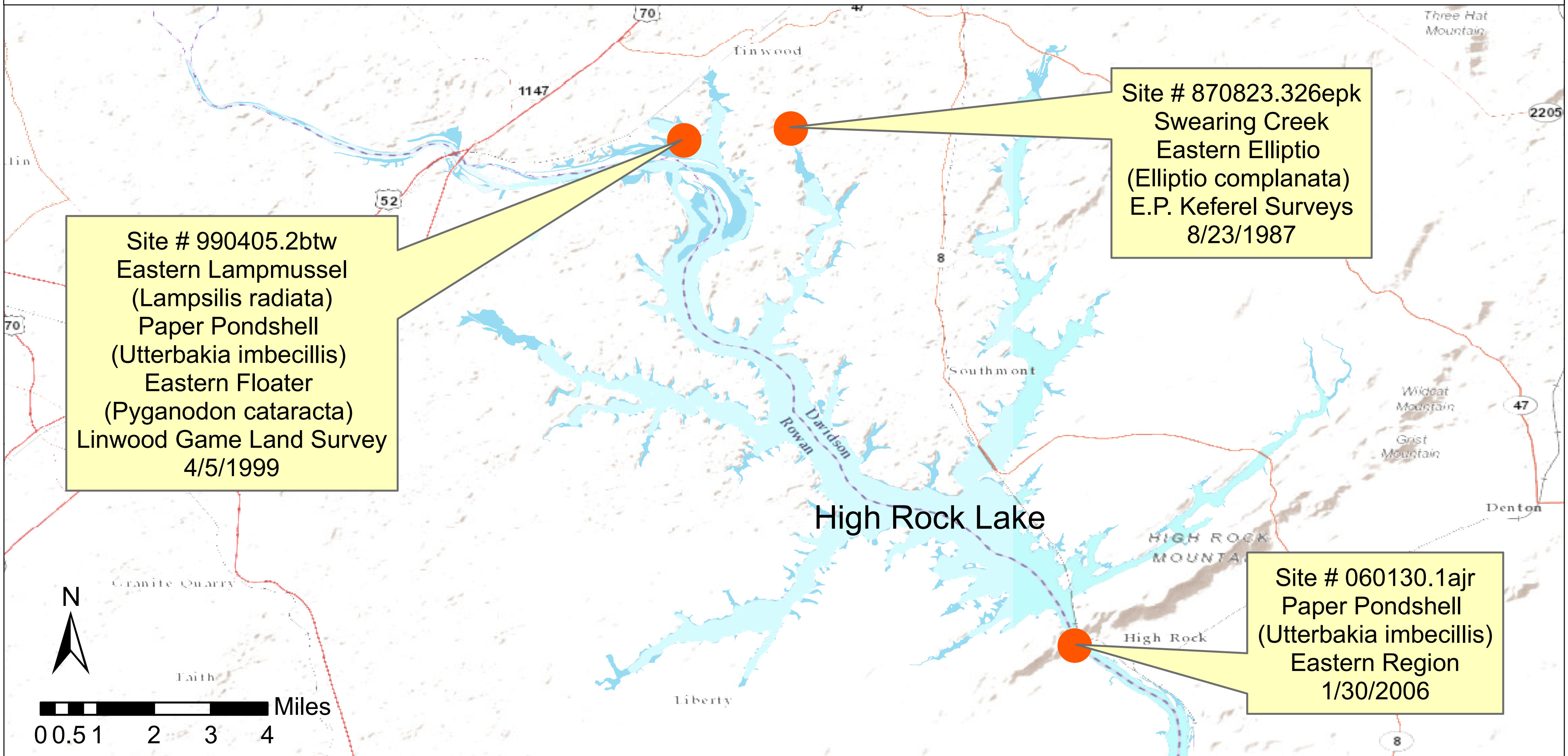
http://deq.nc.gov/about/divisions/water-resources/planning/classification-standards/surface-water-standards

Review of pH Literature for Various Fish found in High Rock Lake

Fish	Impact	Reference
Channel Catfish	Exposure to pH-values above 9 are undesirable and even short-term exposure to waters of pH 10 or above may kill fry and reduce egg matchability.	Southern Regional Aquaculture Center Publication No. 461
	Catfish fry have relatively low tolerance for increasing pH values. An increase in pH of 0.7 units will cause 10% mortality in 8-d posthatch fry, and an increase in 1.4 pH units will cause 50% mortality.	North American Journal of Aquicilture. Vol. 70, No3. Tolerance of Channel Catfish fry to Abrupt pH changes.
Largemouth Bass	Eggs will not hatch if the pH is greater than 9.6	http://www.water.ncsu.edu/watershedss/info/aqlife.html (Camp, Dresser & McKee, 1981)
	Successful reproduction required pH's between 5 and 10. Optimal pH range is 6.5-8.5, but can tolerate short term exposure to pH levels of 3.9 and 10.5	USFWS – FWS/OBS-82/10.16 Habitat Suitability Index Models: Largemouth Bass
	Largemouth bass spawning is inhibited at pH levels of 5.0 and 10.0. 50% mortality of Largemouth bass (1.3 – 5.1 cm) occurred at pH's of 3.9 and 10.5 in 24 hr tests.	USFWS – FWS/OBS-82/10.17 Habitat Suitability Index Models: White Crappie
Hybrid Striped Bass	A pH range of 7.0 to 8.5 is optimal for growth, but a much wider range is tolerated.	Southern Regional Aquaculture Center Publication No. 300
White Crappie	A pH range of 5.0-9.0 is considered safe and a range of 6.5-8.5 is essential for good production. It is assumed that tolerance levels for white crappie would be similar to those for largemouth bass.	USFWS – FWS/OBS-82/10.17 Habitat Suitability Index Models: White Crappie
Black Crappie	Optimum Habitat Requirements: 6.5-8.5	
Bluegill Sunfish	Optimum Habitat Requirements: 6.5-8.5	http://www.state.nj.us/dep/fgw/pdf/fishfact/bluegill.pdf

Prepared by NC DWR: May 16, 2017

Freshwater Mussels in High Rock Lake



Data for freshwater mussel locations obtained
from the NC Wildlife Resources Commission
Portal Access to Wildlife Systems database (P.A.W.S.)

All other data sourced from NCDEQ.

NC Division of Water Resources. May 2017.

Sites with Freshwater Mussels

DWR High Rock Lake Hydrology

Water Quality Criteria for Freshwater Fish

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2

EXTREME pH VALUE

Foreword

The preparation of the original report on extreme pH values and inland fisheries was accomplished largely by Mr R. Lloyd who prepared the basic manuscript to be reviewed and supplemented by other members of the Working Party on Water Quality Criteria for European Freshwater Fish as well as a few experts from outside the region, notably Dr P. Doudoroff, Dr W. A. Spoor, and Dr A. Coche.

Subsequently there has been an upsurge of research on the effects of low pH values on fish in connection with three main areas where acid pollution is becoming increasingly recognized as a problem. These areas are:

(a) Lakes and rivers of Central Europe, Southern Scandinavia, and the U.S.A. (the Adirondacks), where acid rainfall is reducing the pH value of the poorly buffered water draining from granite bedrock.
(b) The Appalachian mountain region of the U.S.A. where extensive strip mining for coal has led to increased acid run-off from the exposed rock.
(c) Areas in the vicinity of smelters, particularly in Canada, where again acid rainfall is responsible for reduced pH values in lakes downwind of the chimneys.

Except for the first area, the increasing acidity of the recipient water is accompanied by an increase in the concentration of heavy metals either from leaching or by atmospheric deposition, which may reach concentrations which are themselves harmful to fish populations. Even in Scandinavia, there is evidence that aluminium salts are leached out by acid rainfall. In response to these problems, a considerable number of field and laboratory studies have been carried out using refined techniques.

Much of the recent literature arising from these studies, especially those on acid rainfall, have been reviewed by Schofield (1976), Hendrey *et al.* (1976) and Leivestad *et al.* (1976); also Wright (1975) has published an annotated bibliography. In general, the extra data provided by the studies supports the guidelines laid out in the original report. Therefore, no attempt is made to review all the recent literature, and only a selection of papers which contribute new information is included.

2.1 Summary

In establishing water quality criteria for European inland fisheries, the acidity or alkalinity of the water is an important factor to be considered. There is a normal range of pH values for waters which support a good fishery. A critical review has been made, therefore, of published and unpublished data on both the direct and indirect effects of extreme pH values on fish, with an emphasis on European species; from this review it is clear that the existing data are not sufficiently comprehensive to enable definite pH criteria to be established for each important fish species and for different environmental conditions, but it is thought that sufficient is known for the following general conclusions to be reached.

There is no definite pH range within which a fishery is unharmed and outside which it is damaged, but rather there is a gradual deterioration as the pH values are further removed from the normal range. The pH range which is not directly lethal to fish is 5–9; however, the toxicity of several common pollutants is markedly affected by pH changes within this range, and increasing acidity or alkalinity may make these poisons more toxic. Also, an acid discharge may liberate sufficient carbon dioxide from bicarbonate in the water either to be directly toxic, or to cause the pH range 5–6 to become lethal.

Below a pH value of 5.0, fish mortalities may be expected, although some species may be acclimated to values as low as 3.7. However, the productivity of the aquatic ecosystem is considerably reduced below a pH value of 5.0, so that the yield from a fishery would also become less. Some acid waters may contain precipitated ferric hydroxide which may also act as a lethal factor.

Relatively little is known of the effects of alkaline discharges on a fishery and this may reflect the lesser importance of the problem. Laboratory data show that pH values between 9 and 10 may be harmful to a few species of fish, and above 10 lethal to the remainder. However, where high pH values are caused by the vigorous photosynthetic activity of aquatic plants, accompanying high temperatures and supersaturation of dissolved gases (together with other factors) may also contribute to a greater or lesser extent to fish mortality, making it difficult to correlate mortality with laboratory data on pH value alone.

There are insufficient data to enable even general criteria to be made for other aspects of this problem, such as the avoidance by fish of zones of extreme pH value, or on the growth of fish or their resistance to disease. Research needs are indicated in this chapter.

2.2 Introduction

Because the pH values of a river or lake water can be readily measured in the field with some accuracy, a considerable number of such measurements have been made and the results used in the description of the general character of the water. In an American survey of 409 locations, Ellis (1937) found that the pH range of those containing a good fish population was 6.3–9.0, with the majority of water-courses being within the range 6.7–8.6. This range of natural pH values can be extended beyond the lower limit by the direct discharge of acid effluents or, as a secondary effect, following the flushing of peat bogs by heavy rainfall, or from mine drainage. Rivers and lakes may be made more alkaline by either the direct discharge of wastes or as a secondary effect of vigorous photosynthetic activity by aquatic plants.

