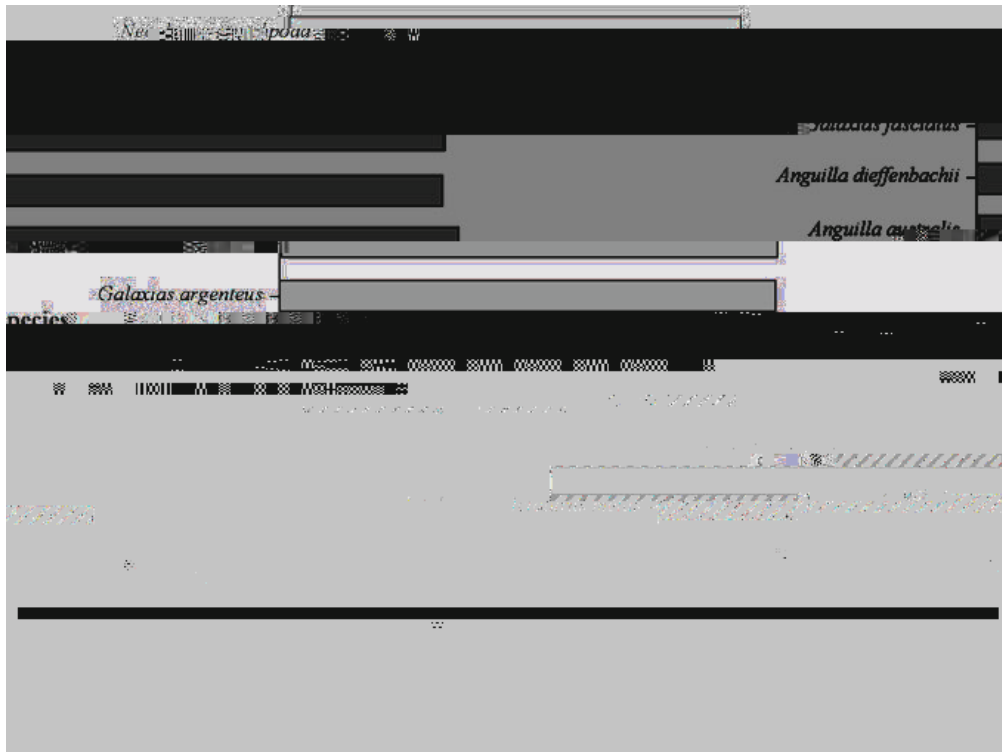


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Naturally acidic freshwaters are found worldwide, yet the fishes of these habitats have been infrequently studied. Systems that formed during the Holocene tend to be depauperate of fishes, yet older, tropical acidic waters are among the most diverse fish habitats. Occupants of naturally acidic waters come from a diverse array of piscine taxa, but geographic location appears to be more important than taxon in driving final fish assemblage structure. Based on studies from relatively rapid exposure, environmental acid is predicted to challenge physiological regulation of many systems across multiple life-history stages of fish. The study of how fish deal with acidity in nature began almost a century ago, and flourished in the last third of the twentieth century as concerns over anthropogenic acidification of

the freshwater components of these systems can be depauperate of fish fauna compared to nearby circumneutral systems (Rahel and Magnuson 1983), or they can be among the most speciose freshwater habitats on the planet (Chao 2001). Naturally acidic waters are most commonly formed through a combination of a drainage basin with either weathering-resistant bedrock or little erosion potential, resulting in very ion-poor water with minimal buffering capacity into which natural organic matter (NOM) is released by biotic processes. Incomplete oxidation of both plant and animal debris generates compounds with acidic functional groups such as humic, fulvic, and tannic acids, among others. Release of these compounds into poorly buffered water will lower the pH and, because this complex mixture of compounds also absorbs light across the visible spectrum, will generally darken the waters causing them to often be referred to as "black waters." "Dystrophic" is a limnological term also often applied to these waters. The fishes from these systems tend to be poorly studied; the few studies come primarily from systems of Holocene origin in North America, Eurasia, Southeast Asia, and New Zealand as well as the much older Rio Negro Basin of South America. Among the temperate Holocene systems, the abundance of hydrogen ion appears to be restricting species diversity in the northern hemisphere (Amarasinghea and Welcomme 2002), but less so in New Zealand (Collier et al. 1990). In Southeast Asia, the black water systems are also of Holocene origin (Wüst et al. 2007), but are characterized by only slightly lower species diversity (Beamish et al. 2003). Considering the incredible species diversity of the older Rio Negro system (over 1,000 fish species, approximately three times the diversity of all of Europe) might lead one to assume that long-term natural acidity promotes speciation, but taken in the context of the overall fish species richness of the neotropics, this assumption would be premature. Certainly,



and gymnotiforms, are well represented amongst the 1,000+ species of the Rio Negro watershed (Goulding et al. 1988). Interestingly, a group not present in the Neotropics and generally thought to be acid-intolerant from laboratory and north temperate studies, the cyprinids, make up a significant portion of the fish assemblages in naturally acidic waters on the Malay peninsula (Beamish et al. 2003) and are found in the most acid waters of Japan (Ikuta et al. 2000). Besides determining whether an animal was present as a naturally acidic system formed, taxon does not appear to be that important in determining final fish assemblage structure. Other biotic factors such as coincident species or whether a given lineage evolved air breathing could be just as important as a species' ability to tolerate acid.