During the past 30 years, reviews of the effect of acids and alkalis on aquatic life have been made by Doudoroff and Katz (1950), Vivier (1954), Marchetti (1962), Jones (1964), and McKee and Woolf (1963). In establishing the water quality criteria for pH values ORSANCO (1955) pointed out that although fish had been found at pH values of 4–10, the safe range was 5–9 and for maximum productivity the pH value should lie between 6.5 and 8.5. These criteria have become widely quoted and the safe range of 5–9 has been accepted and adopted. However, it is not at all certain whether, in field surveys of acid waters, the absence of fish or the presence of a reduced population were caused by the concentration of hydrogen-ions present or by some associated factor such as a lack of chemical nutrients or presence of heavy metals, which may not have been measured. In the same way, fish kills observed in alkaline waters may have been associated with factors other than the concentration of hydroxyl-ions.

It is becoming increasingly clear that no single water quality criterion can be given for a given pollutant irrespective of other environmental variables or factors. Differences in the chemical constituents of the water, and in the sensitivity of various species of fish, may all modify the potential hazard of any given concentration of poison. The purpose of this review is to examine the existing literature on the effect of extreme pH values on fish to see what criteria can be put forward and where further research is necessary. Only the direct or indirect effects of hydrogen and hydroxyl-ions on fish have been reviewed; reference to the effects of those acids such as acetic, benzoic, chromic, or tannic acids, where the anion may be toxic, or alkalis, such as ammonia, where the undissociated molecule is toxic, have not been included. An exception to this has to be made in the case of waters where the low pH value is associated with the presence of humic acids derived from peat; in general, however, the toxicity of such solutions is not dissimilar to those in which the low pH value has been caused by addition of mineral acids and for the purposes of this review it will be assumed that humic acids have a low anionic toxicity.

Prime consideration has been given to literature dealing with species of fish found in Europe, although references to other species are given if they throw additional light on the particular item under discussion. It is thought that most, if not all, of the important published papers on this subject, where relevant to European waters, have been considered in the preparation of this review. Some references have been excluded where the data were incomplete, such as those referring to field observation of mortalities where the pH value of the water is measured some time after the fish were killed. It may also be noted that methods of pH measurement have progressed significantly within the last three decades.

2.3 Literature survey on effects of acid pH values

2.3.1 LABORATORY DATA ON DIRECT LETHAL ACTION

Variables affecting the lethal levels

Concentration of free carbon dioxide The discharge of acid wastes into a water containing bicarbonate alkalinity will result in the formation of free carbon dioxide. If the water is hard, sufficient free carbon dioxide may be liberated to be toxic to fish, even though the pH value does not fall to a level normally considered to be lethal (Doudoroff and Katz, 1950). In well aerated waters the toxic levels of free carbon dioxide are usually above 100 mg/ℓ for rainbow trout (*Salmo gairdneri*) (Alabaster, Herbert and Hemens, 1957). However, Lloyd and Jordan (1964) found that much lower levels can considerably reduce the survival times of fish within a range of low pH values which would not otherwise be lethal. In water containing 10 mg/ℓ free carbon dioxide or less, the median lethal pH value for fingerling rainbow trout was 4.5 after 15 days' exposure, but where the water contained more than 20 mg/ℓ free carbon dioxide, the median lethal pH value rose to 5.7; this increased toxicity was apparent only after a day's exposure to the test conditions. It is, therefore, difficult to interpret some published data where the level of free carbon dioxide in the test conditions is either not given or cannot be calculated.

Total hardness, sodium and chloride It has been shown that although survival times of rainbow trout in rapidly lethal pH values become shorter with a decrease in the calcium content of the water, the median lethal levels after 4 days' exposure are 4.18, 4.22, and 4.25 for water of total hardness of 320, 40, and 12 mg/ℓ as $CaCO_3$ respectively (Lloyd and Jordan, 1964). Recent data have shown that at lower concentrations of calcium the toxicity of acid pH values to fish is increased. Bua and Snekvik (1972) showed that for several species of fish, the hatching success at a given pH value was increased with an increase in calcium concentration; also, for brook trout fry (*Salvelinus fontinalis*) at pH 4.0, the percentage survival after 7 days was 0, 10 and 67 at calcium concentrations of 0.2, 1.0 and 2.0 mg Ca/ℓ respectively (C. L. Schofield, personal communication). Recent data show that the toxic effect of acid pH value is enhanced at low concentrations of sodium and chloride; these results are summarized on p. 30, para. 4 and 6.

Size and age of fish In tests using bluegill sunfish (*Lepomis macrochirus*) of different size groups, Cairns and Scheier (1958) found that the median lethal pH values for four days exposure were 3.6, 3.6, and 3.5 for fish with mean lengths of 3.9, 6.7, and 14.2 cm respectively. Lloyd and Jordan (1964) found no correlation between sensitivity and the size of rainbow trout of any one age group, but a positive correlation existed between age and sensitivity; 16-month old fish survived more than three times as long as those four months old, although the increase in resistance, in terms of lethal pH value for these two age groups, was only 0.3 of a pH unit.

There is increasing evidence that the young stages of the life cycle are more sensitive than the adult fish. The viability of roach (*Rutilus rutilus*) and perch (*Perca fluviatilis*) eggs kept in natural lake waters with a range of acidities was reduced below pH values of 5.5 and 4.7 respectively (Milbrink and Johansson, 1975) (cf. p. 26, para. 3; p. 27); these authors refer to similar work with pike (*Esox lucius*) which gave a corresponding value of 5.0 (cf. p. 27, para. 3). Kwain (1975) found that no rainbow trout eggs survived at pH values of less than 4.5, but that there was a reasonable survival above pH 5.0; yearling rainbow trout were more resistant to acid pH values than were fingerlings. Menendez (1976) found reduced viability of eggs of brook trout at pH values below 5.1, with alevin mortalities occurring below 6.0; however adult mortalities only occurred below 4.5.

Acclimation pH value Although in early literature, it was stated that fish could not withstand sudden changes in pH value, both Brown and Jewell (1926) and Wiebe (1931) found that various North American coarse fish species could withstand rapid transfer between waters of widely different pH values within the normal range. Lloyd and Jordan (1964) found no difference between the susceptibility of batches of rainbow trout acclimated to pH values of 8.40, 7.50, and 6.55 when they were exposed to lethal acid solutions. Falk and Dunson (1977) found that short-term (2–24 h) acclimation to low non-lethal pH values in the range 4–6 did not significantly increase the survival times of brook trout in acutely lethal acid solutions, thus confirming earlier work. However, Trojnar (1977) raised brook trout in waters of pH values 4.65, 4.97 and 8.07 in which survival to hatching was 76.4, 84.2 and 91.1 per cent respectively and, when the fry raised for 78 days at pH values of 4.65, 5.64 and 8.07 were exposed to a pH value of 4.0, 76 per cent of those raised in acid waters survived, whereas all those raised in alkaline waters died. This is in agreement with general Swedish experience in stocking acid lakes with non-acclimated yearling salmonids (M. Grande, personal communication). Although acclimation pH values within the normal range may, therefore, be discounted when comparing the results of toxicity tests, it would be incorrect to assume on this evidence that fish might not be able to acclimate or acclimatize slowly to a progressive decrease in the pH value of the water towards that normally considered to be lethal.

There is some evidence that strains of salmonid species may differ in their resistance to low pH values. Gjvedrem (1976) collected 77 different strains of brown trout from acid waters in Norway, bred them, and found a considerable variation between the resistance of the eggs and alevins to pH values of 4.7 and 5.2. Similar studies with inbred strains of brook trout (Robinson *et al.*, 1976) also demonstrated the possibility of inherited acid tolerance even among fish which had not been selected from acid waters. Therefore, some acclimation to low pH values may occur in the juvenile stages of fish, and there may be some selection in acid-polluted waters for strains which have an inherited resistance to these conditions.

Time of year Sexually mature brook trout were most sensitive to acid pH values in the summer (Dively *et al.*, 1977) although data obtained by Robinson *et al.* (1976) and Falk and Dunson (1977) showed the opposite to be true for immature brook trout.

Other factors There are no reliable data for the effect of low dissolved oxygen concentration on lethal acid pH values. Kwain (1975) found that rainbow trout embryos were more sensitive to sulphuric acid at 5 °C than at 10 °C, the median lethal pH values being 5.52 and 4.75 respectively.

Summary of toxicity data

Salmonids Bishai (1960) found that for young Atlantic salmon (*Salmo salar*), and for sea trout and brown trout (*Salmo trutta*), the lethal pH value was 5.8–6.2 in 2-day tests, but since the water was acidified with free carbon dioxide, it is not clear whether dissolved carbon dioxide or hydrogen-ion concentration was the main toxic agent. Dahl (1927), using water acidified with peat, found that 80 per cent of trout in the yolk sac stage died within 20 days at pH values of 4.7–5.4, and 10 per cent died in the range 5.1–5.7. Salmon in the yolk sac stage held in dilutions of peaty waters were found to have a median lethal pH value of 4.5 at 12 days; also, yearling brown trout taken from a soft acid river (pH 5.85) died within 12–14 h at a pH value of 3.3 and survived a pH value of 4.1 for 7 days (M. Grande, personal communication). Lloyd and Jordan (1964), using hydrochloric acid, found that in water of low carbon dioxide content, the median lethal pH for a 15-day exposure was 4.5 for fingerling rainbow trout. This suggests that the brown trout were more resistant than rainbow trout and, even allowing for the larger size, there is a possibility that these fish were acclimated to some extent to the acid environment. Carter (1964), using a continuous-flow apparatus and acidifying 50 per cent sea water with either hydrochloric or sulphuric acid, and without subsequent aeration, found that the median periods of survival of fingerling brown trout at pH values of 4.5 and 4.6 were 61 and 42 h respectively; however, it is possible that more than 20 mg/ℓ free carbon dioxide was present under these test conditions, and, if so, the results would agree with those of Lloyd and Jordan (1964) for rainbow trout.

M. Grande (personal communication) found that the hatching success of salmon eggs in a water acidified with sulphuric acid to give a pH value of 4.59 was 96 per cent compared with only 48 per cent at a pH value of 4.34; moreover, only 50 per cent of eyed-ova of brown trout hatched in a solution acidified with peaty water to give a pH value of 4.77. No mortalities were observed among trout eggs or alevins (species not given) exposed to water acidified with hydrochloric acid in which pH values fluctuated between 4 and 5 (Krishna, 1953) whereas mortalities occurred below a pH value of 4, but neither the duration of the experiment, nor the concentration of free carbon dioxide, are given.

Other species Using a soft water acidified with nitric acid, Carpenter (1927) found that the survival time of minnow (*Phoxinus phoxinus*) was 28 h at pH 5.0, whereas a pH value of 5.2 had no effect in three days. Under similar conditions, but using hydrochloric acid, stickleback (*Gasterosteus aculeatus*) survived for about 5½ days at pH 4.8 and lived for as long as the control fish (10 days) at pH 5.0 (Jones, 1939). However, the mortality of control fish detracts from these results, and the true lethal limit of pH value may be slightly lower.

Although roach were found to have shorter survival times than rainbow trout in solutions with pH values between 3.0 and 4.1 (Lloyd and Jordan, 1964), the 8-day median lethal pH value was 4.2 for both species. Ellis (1937) found that the 96-hour median lethal pH value for goldfish (*Carassius auratus*) in a hard water acidified with sulphuric acid was 4.0, compared with 4.3 in a soft water and 4.5 for hydrochloric acid in a hard water; it is doubtful whether the differences between these values are of any significance and furthermore the concentration of free carbon dioxide cannot be calculated. A pH value of 4.5, using sulphuric acid, was said to be detrimental to goldfish over a period of two weeks. Lewis and Peters (1956) found that 35-mm common carp (*Cyprinus carpio*) were killed within 4 h at a pH value of 4.9, but the level of dissolved oxygen was low (2.4 mg/ℓ) and the experimental technique almost certainly led to a high level of free carbon dioxide and freshly precipitated ferric hydroxide. Briuchanova (1937) reports a threshold pH value of 5.0 for carp compared with 4.0 for the crucian carp (*Carassius carassius*).

Volodin (1960) showed that the resistance of the various developmental stages of burbot (*Lota lota*) embryos to acid water varied, and successful development could take place only within a narrow pH range. The most sensitive stage was that of embryo segmentation at which a pH value of 6.0 was the critical lower level, but during subsequent development the critical level lowered to 5.0. Dyk and Lucky (1956) found that the period of motility of carp sperm was reduced in water acidified with peat to a pH value of 6.5; Elster and Mann (1950) demonstrated a decreased motility of carp sperm at pH 4.5, and lower pH values were lethal to them.

2.3.2 FIELD OBSERVATIONS

Natural populations Natural populations of brown trout have been found in waters of pH value as low as 4.5 (Menzies, 1927) and 4.9 (Campbell, 1961). Creaser (1930) reported that the brook trout was found in waters with a pH value of 4.1. Results of a survey of fish populations (mainly brown trout) in 1679 lakes in Norway have been summarized by Leivestad *et al.* (1976); few fishless lakes are found with a pH value above 5.5, although a few lakes within the range 4.5–4.7 contain good fisheries. In acid rivers, salmon are reported to be the first species to disappear, with sea-trout and brown trout showing higher resistance. In lakes, perch and eel (*Anguilla anguilla*) appear to be the most resistant species. Similar phased reductions in fish species have been found by Beamish (1974) in acid-polluted lakes in Ontario, where lake trout (*Salvelinus namaycush*) and small-mouth bass (*Micropterus dolomieui*) are the most sensitive and yellow perch (*Perca flavescens*) the most resistant, although the presence of heavy metals may contribute to these findings. From a survey of acid lakes in Sweden, Almer *et al.* (1974) concluded that the reproduction of roach was affected at pH values below 5.5; the associated calcium and conductivity data are not quoted. Surveys of acid Norwegian lakes have confirmed that where low concentrations of calcium are present, self-sustaining brown trout populations are less likely to be present than in similar acid lakes with higher calcium concentrations (Wright and Snekvik, 1978).

Vallin (1953) reports that in L. Blamisus (northern Sweden) the water has a pH value of 2.8–3.1 and an iron content of 6–7 mg Fe/ℓ in the surface waters; the flora and fauna are poor and no fish have been reported there. The water from this lake flows into L. Sladen which has a pH value of 3.7–3.8, an iron content of 0.3–1.2 mg Fe/ℓ, and a slightly more abundant flora and fauna including roach, perch and pike together with bream (*Abramis brama*) during the breeding season. However, in the spring, the pH falls to 3.5–3.7 and some local fish kills of roach have been observed. It is evident that these roach can survive at lower pH values than those found to be lethal in laboratory experiments (p. 25, para. 5) and it is possible that some long-term acclimation has taken place. In L. Sysmajarvi (Finland) Ryhanen (1961) reported that, during summer, the pH value ranged from 3.5 at the outlet of an acid stream to 4.6, with a large zone which had a pH value of 4.2–4.4. Bream, perch, roach and pike were present, but only pike were able to breed in the large zone where the pH values were between 4.2 and 4.4. No under-yearlings of bream, perch or roach were present and the older fish presumably migrated from the more alkaline streams feeding the lake. Dyk (1940) states that tench (*Tinca tinca*) can be kept for two weeks in a water of pH 3.6–3.8 without adverse effect, although these values adversely affect carp.

Although there are several field studies published on the fish population of

American waters polluted by strip-mining activities, the results are difficult to interpret since high hydrogen-ion concentrations are associated with high heavy metal content. A comprehensive survey of six lakes with pH ranges between 2.5–3.2 and 7.4–8.2 has been made by Smith and Frey (1971). The two most acid lakes (pH ranges of surface water of 2.5–3.2 and 3.0–3.4 respectively) were fishless but green sunfish (*Lepomis cyanellus*) only were caught in a lake with a surface pH range of 3.6–6.4; five species of fish were present in a lake with a surface pH range of 4.5–7.6. However, the two most acid lakes contained 2.9 and 0.8 mg Zn/ℓ and 82 and 4.7 mg Fe/ℓ respectively.

A survey of the acid lakes in the vicinity of Sudbury, Ontario, has been made by Beamish (1976); some sensitive species of fish declined in numbers as the pH fell below 6.0, but increasing acidity was accompanied by increased contamination by heavy metals, which may have contributed to the toxicity of the water. Although this was held not to be the case, the data on heavy metal toxicity used for the comparison were for other species of fish and in water of different chemical characteristics.

It is becoming clear that it is not possible to give precise limits of pH value above which a good population of a fish species would be expected. Genetically determined differences between strains of species, selection and acclimation may affect the sensitivity of the fish, and low concentrations of sodium, calcium, and chloride may decrease their ability to osmoregulate (p. 29, para. 6). Data from chronic tests carried out in the laboratory may tend to overestimate the long-term effects of acid pH values on natural fish populations, for example, through not having taken into account the influence of minor components in the water.

Fish kills Fish kills occur with two main types of acid pollution. Heavy rainfall may flush out peat bogs or strip mining areas and produce a sudden flush of acid water, or acid discharges from industrial sources may temporarily lower the pH value of the water to a lethal level. In both cases, the pH value of the water is usually measured after the fish kill has occurred and, therefore, the figures may bear little relation to the pH values which were actually responsible for the mortality.

The position is further complicated in that these acid run-offs can contain considerable quantities of dissolved ferric sulphate which may become hydrolysed at pH values above 3.0 to form ferric hydroxide (Dahl, J., 1963), a process which might be accelerated by the presence of *Thiobacillus* species (Fjerdingstad, 1958; Dahl, J., 1963). Roach which have been killed in such waters have had brown deposits on their gills (Vallin, 1953). Schiemenz (1937) states that pH values below 5.4 are dangerous to common carp and tench, but a water containing much iron is dangerous at a pH value of 5.4. Haupt (1932) found that one-year-old carp died within five days in a water of pH 4.3–4.4 containing 1.2–10.5 mg Fe/ℓ. Larsen and Olsen (1948) found that fish kills occurred in a trout hatchery when the pH value of the water was 6.2–7.0 and the water contained 1.5–20 mg Fe/ℓ; the cause of death was attributed to the precipitation of ferric hydroxide on the gills, since the pH value of the water was higher than the lethal value. In laboratory experiments, Jones (1939) found that the toxicity of solutions of ferric chloride in soft water could be wholly accounted for by the low pH value, and he concluded that ferric salts had a very low toxicity. However, only 1 mg Fe/ℓ was required to give the threshold pH value of 5.0 with the dilution water used, and it is possible that this concentration was too low to have a toxic action if precipitated. If fish are killed by ferric hydroxide in suspension, the concentrations which appear to be lethal are lower than that found for inert suspended material (Chapter 1), but the presence of the precipitate on the gills of dead fish does not necessarily indicate that this was the primary cause of death. Lewis and Peters (1956), using green sunfish and largemouth bass, found that high concentrations of precipitated ferric hydroxide (up to 27 mg Fe/ℓ) had no effect on these fish in acid waters during a two- or three-day test in which the pH values varied within the range 3.7–4.7.

Recent experiments by Decker and Menendez (1974) showed that the 96-h LC50 for iron to brook trout was 1.75 mg/ℓ at pH 7.0, 0.48 at pH 6.0 and 0.41 at pH 5.5; a constant-flow experimental technique was used which ensured that a continuous supply of freshly-precipitated iron hydroxide was brought into contact with the test fish. However, Sykora *et al.* (1975) found that the maximum level which allowed the normal survival and growth of brook trout was 7.5–12.5 mg/ℓ; in these experiments a 1½-h delay tank was introduced to ensure the oxidation of ferrous hydroxide to the ferric state. It is possible that experimental techniques which can affect the particle size and chemical nature of the suspension may exert a considerable influence on the results. Smith, Sykora and Shapiro (1973) found that fathead minnow were more sensitive, with hatchability and growth being reduced at the lowest concentration tested, 1.5 mg Fe/ℓ.

Surber (1935) found that after rainbow trout were transferred from water with a pH value of 7.1 to a soft hatchery water of pH 5.4, 35 per cent of them died. Lloyd and Jordan (1964) point out that the water was probably high in free carbon dioxide (about 40 mg/ℓ) and the observed mortalities were similar to those which would be predicted for these conditions from their laboratory data, and therefore the mortality was not caused simply by the change in pH value alone.

Vallin (1962) stated that when the R. Morrumsan in southern Sweden (pH value 6.0) was polluted by an increased discharge from a sulphite cellulose factory, the pH value fell to 4.0–4.5 and mortalities of tench, roach and bream were recorded, whereas perch and pike were more resistant. Neutralization of the effluent with lime raised the pH value to above 5.0 and further fish kills were avoided, so that it is very likely that this effect was caused either directly or indirectly by the concentration of hydrogen-ions in the water.

In the cases where the toxicity was not complicated by the presence of ferric salts, the data on fish kills are in reasonable agreement with the results of laboratory experiments.

2.3.3 MODE OF TOXIC ACTION

The toxic action of hydrogen-ions on goldfish has been ascribed by several authors to the precipitation of mucus on the gill epithelium causing death by suffocation, or by precipitation of proteins within the epithelial cells (Ellis, 1937; Westfall, 1945). Kuhn and Koecke (1956), using solutions of hydrochloric and sulphuric acids in distilled water, found that the exposure of goldfish for one hour to a pH value of 4.0 led to complete destruction of the gill epithelium, a rather rapid degeneration since this pH value has been found to be the 4-day median tolerance limit (Ellis, 1937).

Lloyd and Jordan (1964) found no evidence of gill tissue damage or precipitated mucus in rainbow trout taken at death after a 7½-h exposure to a solution of pH value 3.4. Histopathological studies by Daye and Garside (1976) on surficial tissues of brook trout exposed for up to 7 days to a range of pH values above 2.2 showed that the gills were the most sensitive, with hypertrophy of the mucus cells at the base of the filaments at pH 5.2 and accumulation of mucus on the gills of surviving fish. In acutely lethal solutions the gill epithelium became detached from the pilaster cells. The lethal pH limit for this species for a 7-day exposure period was 3.5 (Daye and Garside, 1975). Dively *et al.* (1977) also noted that mucus accumulated on the gills of brook trout in acid solutions when respiratory distress was at a maximum.