where inhibition of ion-transport proteins in gill ionocytes and disruption of the integrity of intercellular junctions are frequently reported lesions (Reid 1995; Wood 2001; Kwong et al. 2014; Fig. 2). Investigations into acid precipitation and fish kills generally found that fish were extirpated from waters at pH levels substantially higher than were distressful to adult fish in the laboratory. There are many potential explanations for this finding. Two of the most important turned out to be: 1) that aluminum was commonly released into the waters of acidifying watersheds and had a complex synergistic toxicity that varied with pH level and dissolved organic molecules, and 2) that for most species, individuals were more vulnerable to reduced environmental pH during reproductive life-history stages (Sayer et al. 1993). Aluminum toxicity at low pH is a complex function of oxidation state, pH, environmental $[Ca^{++}]$

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Relative to comparison species and conspecific populations, animals indigenous to acidic habitats have been reported to (1) be more tolerant of low pH levels (Dunson et al. 1977; Rahel 1983; Dederen et al. 1986; Wilson et al. 1999; Gonzalez et al. 1998); (2) have less disruption of monovalent ion balance during acid exposure (McWilliams 1982; Gonzalez and Dunson 1987, 1989a; Wilson et al. 1999; Gonzalez et al. 1998, 2002); (3) exhibit greater blood oxygen transport capacity (Rask and Virtanen 1986; Nelson et al. 1988; Wood et al. 1998); (4) have

sophisticated flux measurements on some of the most acid-tolerant Neotropical species from black waters by obtaining them from aquarium dealers in North America (e.g., Gonzalez and Preest [1999](#); Gonzalez and Wilson [2001](#)). Some of these fish exhibited branchial permeabilities on par with acid-intolerant species, whereas others had very unremarkable Na⁺ uptake kinetics. Some of these species did exhibit monovalent transport kinetics fairly independent of pH while others

A few studies using intraspecific comparisons of fish from naturally acidic waters conflict with these results. Lyons (1982) and Vinogradov and Komov (1985) showed no differences in monovalent ion loss between fish from naturally acidic waters and conspecifics from neutral waters upon acid exposure. Furthermore, Nelson and Mitchell (1992) compared plasma ion levels of yellow perch populations from a naturally acidic lake with conspecifics from neutral lakes after 16 h of swimming in acid water and found no difference between them. These latter results support the conclusion from the interspecific comparative studies (reviewed in Gonzalez et al. 2005) that adjustments to monovalent ion regulatory parameters

fish exposed to acid water are quite variable across studies (reviewed in Wood and McDonald 1982). Many of the changes reported could not be separated from cell swelling expected from plasma ion losses or adrenergic activation of erythrocytes (Milligan and Wood 1982). If oxygen loading is being compromised in the gills of fish from low pH waters, we would expect to see some compensation for this in fish spending thousands to millions of generations in naturally acidic systems. Indeed, Rask and Virtanen (1986) found that European perch from a naturally acidic lake had a higher hematocrit than conspecifics from a circumneutral lake; even more interesting was that the acidic lake perch increased their hematocrit in response to reductions in pH, without changes in osmolality, whereas the neutral lake perch did not (Rask and Virtanen 1986). Nelson et al. (1988) found blood sampled from

acidic lake (Nelson et al. [1988](#)) could account for some of the increase in plasma $[\text{HCO}_3^-]$

fairly extreme. For example, Waiwood and Beamish (1978) found no effect on critical swimming speed (U_{crit}) when the pH was reduced to 6.0 in rainbow trout, but West and Garside (1986) found a significant depression of U_{crit} at pH 5.0–6.0. Graham and Wood (1981) found a linear decrease in U_{crit} as pH was progressively depressed below pH 6.0 in the same species. Fish from naturally acidic waters have been shown to have their swimming performance less diminished by acid water, but this result is context dependent: Nelson (1989) reanalyzed the data reported by Holeton and Stevens (1978) to show that *Tripottheus angulatus* (Characiformes) acclimated to white water and swimming in black water had reduced critical

phosphate, and inosine mono-phosphate and suggested that fish that pushed adenylate depletion and glycolysis to extremes had been selected against in this



The overwhelming conclusion from this review is that fish from naturally acidic systems merit far more study. Today, we cannot even generalize as to whether acidic habitats promote or restrict piscine diversity nor do we understand what the biological characteristics are that allow some species to thrive in acidic habitats. Considering the fact that we find jawless lampreys and ancestral teleosts among the fauna of naturally acidic systems and that the earth has experienced prior massive acidification events (e.g., Permian-Triassic boundary, 250 MYA; Ogden and Sleep 2012) within the evolutionary history of today's fishes, we would expect the ability to occupy acidic habitats to be pleisiomorphic. This may explain why we find so many diverse fish taxa in extant acidic ecosystems, but the question then becomes, why have so many fishes lost the ability to thrive in acid waters? Minna Jewell (1922) postulated almost a century ago that because of the physiological challenges posed by high environmental $[H^+]$, species and populations occupying naturally acidic waters were likely to be special in some way. Today, interest in animals from acidic ocean seeps is surging as scientists seek to predict organismal and ecosystem consequences of human-generated ocean acidification, yet we still know little about how fishes deal with the more extreme acidity they encounter in naturally acidic freshwaters. Understanding how fish acclimatize to, adapt, or even speciate in acidic habitats will not only enrich our knowledge of freshwater fish evolution

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