Dahl, K. (1927) found that salmon held at a pH value of 4.7–5.4 (which had killed 80 per cent of them in 17 days) recovered on transfer to clean water (pH value 6.4). Lloyd and Jordan (1964) found that rainbow trout which had overturned after 24 h in a solution of pH value 3.8, recovered on transfer to clean water at pH 8.2. It would appear, therefore, that salmonids do not suffer any permanent damage from exposure to acid solutions for periods of time too short to cause death. The pH value of the venous blood of rainbow trout killed by highly acid water (pH value 3.15) was 0.2 units lower than that of control fish in water where little free carbon dioxide was present, and 0.55 units lower in fish dying in water of pH value 4.50 and containing 50 mg/ℓ free carbon dioxide (Lloyd and Jordan, 1964). These authors were of the opinion that, in the rainbow trout, the cause of death is acidaemia.

Dively *et al.* (1977) found an increase in the P_{CO_2} of arterial blood of brook trout, and also increases in gill ventilation rate, haematocrit and activity when the fish were exposed to a pH value of 4.2; little change occurred in the blood pH value. They also found a reduction in serum sodium content, which agrees with the findings of Packer and Dunson (1970, 1972) for this species. Leivestad and Muniz (1976) found that brown trout dying in an acid Norwegian river (pH value approx. 5.2) had low plasma sodium and chloride concentrations (but normal P_{CO_2} and haematocrit) and suggest that inability to osmoregulate is a major cause of mortality. Addition of sodium chloride to snow melt water containing 1.65 mg Na/ℓ to raise the sodium content to 14.4 mg/ℓ increased the survival of brown trout alevins from 30 per cent to 83 per cent at a pH value of 4.9; similar results were obtained with salmon, sea-trout and Arctic char (*Salvelinus alpinus*) (Bua and Snekvik, 1972, quoted in Leivestad *et al.,* 1976). Packer and Dunson (1970) also found that increasing the sodium content of the water prolonged the survival of brook trout exposed to acute lethal pH values; at death the sodium concentration in the blood plasma was normal and it is likely that death was caused by other factors. In other tests at a pH value of 3.0, the blood pH value was reduced by 0.44 units within a 1½-h exposure period.

The influence of acidity on the sodium balance of brown trout has been studied using radio-tracers (P. G. McWilliams and W. T. W. Potts, personal communication). At pH levels greater than 5.0, influx and outflux are approximately equal and body sodium is maintained; below pH 5.0 the influx is increasingly reduced, and the efflux is increased. While the influx is most sensitive to acid pH values, the efflux is more responsive to the calcium concentration of the water; it is thought that lack of calcium increases cell membrane permeability. Brown

trout of different strains and different acclimation histories have different sodium exchange rates and so react differently to acid stress. Transfer of these fish to a more acid water produces an initial reduction in sodium uptake followed by an increased level within 1–2 days.

It seems that the prime mode of toxic action is still unresolved; disruption of the gill epithelium, production of mucus on gills, inability to osmoregulate and acidosis of the blood have all been found to be associated with harmful acid pH values.

There are few data on the sublethal effects of hydrogen-ion toxicity; Neess (1949) states that below a pH value of 5.5, carp develop a hypersensitivity to bacteria, and it is commonly believed in fish farming practice that a low pH value increases the susceptibility of fish to disease. It is quite possible that fish weakened by acid pH values may be more susceptible to disease, but there are no controlled laboratory experiments known to us which demonstrate this effect. In the case of field observations, it is difficult to separate pH value from other associated environmental variables, including water hardness, which may also be of importance.

The life cycles of some fish parasites are affected by pH value. *Ichthyophthirus* can reproduce normally within the pH range 7.2–8.7, and can become attached to the host fish only within the range 5.5–10.1; on the other hand, both *Costria necatrix* and *Chilodonella* require an acid environment for reproduction (Bauer, 1959). Frost (1939) found no difference between the incidence of parasites in a natural population of trout living in water at a pH value of 5.6 and those at a pH value of 7.8–8.0.

2.3.4 AVOIDANCE REACTIONS

Several authors have measured the ability of fish to detect and avoid acid pH levels under laboratory conditions. In some of these experiments it is difficult to judge whether the fish were detecting changes in hydrogen-ion concentration or differences in the level of free carbon dioxide.

Jones (1948) found that stickleback definitely avoided acid waters with pH values of up to 5.4, which was slightly above the lethal level of 4.8–5.0, and showed a very vague negative reaction to a pH value of 5.8, when the alternative choice was water with a pH value of 6.8. Ishio (1965) found that carp and goldfish avoided pH values in the range 5.5–7.0, with preference values of 8.4 and 7.2 respectively. Höglund (1961) separated the effects of free carbon dioxide from that of hydrogen-ion concentration and showed that roach tend to avoid pH values below 5.6 and salmon parr pH values below 5.3.

Höglund also found that pH values in the range 5.6–10.5 were non-directive for roach, and that the range 5.3 to at least 7.4 was non-directive for salmon parr. Brown and Jewell (1926), using populations of fish from an acid lake (pH values 6.4–6.6) and from an alkaline lake (pH values 8.4–8.6) found that, in a gradient tank where there was a choice between these two waters, the fish from the acid lake preferred the acid water and those from the alkaline lake the alkaline water. It is not established, however, that the fish were reacting to pH *per se*.

In the discussion to Ishio's paper (1965), Doudoroff questioned the ecological significance of experiments in which fish were exposed to steep concentration gradients of substances, and thought that reactions in the field, where changes in concentration occurred either over a longer distance or during a longer period of time, might well be different since progressive adaptation to the changing conditions might occur.

There are no accurate field data to suggest that fish migrate to an area of optimum hydrogen-ion concentration. The fact that various species of fish have been observed at pH values considerably lower than 5.0 indicates that laboratory tests demonstrate only the ability of fish to detect changes in the pH value of the water, and it does not necessarily follow that changes will be avoided in the field where the fish are also exposed to other, perhaps more powerful, stimuli. Although there are reports of fish moving downstream when an acid flush lowered the pH value of the water (Högbom, 1921; Parsons, 1952), there are no data on the pH value to which these were acclimated, nor on the acidity required to initiate movement.

2.3.5 EFFECT ON GROWTH

It is well known that the growth rate of fish in acid waters is usually less than that under alkaline conditions. Frost (1939) came to the conclusion that some factor other than the amount of food available was responsible for the lower growth rates of trout in the acid head waters of the R. Liffey compared with alkaline reaches further downstream. Campbell (1961) found that there was no correlation between pH value and growth rate of brown trout in nine lakes with pH values ranging from 4.9 to 8.4; however, he suggested that in some acid lakes, where there were ample spawning grounds, the slow growth rates were due to a too high population density for the available food supply. In an acid lake with no natural spawning grounds, the growth rate of trout artificially stocked at a low density was equal to that of fish in alkaline lakes. A similar observation was made by Pentelow (1944). From data supplied by the Department of Agriculture and Fisheries of Eire (E. Twomey, personal communication), the growth rate of brown trout in Irish rivers and lakes was generally higher in alkaline waters, but the best growth rate recorded was in a lake with a pH value of 5.4.

Experiments have now been carried out on the growth rate of fish kept at different pH values and fed the same ration. No difference was found in the growth rate of 18-month-old brown trout kept at pH values 6.26, 5.44 and 5.00 and fed with a daily ration of 2.9 per cent of initial body weight (Jacobsen, 1977). However, Menendez (1976) found that brook trout grew more slowly at pH values of 5.0–6.5 compared with that of the controls, although growth rates after ten weeks exposure appeared to be similar. Muniz and Leivestad (quoted in Leivestad *et al.*, 1976) also found that brook trout grew more slowly in an acid water (pH value 4.2–5.0) over a period of a year, compared with fish kept in the same water supply but neutralized with calcium carbonate to give a pH value of 5.2–6.5. It is not clear whether these apparently contradictory results are due to species difference or to the experimental techniques used. However, Leivestad *et al.* (1976) also quote Scandinavian studies which indicate that acidification of waters can initially increase growth rate of fish because of reduced competition for food.

Briuchanova (1937) found that crucian carp and common carp appeared to feed normally over the tolerated pH range, but that maximum growth was

achieved at a pH value of 5.5 for crucian carp and 6.0–6.2 for common carp. In northern Germany the optimum pH range for carp growth was 6.8–7.5; below pH 6.0 the growth rate is reduced, and this is associated with a reduced food supply (H. Mann, personal communication). Parsons (1952) reports 'amazing growth' of bluegill sunfish in a pool at a pH value of 4.5.

The relation between growth rate and hydrogen-ion concentration is unclear, and it is possible that other ions present, such as sodium, calcium, and chloride, may exert a modifying effect.

2.3.6 EFFECT ON FOOD SUPPLY

A major factor in the poor productivity of naturally acid waters is the low concentration of dissolved mineral nutrients entering the ecosystem from surface drainage. It has been estimated that in Belgium, the productivity of ponds is three times greater in the alkaline areas (pH values 7.0–7.5) than in the acid areas (pH values 5.0–5.6) but the difference between the productivity of rivers in these areas is not so great (Huet, 1941).

However, there are several references suggesting that low pH values resulting from pollution affect the recirculation of nutrients in the aquatic ecosystem by reducing the rate of decomposition of organic matter and by inhibiting nitrogen fixation (Neess, 1949; ORSANCO, 1955). Harrison (1956) found that acid pollution from gold mining in South Africa produced typical peat bog conditions, with large accumulations of undecayed plant debris, in a stream with a pH range of 3.7–4.8. It is a common fish culture practice to add calcium carbonate to ponds where the pH value of the water or pond bottom is too low.

Certain species of invertebrates can withstand very high hydrogen-ion concentrations. Lackey (1938) found *Gammarus* species in two streams with pH values of 2.2 and 3.2 respectively, mosquito larvae in a stream at pH 2.3, and caddis larvae (Trichoptera) at pH 2.4. He points out that a wide variety of different species of animals and plants does not occur in waters with pH values below 6.2 but that large numbers of some species may occur in highly acid waters. Harrison (1956) found that species common to alkaline or neutral waters were found at pH values down to 4.0, but a specialized flora and fauna developed below 5.0 to at least as low as 2.9; Robeck (1965) reports six genera of caddis from water of pH value 3.0. Since these lower pH values are well below those lethal to fish, it would seem that absence of invertebrates is unlikely to be a limiting factor for fish in acid waters. Although *Gammarus* is frequently absent from acid streams, this may be correlated with low calcium content, dissolved oxygen distribution or current speed, rather than hydrogen-ion content (Huet, 1941).

There have been no data published since 1969 which indicate that lack of food organisms may be a limiting factor for fish populations in acid waters (except where precipitated iron salts are present) although the number of species present and the productivity of the water may be reduced; recent Scandinavian data have been reviewed by Hendry *et al.* (1976). Also, Tomkiewicz and Dunson (1977) concluded that sufficient fish food organisms were present in a stream at pH 4.5–5.0 to support a limited population of fish.

2.3.7 TOXICITY OF OTHER POISONS

A change in the pH value of the water following the discharge of an acid effluent may modify the toxicity of other poisons already present, particularly those which dissociate into an ionized and an un-ionized fraction of which one is markedly toxic. A classic example is the nickelocyanide complex which is 500 times more toxic at pH 7.0 than at 8.0 (Doudoroff, 1956) because the complex dissociates into cyanide and nickel ions and a proportion of the cyanide forms the highly toxic undissociated HCN. Conversely, ammonia is almost one tenth as toxic at pH 7.0 as at 8.0 (Wuhrmann and Woker, 1948). Other substances whose toxicities are affected by the pH value of the water are cyanide alone (Wuhrmann and Woker, 1948) and sodium sulphide (Longwell and Pentelow, 1935; Bonn and Follis, 1967). Recently, Mount (1966) has shown that the toxicity of zinc to fathead minnows (*Pimephales promelas*) decreases with a fall in pH value from 8.6 to 6.0 (the 4-day median lethal concentration (LC50) being 6.4 and 21.8 mg Zn/ℓ respectively in water of total hardness of 100 mg/ℓ as $CaCO_3$) but there was no further decrease in toxicity when the pH value was reduced further to 5.0. There are other poisons, the toxicities of which are affected by pH changes, but these cannot be considered here.

Poisons which are known to be not affected by changes in pH value of the water within the normal range include ABS (Marchetti, 1966) and gas-liquor phenols (Herbert, 1962).

The discharge of acids to water with a high bicarbonate alkalinity will liberate free carbon dioxide in concentrations high enough to be directly lethal to fish, even though the pH value of the water does not fall to a level considered to be harmful (Doudoroff and Katz, 1950). Sublethal levels of free carbon dioxide may increase the sensitivity of fish to low levels of dissolved oxygen (Alabaster, Herbert and Hemens, 1957) unless given prior acclimation (Doudoroff and Warren, 1965). It is not known whether sudden exposure to high but sublethal levels of free carbon dioxide increases the sensitivity of fish to other dissolved poisons.

Although there is reasonable agreement between laboratory data and field observations of fish kills, there is good evidence that some fish populations can tolerate pH levels lower than those which would be considered lethal from these studies. Moreover, this also indicates that such acid conditions are not necessarily actively avoided. In general, coarse fish appear to be at least as resistant as salmonid species to acid pollution and some species may be more resistant. However, a chronic acid discharge which lowers the pH value of a river or lake to below 5.0 will reduce the primary productivity and therefore the food supply, so that if fish are still present, either their numbers or their growth rate will be reduced. A more detailed summary of the data is given at the end of this review in *Table 2.1*.

There is considerable scope for further research in this field. There is conflicting evidence on the effect of iron salts on fish in acid waters; the presence of soluble iron salts does not appear to harm fish but the precipitated hydroxide may be more toxic than would be expected from studies on other suspended solids. There is little information on the relation between pH value and the resistance of fish to disease, or on their growth rate, or food/body-weight conversion ratios.

2.4 Literature survey on effects on alkaline pH values

2.4.1 LABORATORY DATA ON DIRECT LETHAL ACTION

Variables affecting the lethal levels

Effect of size Using sodium hydroxide, Cairns and Scheier (1958) found that the 4-day median tolerance limits of pH value for bluegill sunfish were 10.5, 10.5 and 9.9 for fish with mean lengths of 39, 61, and 142 mm respectively, showing that susceptibility increases with size. Bandt (1936), however, states that the median tolerance levels of alkaline pH values are 0.2 units higher for large fish and Mantelman (1967) has shown that the resistance of *Coregonus peled* and common carp increases with age.

Acclimation pH value Jordan and Lloyd (1964) showed that although the acclimation pH value had no effect on the resistance of rainbow trout to pH values high enough to kill in a few hours, the 1-day median lethal values were 9.86, 9.91 and 10.13 for batches acclimated to pH values of 6.55, 7.50 and 8.40 respectively, and that this difference, although small, was statistically significant.

Dissolved oxygen concentration (DO) There are no accurate data on the effect of high pH values on fish at different levels of dissolved oxygen, although this might be important since alkaline conditions following from intense photosynthetic activity of aquatic plants are normally accompanied by high levels of dissolved oxygen. Wiebe (1931) found that bluegill sunfish showed distress, and some died, in water of pH value 9.6 and a DO of 5 mg/ℓ, but were unaffected by a pH value of 9.5 and a DO of 10 mg/ℓ. If the toxicity of an alkaline solution is related to the pH value at the gill surface and not to the pH value of the bulk of the solution, then an increase in DO in the water may lead to an increased concentration of excreted free carbon dioxide at the gill surface (Lloyd, 1961) and therefore to a lower pH value there. The extent to which the pH value at the gill surface is changed would also depend in part on the buffering capacity of the water; none of these factors has been the subject of controlled experimentation.

Other factors There are no data for the effect of temperature, or water hardness, on the toxicity of hydroxyl-ion concentrations.

Summary of toxicity data

Salmonids In tests using concrete blocks as a source of alkali, Bandt (1936) found that the minimum lethal pH value for trout was 9.2. This is slightly lower than the values found for rainbow trout by Jordan and Lloyd (1964) who found that the median lethal pH value for a 15-day exposure was 9.5, but the difference between these results may be that between the minimum values, which presumably killed no fish, and the median values which killed 50 per cent of a batch. Sprague (1964) reports that only 5 per cent of a batch of 40 yearling Atlantic salmon died within six weeks when kept in a water supply carried through asbestos-cement pipelines and having a pH value of 9.5. Carter (1964) acclimated brown trout to full strength sea water and exposed them to alkaline saline solution; a pH value of 9.6 gave a median lethal period of 20 h, whereas fish at a pH value of 9.5 survived for more than four days. Survival times of these fish in lethal alkaline solutions were considerably less than that for rainbow trout in fresh water at similar pH values (Jordan and Lloyd, 1964). Rosseland (1956) reports that an alkaline effluent was toxic to young salmon and brown trout, a pH value of 9.7 being lethal within a day, whereas none died during $1\frac{1}{2}$ days at pH 9.0. Long-term experiments with young stages of *Coregonus peled* showed that the highest safe pH value was 8.6-9.2 (Mantelman, 1967).

Krishna (1953) found that with eggs and alevins of trout, mortalities occurred above a pH value of 9.0, but the period of exposure is not given.

Other species Bandt (1936), in experiments similar to that on p. 35, para. 5, found that the minimum lethal value for perch was 9.2, roach 10.4, carp 10.8, pike 10.7, and tench 10.8. Jordan and Lloyd (1964) found that the median lethal pH value for a 10-day exposure was 10.15 for roach, slightly less than that given by Bandt, and Mantelman (1967) gives the highest safe concentration for common carp as 9.2-9.6. Sanborn (1945), using sodium hydroxide, found that goldfish died within 3-20 h at a pH value of 10.9, and lived for more than seven days at a value of 10.4. Experiments using sodium carbonate and calcium hydroxide gave similar results, so that these cations appear to have no effect on the toxicity of the hydroxyl-ions. Rosseland (1956) found that minnow were slightly more sensitive than brown trout to the alkaline effluent described on p. 35, para. 5.

The various developmental stages of burbot eggs showed different sensitivities to alkaline waters, the most sensitive stage being that of embryo segmentation, when a pH value of 8.0 killed half the eggs (Volodin, 1960). Resistance increased after this stage, but even at pH 9.0 hatching was delayed. Sperm of common carp had a lower period of motility when the pH value of the water was raised to 8.2-9.5 (Dyk and Lucky, 1956), and pH values above 9.0 were found to be lethal (Elster and Mann, 1950).

2.4.2 FIELD OBSERVATIONS

Fish kills In lakes and rivers, where there exists a combination of high plant density (including algae), high temperature, and strong sunlight, vigorous photosynthetic activity can raise the pH value of the water to high levels for short periods. This is usually followed by lower pH values during the night with minimum values just before dawn. Such a diurnal variation was measured in the R. Tweed in 1956 (Jordan and Lloyd, 1964). These authors point out that the harmful effect of these conditions is determined in part by the length of time for which these high pH values are maintained, and in part by the maximum pH value reached. Other factors include temperature and the high level of dissolved oxygen accompanying the high pH value (p. 35, para. 3). Furthermore, other possible lethal factors under these conditions are an increase in the dissolved gas content of the water to values greater than atmospheric pressure, which may give rise to 'gas bubble' disease (Doudoroff, 1957), and also certain algal blooms present may produce toxic by-products.

Since the pH values can show a considerable diurnal fluctuation under these natural conditions, it would be necessary to make frequent analyses of the water in order to correlate pH value with fish kills. Eicher (1946) reports that some rainbow trout in a lake were killed when the pH value rose above 10.2, but that fish in a river tolerated a rise to 9.4. For the reasons given above, this observation cannot be correlated directly with laboratory data but it is not at variance with them. Dahl, J. (1957) records a fish kill in L. Lyngby (Denmark) where the pH value rose to 10.3-10.6. In deep lakes, the high pH values may be limited to surface waters only, and fish may be able to survive in the deeper portions where pH values are lower. Mortalities among pike-perch (*Stizostedion lucioperca*) occurred at Ronninge (south of Stockholm) in 1966 when the pH value of the water rose to 8.4-9.5 (T. Hasselrot, personal communication); it is thought, however, that toxins from the accompanying algal bloom may have contributed to the death of the fish.

Natural populations Although Neess (1949), referring to carp ponds at Wielenbach, southern Bavaria, states that a high fish production is maintained there even though the pH value of the water reaches 12, this is an unusually high alkalinity if produced by photosynthetic activity and might be regarded as inaccurate. However, pH values of about 10.0 often occur there during the summer (H. Reichenbach-Klinke, personal communication).

An alkaline discharge to the Austrian Millstätter See raised the pH value of the water to 9.3 over an 8-year period (Findenegg, 1962) but primary productivity appeared to be unaffected although some qualitative changes in the composition of the plankton and fish population were observed.

2.4.3 MODE OF TOXIC ACTION

According to several authors (Kuhn and Koeche, 1956; Bandt, 1936; Schäperclaus, 1956) a toxic action of hydroxyl-ions is to destroy the gill and skin epithelium. Daye and Garside (1976) found that the gills of brook trout were the most sensitive of the surficial tissues to high pH values within a 7-day exposure period, with a threshold pH value of injury of 9.0; mucus cells at the base of the gill filaments became hypertrophic and separation of the epithelium from the pilaster cells occurred at high pH values. Eicher (1946) reported that trout found dying at a pH value of 10.2 (p. 37, para. 2) had frayed dorsal and caudal fins and were blind, and a similar condition was reported by Ivasik (1965) for carp in a heavily weeded pond where the pH value rose to above 9.0, but it is not clear whether these symptoms were a direct result of the high pH value. Damage to the eye lens and cornea of brook trout occurred above a pH value of 9.5 (Daye and Garside, 1976); the lethal pH limit for this species within a 7-day exposure period was 9.8.

2.4.4 AVOIDANCE REACTIONS

Jones (1948) showed that stickleback avoided solutions of sodium hydroxide with a pH value above 11.0 but the range 7–11 produced no avoidance response from fish given the choice between tap water at a pH value of 6.8 and the experimental solutions. Ishio's (1965) results suggest that common carp and goldfish avoid lower levels, the median avoidance pH for these species being 9.30 and 8.64 respectively. However, the comments made by Doudoroff to Ishio's paper mentioned on p. 31, para. 7 are pertinent here also.

2.4.5 EFFECT ON GROWTH

There are no data known to us on the effect of high pH values on the growth rate of fish.

2.4.6 EFFECT ON FOOD SUPPLY

There are no data on the effect of high pH values on food supply of fish apart from the observations by Findenegg (1962) on the Millstätter See (p. 37, para. 4).

2.4.7 TOXICITY OF OTHER POISONS

The section on the effect of low pH values on the toxicity of other poisons is applicable here, in respect of those poisons, such as cyanide and ammonia, whose toxicity is affected by the degree of ionization. This is particularly important in the case of ammonia, the toxicity of which increases with an increase in pH value. Although zinc in solution may be precipitated as the basic carbonate at alkaline pH values, the precipitate can be highly toxic to fish if it is kept in suspension (Lloyd, 1960; Herbert and Wakeford, 1964; Mount, 1966). It is not known whether other heavy metals are toxic when precipitated as basic carbonates.

In summary, it appears that chronic exposure to pH values above 10.0 is harmful to all species studied, while salmonid and some other species are harmed at values above 9.0, and that tentative water quality criteria can be based on the existing data. However, it is difficult to correlate laboratory data with field observations on the effect of alkalinity caused by photosynthetic activity because of the possible additional effect of concomitant high dissolved oxygen levels, and the possibility that the water was also supersaturated with dissolved gases or contained toxic algal by-products, or subsequently became deoxygenated during the hours of darkness. If this problem is sufficiently serious to warrant further research, more attention will have to be given to measuring these factors in the field and making the appropriate laboratory experiments.

Table 2.1 SUMMARY OF THE EFFECTS OF pH VALUES ON FISH

Range	*Effect*
3.0–3.5	Unlikely that any fish can survive for more than a few hours in this range although some plants and invertebrates can be found at pH values lower than this.
3.5–4.0	This range is lethal to salmonids. There is evidence that roach, tench, perch and pike can survive in this range, presumably after a period of acclimation to slightly higher, non-lethal levels, but the lower end of this range may still be lethal for roach.
4.0–4.5	Likely to be harmful to salmonids, tench, bream, roach, goldfish and common carp which have not previously been acclimated to low pH values, although the resistance to this pH range increases with the size and age of the fish. Fish can become acclimated to these levels, but of perch, bream, roach and pike, only the last named may be able to breed.
4.5–5.0	Likely to be harmful to the eggs and fry of salmonids, and to adults particularly in soft water containing low concentrations of calcium, sodium and chloride. Can be harmful to common carp.
5.0–6.0	Unlikely to be harmful to any species unless either the concentration of free carbon dioxide is greater than 20 mg/ℓ, or the water contains iron salts which are freshly precipitated as ferric hydroxide, the precise toxicity of which is not known. The lower end of this range may be harmful to non-acclimated salmonids if the calcium, sodium and chloride concentrations, or the temperature of the water are low, and may be detrimental to roach reproduction.
6.0–6.5	Unlikely to be harmful to fish unless free carbon dioxide is present in excess of 100 mg/ℓ.
6.5–9.0	Harmless to fish, although the toxicity of other poisons may be affected by changes within this range.
9.0–9.5	Likely to be harmful to salmonids and perch if present for a considerable length of time.
9.5–10.0	Lethal to salmonids over a prolonged period of time, but can be withstood for short periods. May be harmful to developmental stages of some species.
10.0–10.5	Can be withstood by roach and salmonids for short periods but lethal over a prolonged period.
10.5–11.0	Rapidly lethal to salmonids. Prolonged exposure to the upper limit of this range is lethal to carp, tench, goldfish and pike.
11.0–11.5	Rapidly lethal to all species of fish.

Reference is made to different species on the basis of information known to us; the absence of a reference indicates only that insufficient data exist.

2.5 Conclusions

2.5.1 TENTATIVE WATER QUALITY CRITERIA

It is becoming increasingly clear that, for many pollutants, no single level or concentration can be put forward as the dividing line between safe and harmful which is universally applicable for all aquatic situations. Effects of the environment on both the toxicity of the pollutant and the susceptibility of the fish, as well as differences between the susceptibility of the various species of fish and the presence of other pollutants, have to be taken into account when attempting to formulate criteria for safe levels.

Although the existing data on the effect of extreme pH values on fish are neither as comprehensive, nor as accurate, as would be ideally required for the formulation of definite criteria, the information presented in this review does, nevertheless, allow general predictions to be made of the effects of acid or alkaline discharges on a fishery. Such effects are summarized in *Table 2.1*; it should be emphasised that these may have to be revised in the light of future experience and research. Data on avoidance reactions have not been taken into account because of the difficulty in correlating laboratory data with field conditions; also, there is no information on a direct effect of pH value on growth. For the alkaline range, the effect of high levels of dissolved oxygen on the susceptibility of fish has not been considered since there are no relevant quantitative data. There is some evidence that the resistance of fish to extreme pH values increases with age.

2.5.2 SCOPE FOR FURTHER RESEARCH

In order to define water quality criteria more fully, further laboratory research is required on the toxicity to fish of acid waters containing iron salts, and on the growth rates of fish in acid waters. Field studies on the productivity of acid polluted streams are also required. There may be a need for laboratory studies on the effect of high dissolved oxygen levels on the resistance of fish to alkaline pH values, together with those other associated factors which may occur in the field.

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Technical Memorandum

pH Requirements of Freshwater Aquatic Life

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May 2004

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The pH of surface waters is important to aquatic life because pH affects the ability of fish and other aquatic organisms to regulate basic life-sustaining processes, primarily the exchanges of respiratory gasses and salts with the water in which they live. Failure to adequately regulate these processes can result in numerous sub-lethal effects (e.g., diminished growth rates) and even mortality in cases when ambient pH exceeds the range physiologically tolerated by aquatic organisms.

DIRECT EFFECTS OF PH ON AQUATIC LIFE

The effects of pH on fish and other freshwater aquatic life have been reviewed in detail (e.g., Doudoroff and Katz 1950; McKee and Wolf 1963; EIFAC 1969; Katz 1969; NAS 1972; AFS 1979; Alabaster and Lloyd 1980). The pH of water affects the normal physiological functions of aquatic organisms, including the exchange of ions with the water and respiration. Such important physiological processes operate normally in most aquatic biota under a relatively wide pH range (e.g., 6-9 pH units). There is no definitive pH range within which all freshwater aquatic life is unharmed and outside which adverse impacts occur. Rather, there is a gradual “deterioration” in acceptability as pH values become further removed from the normal range (EIFAC 1969; AFS 1979; Alabaster and Lloyd 1980). The acceptable range of pH to aquatic life, particularly fish, depends on numerous other factors, including prior pH acclimatization, water temperature, dissolved oxygen concentration, and the concentrations and ratios of various cations and anions (McKee and Wolf 1963).

Alabaster and Lloyd (1980) identified the pH range that is not directly lethal to freshwater fish as 5.0-9.0. With few exceptions, pH values between 6.5 and 9.0 are satisfactory, on a long-term basis, for fish and other freshwater aquatic life. The pH of most inland fresh waters containing fish ranges from about 6 to 9 (Ellis 1937), with most waters, particularly those with healthy, diverse, and productive fish and macroinvertebrates communities having a pH between approximately 6.5 and 8.5 units (Ellis 1937; McKee and Wolf 1963; NTAC1968; NAS 1972). In establishing water quality criteria for pH, ORVWSC (1955) stated that, although fish had been found at pH values from 4-10, the safe range was 5-9 and for maximum productivity the pH should be maintained between 6.5 and 8.5. Some aquatic organisms (e.g., certain species of algae) have been found to live at pH 2 and lower, and others at pH 10 and higher (NAS 1972). However, there are few such organisms, and their extreme tolerances are not reflective of the pH tolerated by the majority of organisms occurring in a given aquatic ecosystem.

Limiting pH Values			
Minimum	*Maximum*	*Remarks*	*References*
3.3	10.7	Trout survived without adverse effects	1467
3.6	---	Tench survived two weeks but carp died	1302
3.6	10.5	96-hour TL_m range for bluegill sunfish	2934
3.8	10.0	Fish eggs could be hatched, but abnormal young were produced of extreme pH's	1468
4.0	10.0	The most resistant fish can tolerate such extreme pH values indefinitely after acclimatization	1460
4.0	10.1	Limits for the most resistant species	361
4.0	10.4	Limits for bluegill sunfish with HCl and NaOH	3606
4.1	8.5	Range tolerated by speckled trout in nature	1467
4.1	9.5	Range tolerated by trout	862
4.3	---	Carp died in 5 days	1303
4.4	8.7	Toxic limits for trout	3609
4.5	8–9	Trout eggs and larvae develop normally	1636
4.6	9.5	Toxic limits for perch	3609
4.6	---	Tench died in two days	2977
4.8	---	Lower limit for trout	1304
4.8	---	Illness and early death for carp	2977
4.8	9.2	Toxic limits for fish	1305
5.0	---	Toxic limit for sticklebacks	2941
5.0	9.0	Tolerable range for most fish	361, 2409, 3609
---	8.7	Upper limit for good fishing water	717
5.4	---	Lower limit for carp and tench	1306
---	9.2	Upper limit for trout and perch	2977
5.5	---	Lower limit for general fish protection	1307
5.4	11.4	Fish avoided waters beyond these limits	1046
6.0	11.0	Fish did not avoid waters in this range	1046
6.0	7.2	Optimum range for fish eggs	1468
6.5	8.4	Range tolerated by most fresh-water fish	1460
For other aquatic organisms, ranges were reported as follows:			
1.0	---	Mosquito larvae destroyed at this value	1308
2.5	---	Tolerated by *Chlamydomonas*, *Fragilaria*, *Asterionella*, *Aphanizomenon*	2168
3.3	4.7	Mosquito larvae thrived in this range	1309
4.0	---	Toxic for *Paramecium*, *Volvox*, *Asplanchna*	2977
7.5	8.4	Good range for plankton production	1021
---	8.5	Algae are destroyed above this value	

Source: McKee and Wolf (1963).

A Summary of Some Effects of pH on Freshwater Fish and Other Aquatic Organisms

pH	Known effects
11.5–12.0	Some caddis flies (Trichoptera) survive but emergence reduced.
11.0–11.5	Rapidly lethal to all species of fish.
10.5–11.0	Rapidly lethal to salmonids. The upper limit is lethal to carp (Cyprinus carpio), goldfish (Carassius auratus), and pike. Lethal to some stoneflies (Plecoptera) and dragonflies (Odonata). Caddis fly emergence reduced.
10.0–10.5	Withstood by salmonids for short periods but eventually lethal. Exceeds tolerance of bluegills (Lepomis macrochirus) and probably goldfish. Some typical stoneflies and mayflies (Ephemera) survive with reduced emergence.
9.5–10.0	Lethal to salmonids over a prolonged period of time and no viable fishery for coldwater species. Reduces populations of warmwater fish and may be harmful to development stages. Causes reduced emergence of some stoneflies.
9.0–9.5	Likely to be harmful to salmonids and perch (Perca) if present for a considerable length of time and no viable fishery for coldwater species. Reduced populations of warmwater fish. Carp avoid these levels.
8.5–9.0	Approaches tolerance limit of some salmonids, whitefish (Coregonus), catfish (Ictaluridae), and perch. Avoided by goldfish. No apparent effects on invertebrates.
8.0–8.5	Motility of carp sperm reduced. Partial mortality of burbot (Lota lota) eggs.
7.0–8.0	Full fish production. No known harmful effects on adult or immature fish, but 7.0 is near low limit for Gammarus reproduction and perhaps for some other crustaceans.
6.5–7.0	Not lethal to fish unless heavy metals or cyanides that are more toxic at low pH are present. Generally full fish production, but for fathead minnow (Pimephales promelas), frequency of spawning and number of eggs are somewhat reduced. Invertebrates except crustaceans relatively normal, including common occurrence of mollusks. Microorganisms, algae, and higher plants essentially normal.
6.0–6.5	Unlikely to be toxic to fish unless free carbon dioxide is present in excess of 100 ppm. Good aquatic populations with varied species can exist with some exceptions. Reproduction of Gammarus and Daphnia prevented, perhaps other crustaceans. Aquatic plants and microorganisms relatively normal except fungi frequent.
5.5–6.0	Eastern brook trout (Salvelinus fontinalis) survive at over pH 5.5. Rainbow trout (Salmo gairdneri) do not occur. In natural situations, small populations of relatively few species of fish can be found. Growth rate of carp reduced. Spawning of fathead minnow significantly reduced. Mollusks rare.
5.0–5.5	Very restricted fish populations but not lethal to any fish species unless CO_2 is high (over 25 ppm), or water contains iron salts. May be lethal to eggs and larvae of sensitive fish species. Prevents spawning of fathead minnow. Benthic invertebrates moderately diverse, with certain black flies (Simuliidae), mayflies (Ephemerella), stoneflies, and midges (Chironomidae) present in numbers. Lethal to other invertebrates such as the mayfly. Bacterial species diversity decreased; yeasts and sulfur and iron bacteria (Thiobacillus-Ferrobacillus) common. Algae reasonably diverse and higher plants will grow.
4.5–5.0	No viable fishery can be maintained. Likely to be lethal to eggs and fry of salmonids. A salmonid population could not reproduce. Harmful, but not necessarily lethal to carp. Adult brown trout (Salmo trutta) can survive in peat waters. Benthic fauna restricted, mayflies reduced. Lethal to several typical stoneflies. Inhibits emergence of certain caddis fly, stonefly, and midge larvae. Diatoms are dominant algae.
4.0–4.5	Fish populations limited; only a few species survive. Perch, some coarse fish, and pike can acclimate to this pH, but only pike reproduce. Lethal to fathead minnow. Some caddis flies and dragonflies found in such habitats; certain midges dominant. Flora restricted.
3.5–4.0	Lethal to salmonids and bluegills. Limit of tolerance of pumkinseed (Lepomis gibbosus), perch, pike, and some coarse fish. All flora and fauna severely restricted in number of species. Cattail (Typha) is only common higher plant.
3.0–3.5	Unlikely that any fish can survive for more than a few hours. A few kinds of invertebrates such as certain midges and alderflies, and a few species of algae may be found at this pH range and lower

Source: USEPA (1973). Table incorporates information presented by Alabaster and Lloyd (1980).

In response to the acid rain problems occurring in the eastern United States and Canada, the physiological effects of acid stress on fish and other aquatic life have been well documented (e.g., see Alabaster and Lloyd 1980; AFS 1982). A number of researchers have proposed that the toxic action of hydrogen ions on fish under acidic conditions involves production of mucus on the gill epithelium, which interferes with the exchange of respiratory gasses and ions across the gill; precipitation of proteins within the epithelial cells; and/or acidosis of the blood (also affecting oxygen uptake) (Ellis 1937; Westfall 1945; Leivestad, in AFS 1982; Boyd 1990). Hence, respiratory distress and osmotic imbalance are the primary physiological symptoms of acid stress in fish. Less research has been conducted on the effects of acid stress on macroinvertebrates. However, those species that exchange respiratory gasses and regulate ions through their gills (e.g., mayflies and stoneflies) and/or species affected by blood acid-base balance may experience effects similar to fish.

Below a pH of 5.0, mortality occurs in some life stages of certain fish species, although some fishes can be acclimated to pH levels below 4.0. Certain species of macroinvertebrates can tolerate very low pH values. Lackey (1938) found Gammarus spp. in two streams with pH values of 2.2 and 3.2, mosquito larvae in a stream at pH 2.4, and caddis fly larvae (Trichoptera) at pH 2.4. Nevertheless, the primary productivity of freshwater aquatic ecosystems is reduced considerably below pH 5.0, which, in turn, reduces the food supply for higher organisms. Hence, fish that remain present would likely experience reduced numbers and/or growth rates (Alabaster and Lloyd 1980).

The physiological effects on aquatic life induced by high pH (>9) have been studied less than those at low pH. This is likely because high pH waters are less common (Doudoroff and Katz 1950; Alabaster and Lloyd 1980). Several researchers concluded that the toxic mode of action of hydroxyl ions (i.e., high pH values) is hypertrophy of mucus cells at the base of the gill filaments and destruction of gill and skin epithelium, with effects on the eye lens and cornea (Alabaster and Lloyd 1980; Boyd 1990).

Studies have shown that pH values of between 9 and 10 can result in partial mortality for bluegill sunfish (Lepomis macrochirus), rainbow trout (Oncorhynchus mykiss), brown trout (Salmo trutta), salmon, and perch. The majority of freshwater fishes and macroinvertebrates experience harmful effects (lethal or sublethal) at one or more life stages at pH values above 10 (Weibe 1931; AFS 1979; Alabaster and Lloyd 1980). Where high pH is caused by aquatic plant photosynthesis, high water temperatures and supersaturation of dissolved gasses may also occur and may contribute to physiological effects experienced by aquatic organisms, making it difficult to correlate mortality with laboratory data on pH alone. Based on their review of the literature, Alabaster and Lloyd (1980) stated that chronic exposure to pH values above 10 was harmful to all species studied, while salmonids and some other species were harmed at pH values above 9.

The USEPA has concluded that a pH range of 6.5 to 9.0 provides adequate protection for the life of freshwater fish and bottom-dwelling macroinvertebrates. Outside this range, fish suffer adverse physiological effects that increase in severity as the degree of deviation increases until lethal levels are reached (USEPA 1976, 1986).

EFFECTS OF DIURNAL FLUCTUATIONS AND RAPID PH CHANGES ON AQUATIC LIFE

The pH of lakes and streams often changes during the day in response to photosynthetic activity. In ponds having poorly buffered (low alkalinity) waters, the pH may fall to approximately 7 in the early morning and increase to 9 or more in the afternoon (Boyd 1990). Good fish production usually can be maintained in spite of these daily fluctuations. In most lakes and ponds, diurnal pH fluctuations during the summer, when photosynthetic activity peaks, are generally less than 2 pH units, while in streams are generally less (e.g., 0.5-1.0 units). Unless diurnal fluctuations result in ambient pH falling below 6 or being elevated above 9, they generally have no adverse impact on aquatic life. This is supported by the study findings discussed below.

Although it was once believed that fish could not tolerate sudden pH changes, studies conducted by Brown and Jewell (1926) and Wiebe (1931) showed that certain fish species could tolerate such rapid changes, within the normal pH range. Brown and Jewell (1926) observed catfish and perch living in a bog lake having a pH of 4.4-6.4, and also in a nearby glacial lake having a pH of 8.2-8.7. These researchers demonstrated that the fish from both lakes survived transfer from one lake to another.

Wiebe (1931) reported that sunfish (Lepomis spp.) and goldfish (Carassius auratus) survived rapid changes from pH 7.2 to 9.6 (2.4 units); largemouth bass (Micropterus salmoides) from pH 6.1 to 9.6 (3.5 units); and smallmouth bass (Micropterus dolomieui) from pH 6.6 to 9.3 (2.7 units). Witschi and Ziebell (1979) transferred rainbow trout from water of pH 7.2 to waters of pH 8.5, 9.0, 9.5, and 10.0. Survival after 48 hours was 100% for fish transferred to pH 7.2 and 8.5, 88% for those transferred to pH 9.0, 68% for pH 9.5, with complete mortality occurring for fish transferred to pH 10.0. This study clearly demonstrated that rainbow trout could handle rapid pH changes of 1.3 units (from 7.2 to 8.5) without experiencing acute mortality. The acute mortality that occurred when transferred to pH 9.0, 9.5, and 10.0 water was more likely due to being transferred to a pH outside the acceptable range for the species than due to the pH change itself (Modin, pers. comm., 1998). If no acute mortality occurs, no chronic effects would be expected because of physiological acclimation to the new pH, which occurs within a short period of time (i.e., hours to days).

This work demonstrated that the fish species studied tolerated rapid pH changes of 1.3 to 3.5 units when these changes occurred within the physiological-tolerance pH range. When the pH changed to a value that approached the species' normal upper tolerance level (i.e., 9.0) or exceeded their upper tolerance limit (9.5 and 10.0), mortality occurred (Witschi and Ziebell 1979). Based on findings from these studies and personal communications with CDFG fish pathologists (Modin, pers. comm., 1998), it is concluded that neither acute mortality nor chronic sub-lethal effects would be expected in fish experiencing rapid pH changes when all pH levels to which fish are exposed remain within the range of 6.5 to 8.5. Conversely, these studies suggest that small pH changes (e.g., 1 unit) could have adverse impacts when the resulting pH value falls outside the physiologically acceptable range for a given species. For example, rainbow trout acclimated to pH 9.0, which is at or near the species' upper limit, would be expected to experience high mortality if transferred to pH 10.0 and, in fact, would be expected to experience mortality if transferred to pH 9.5 – a change of just 0.5 units (Witschi and Ziebell 1979; Modin, pers. comm., 1998).

The ability of fish to rapidly acclimate to waters having substantially different pH values is further demonstrated by hatchery stocking programs and the freshwater tropical fish (aquarium) industry, where it is common to move fish from one water body or aquarium to another that differ by at least 0.5 pH units, and often by more than 1.0 pH unit. However, it should be noted that this "stocking" of fish typically involves waters with pH values in the range of 6.5 to 8.5 units so that the fish are transferred to waters with pH values well within the range that is physiologically acceptable to them. Available data regarding pH values tolerated by macroinvertebrates suggest that, like fish, they can rapidly adapt to changes in ambient pH levels within their natural pH range (Alabaster and Lloyd 1980; Boyd 1990).

A technical review of the effects of rapid pH changes on benthic macroinvertebrates revealed evidence indicating that macroinvertebrates rapidly exposed to pH changes of one unit or more, when pH is maintained within the 6.5 to 8.5 range, would not experience mortality, or other long-term adverse effects. Information supporting this finding is discussed further below.

The available scientific literature on the effects of rapid pH reductions on benthic macroinvertebrates provides evidence to suggest that rapid pH reductions of one unit or more, when pH is maintained between 6.5 and 8.5, would not cause chronic, adverse effect on individual macroinvertebrates or their populations. A thorough review of the scientific literature was conducted to identify studies that investigated the effects of rapid pH changes on macroinvertebrates, when pH was maintained between 6.5 and 8.5. No such studies were found. The fact that no studies of this nature could be found in the literature further supports the contention that rapid pH changes within the 6.5 to 8.5 range are not problematic to benthic macroinvertebrates. Based on the commonality of their experimental approaches, the acidification studies that are available in the scientific literature suggest that significant adverse effects to individual macroinvertebrates and their communities would not be expected to occur upon experiencing a rapid pH reduction unless the ending pH is below 6.0. Several studies that investigated the effects of stream acidification on benthic macroinvertebrate communities, where ending pH was below 6.0, shed additional light on how a pH gradient within a point source discharge mixing zone would affect benthic macroinvertebrates drifting through the zone; hence, findings from these studies are briefly summarized below.

Bernard et al. (1990) acidified experimental reaches of a British Columbia stream from pH 7.0 to 5.9 within 30 minutes to assess the effect of mild acidification on short-term invertebrate drift. They reported that small Ephemeroptera showed no initial response to pH reductions from 7.0 to 5.9, but that their drift increased after about 6 hours. Increased drift was observed for Chironomid and Trichoptera within an hour of reaching pH 5.9. Harpactacoid copepods, Hydrcarina, simulid Diptera, Plecoptera, and large Ephemeroptera did not respond. Lack of a drift response induced by rapid pH reduction in certain taxa demonstrates that the organisms were not adversely affected enough to move, and consequently, would not be affected enough to experience mortality. Kratz et al. (1994) reported that Simuliids (black flies) did not respond to rapid depressions of 1 pH unit below ambient, with an ending pH of below 6.0. Also, Hall et al. (1987) reported no effect on daytime drift rates in acidic Norris Brook, where pH was reduced from 6.4 to 5.2-5.5. Bernard et al. (1990) surmised that the rapid, large increases in drift exhibited by chironomids were avoidance behavior. Sensitive organisms may escape by drift to more suitable conditions downstream. Bernard (1985) (cited in Bernard et al. 1990) supported this hypothesis by showing that rapidly responding mayflies collected in a stream rapidly acidified to pH 5.7 had greater than 95% survival when subsequently held in circumneutral water for 24 hours. Kratz et al. (1994) concurred with these findings, suggesting that mild pH reductions (i.e., those with an ending pH near 6.0 or above) would likely elicit increased drift in some species due to behavioral responses rather than from causing pH-related mortality, whereas mortality-induced drift would increase as ending pH decreases, and reached lethal levels (e.g., 5.5 or lower).

To determine the direct effects of water chemistry on invertebrates sensitive to pH reductions, Rosemond et al. (1992) transplanted three mayfly species (i.e., *Drunella conestee (*Family Ephemerellidae) and *Stenonema* sp. and *Epeorus pleuralis* (Family Heptageniidae)) from a stream having pH of 6.6-6.8 to: 1) the stream from which they were collected (i.e., back into pH 6.6-6.8), and 2) a stream of pH 5.0 (a rapid pH change of 1.6-1.8 units). In the first *in situ* transplant experiment, there was no significant difference in mortality among the individuals of *Drunella conestee* transplanted into the two sites through 9 days post transplant. Mortality rates were 32% for organisms transplanted back into the same pH, and 28% for those transplanted into pH 5.0. In the second *in situ* experiment, using *Stenonema* sp., and *Epeorus pleuralis*, both species transplanted into the pH 5.0 stream experienced significantly higher mortality that those transplanted back into the original stream. In addition, the ultimate mortality experienced by these two species transplanted into the pH 5.0 stream differed significantly. These researchers concluded that the different sensitivities of the three species was due to differences in sensitivities to ending pH and acquired body burdens of aluminum, rather than to the initially-experienced rapid change in pH. This was supported by the fact that it took 2-6 days for mortality rates to differ between transplant groups for the same species. An inability to tolerate the initial pH shock (an acute phenomenon) would be expected to become apparent within a matter of hours rather than days. This is of particular relevance because macroinvertebrates drifting through a mixing zone would typically pass through the zone in a matter of minutes to hours.

Bell and Nebeker (1969) investigated the tolerance of aquatic insects to low pH. In this study, caddisfly, stonefly, dragonfly, and mayfly nymphs were exposed to a range of pH levels for 96 hours (4 days) to determine the pH levels at which 50% of the test organisms died (96-hr TL_{50}). Field-collected nymphs were acclimated to the laboratory for one week at pH 7.8. However, no gradual acclimation to test pH levels was reported. In fact the methods stated: "*If the test pH deviated by more than 0.25 pH units from the desired pH, the test was terminated*." Hence, test organisms were taken directly from their laboratory acclimation tank (pH 7.8), and placed directly into test tanks maintained at pH 1.0-7.0. The 96-hr TL_{50} values reported for the 10 species tested (from the families identified above) ranged from a low of 1.5 (the caddisfly *Brachycentrus americanus*) to a high of 4.65 (the mayfly *Ephemerella subvaria*) pH units. All 10 species tested showed 100% survival at pH 6.0, a 1.8 unit change from their acclimated pH of 7.8. The mayfly *Ephemerella subvaria* began to experience some mortality at test pH levels below 6.0. However, the caddisfly *Hydropsyche betteni*, stonefly *Acroneuria lycorias*, dragonfly *Boyeria vinosa*, and mayfly *Stenonema rubrum* all showed 100% survival at test pH levels as low as 5.5. Hence, these species showed no mortality when transferred from the acclimation tank at pH 7.8 to test tanks at pH 5.5, thereby experiencing a rapid pH change of 2.3 pH units. The caddisfly *Brachycentrus americanus* showed 100% survival to pH levels of 4.5, thereby experiencing a rapid pH change of 3.3 pH units.

In a follow-up study, Bell (1970) performed similar experiments with the same species of benthic macroinvertebrates, but extended the test period from 96 hours to 30 days. Findings were similar to the 96-hr study, except that the 30-day TL_{50}s were somewhat higher (i.e., higher pH levels) than those reported for the 96-exposure. These studies' findings concur with those of the studies discussed above, indicating that the ending pH is more important in determining mortality than the magnitude and rate of initial pH change.

These studies showed that rapid pH reductions of up to 1.6 pH units, with an ending pH below 6.0, did not cause elevated mortality in mayflies, a taxa of benthic macroinvertebrates shown through numerous studies (e.g., Kratz et al. 1994; Feldman and Connor 1992; Rosemond et al. 1992) to be the most sensitive taxa to pH reductions. Mortality was not shown to occur in sensitive mayfly species, or other macroinvertebrate taxa, when the ending pH was maintained at or above 6.5, as would always occur under compliance with the proposed pH objective.

Personal communications with several macroinvertebrate experts provide evidence in support of the conclusions pertaining to rapid pH changes stated above. S. Cooper (U.C. Santa Barbra, pers. comm., 1999), R. Haro (U.W. LaCrosse, pers. comm., 1999), and J. Harrington (CDFG, pers. comm., 1999) all concurred that the lack of studies in the scientific literature addressing pH changes within the 6.5 to 8.5 range suggest that rapid changes within this range are unlikely to adversely affect macroinvertebrates. Moreover, none of these experts were aware of any studies reported in the literature that document mortality to macroinvertebrates resulting from rapid pH changes with in the 6.5 to 8.5 range.

When asked to give their professional opinion regarding potential effects of rapid pH changes on benthic macroinvertebrates within the context of what can occur across the mixing zone associated with a municipal effluent discharge, the following statements were made.

A pH change from 8.5 to 7.0 would not be expected to have a lethal effect, but could have a sublethal (e.g., behavioral) effect. Nevertheless, sublethal effects would be expected to cease when the macroinvertebrates acclimated to the new pH. One would not expect to see lethal effects until the ending pH fell outside the normal pH range, perhaps 5.5 or 5.0 pH units (Cooper, pers. comm., 1999). S. Cooper is considered to be the leading expert on the West Coast regarding the effects of acid pulses on stream benthic macroinvertebrates.

As long as pH remained within the 6.5 to 8.5 range (referred to as circumneutral), there generally would not be any substantial adverse effects to macroinvertebrates drifting downstream into the effluent-dominated portion of the creek, where pH could be 1-2 units lower. Short-term sublethal (e.g., behavioral) effects could occur in some species (Haro, pers. comm., 1999).

In discussions with Jim Harrington of CDFG, regarding ranges of pH acceptable to aquatic life, he stated the following, *"The pH range of 6.5 to 8.5 is accepted to represent safe levels, and this is probably why there is not much literature on its effects to the aquatic system. When I write biological significance reports on pH-related spill events, I would conclude that there would be no deleterious effects within this range."* (Harrington, pers. comm., 1999).

The USEPA's past and current national pH criteria for the protection of aquatic life provide evidence to suggest that rapid pH changes, when pH is maintained within the 6.5 to 8.5 range, would not cause adverse impacts to benthic macroinvertebrates or their communities. Based on the language used by the NAS in its 1972 criteria referring to pH changes above or below the "…natural seasonal", it is clear that the 0.5 unit of change allowed under the "nearly maximum level of protection" was defined to limit the ambient pH range, not the magnitude of rapid change within this range. In fact, no quantitative criterion was assigned to limit rapid pH changes within the preferred pH range of 6.5 to 8.5. Similarly, the USEPA's current pH criterion for the protection of freshwater aquatic life (USEPA 1986, 1999a) simply defines an acceptable ambient pH range (i.e., 6.5-9.0), but does not quantitatively limit the magnitude of rapid change that organisms can be exposed to within this range (e.g., during movement through mixing zones associated with point-source discharges). Because the magnitude of rapid change to which freshwater aquatic life are exposed, within acceptable ambient pH ranges, has never been regulated as part of any national pH criterion, it can be reasonably concluded that all available scientific data on this issue indicate that the effects of rapid pH changes are insignificant when pH is maintained within the acceptable ambient range (e.g., 6.5-8.5).

Based on the above discussion, the proposed pH amendment is strongly supported by the current science regarding pH requirements of freshwater aquatic life and would be consistent with, but somewhat more restrictive than, USEPA's current national recommended criteria for the protection of freshwater aquatic life.

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