

Review of the suitability of EPA's 1999 ammonia criteria for Idaho

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Regulatory Background

Under section 304(a) of the Clean Water Act, EPA is to develop and publish water quality criteria that reflects the latest scientific knowledge on the kind and extent of all identifiable effects on health and welfare. These include effects on fish, other aquatic life and wildlife, recreation, and biological community diversity, productivity, and stability. Technically, these criteria are published as non-regulatory "recommendations," for states and authorized tribes to use in setting their standards (EPA 1999a). As a practical matter, EPA uses their published criteria as one factor for determining whether to approve or disapprove a state's water quality standards.

Over the years EPA and its predecessors have developed and revised criteria for many pollutants in ambient waters starting with the 1968 "Green Book", the 1972 "Blue Book", the 1977 "Red Book", the 1986 "Gold Book", and the 1998 "National Recommended Water Quality Criteria; Republication". Since 1985, these revisions have generally followed the same approach: toxicity test data for a large number of taxa from a variety of taxonomic groups were compiled, rank-ordered by sensitivity, and then criteria values are calculated to protect all but a small percentage of the most sensitive species. The small percentage was set at 5% because higher or lower percentages resulted in criteria that seemed too high or too low in comparison with the sets of data from which they were calculated. Further, the use of the 5th percentile of sensitivity in aquatic life criteria development was considered appropriate in part because aquatic ecosystems can tolerate some stress and occasional adverse effects, protection of all species at all times and places was not deemed necessary in deriving most aquatic life criteria (Stephan et al. 1985). Through these criteria updates, the recommended *values* to achieve this level of protection may go up or down in reflection of the more recent scientific knowledge. Thus, according to EPA, updated criteria are not more or less stringent, instead they reflect latest scientific knowledge to achieve the same level of protection.

Because EPA develops criteria to protect 95% of aquatic species, if an unusually sensitive species is ecologically, economically, or recreationally important at a site, more stringent, site-specific modifications to the criteria could be needed. With threatened or endangered species, if sufficient data exist indicating that they are more sensitive to a pollutant than the species upon which the criteria were developed, or if exposure to criteria concentrations at the, frequency and durations specific would likely result in adverse effects, then site-specific modifications should be made to reduce the criteria (EPA 1999a).

Ammonia water quality concerns

Ammonia is one of the most important pollutants in the aquatic environment because of its relatively highly toxic nature and its ubiquity in surface water systems. Ammonia can enter natural water systems from several sources, including industrial wastes, sewage effluents, fuel conversions and refining, and runoff from agricultural fields where commercial fertilizers and animal manure are applied. It is a natural biological degradation product of nitrogenous organic matter (Russo 1985).

Ammonia buildup and toxicity can be a problem in fish aquaculture. Consequently, a great deal of information on the toxicity of ammonia to fish and other aquatic organisms is available in the literature. While reports vary, most literature supports the following: the toxicity of ammonia varies with pH and to a lesser degree temperature and other factors. Wicks et al. (2002a) found that at constant pH, increasing calcium hardness decreased ammonia toxicity. Ammonia exists in two forms in natural waters, ammonium (NH_4^+) and un-ionized (NH_3) ammonia. Of the two forms, un-ionized is by far the more toxic, since it is a neutral molecule that can readily pass through epithelia. Together, they are referred to a total ammonia (Russo 1985, EPA 1999b). EPA's 1999 ammonia criteria are expressed in terms of nitrogen, i.e. as mg N/L because most permit limits for ammonia are expressed in terms of nitrogen ammonia (EPA 1999b). Emerson (1975) provides aqueous equilibrium equations for expressing estimated concentrations of the different forms, so that differently expressed test results, criteria, etc. may be compared.

Rather than single numbers, both the previous criteria and 1999 updates use nonlinear polynomial equations to describe the criteria for a given temperature and pH (Equations 1-3, EPA 1985, 1999b).

Equation 1. Criterion maximum concentration (“acute criterion”) from EPA (1999), where salmonids are present.

$$CMC = \frac{0.275}{1 + 10^{7.204 - pH}} + \frac{39.0}{1 + 10^{pH - 7.204}}$$

Equation 2. Criterion continuous concentration (“chronic criterion”) from EPA (1999), where early-life stages of fish are present.

$$CCC = \left(\frac{0.0577}{1 + 10^{7.688 - pH}} + \frac{2.487}{1 + 10^{pH - 7.688}} \right) \bullet \text{MIN}(2.85, 1.45 \cdot 10^{0.028 \cdot (25 - T)})$$

Equation 3. Criterion continuous concentration (“chronic criterion”) from EPA (1999), when early-life stages of fish are absent.

$$CCC = \left(\frac{0.0577}{1 + 10^{7.688 - pH}} + \frac{2.487}{1 + 10^{pH - 7.688}} \right) \bullet 1.45 \cdot 10^{0.028 \cdot (25 - T)}$$

The 1999 criteria values are higher than the 1984 criteria values. (Figures 1-4). EPA's 1999 ammonia update has two recommended acute criteria, with or without salmonids present. It also has two recommended chronic criteria, with or without early-life stage fishes present. The Idaho application of the EPA 1999 criteria for coldwater and seasonal coldwater aquatic life uses the acute criteria with salmonids present, and the chronic criteria for early life stage fishes present. Both are the more restrictive of the available options given by the 1999 criteria update. Salmonids are found throughout Idaho. Because both fall and spring spawning fish occur in many rivers, fish early life stages would be expected to occur at different times of the year (Figure 1, Table 1). Fry from fall spawning salmonids typically emerge from stream gravels the following March or April, thus early life stages would be present over-winter in waters with fall spawning fish. Thus to apply the early life stages present-absent provisions of the 1999 criteria (EPA 1999a) would be quite complex, and in many cases very limited. For the many waters where both spring and fall spawning fishes are present, early life stages could be present for all but about two months in summer. Since ammonia removal from wastewater is most difficult in cold weather (EPA 1999a), the early life stage absent criterion may offer little relief to most dischargers, and have limited applicability in most waters of Idaho.

Table 1. Common core-periods for early-life stages to be present in Idaho streams for several native and introduced salmonids

Species	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Chinook salmon (spring/summer)												
Kokanee salmon												
Steelhead trout												
Cutthroat trout												
Bull trout												
Mountain whitefish												
Rainbow trout												
Brown trout												
Brook trout												

Source: *Time Periods for Salmonid Spawning*, Appendix F to Grafe et al. (2002). Time periods shown include spawning, egg incubation through emergence. Beginnings and ends of bars indicate early or mid-month, no higher precision is intended.

Table 2. Example of fish species with spring or fall spawning habits.

Family	Common Name	Scientific name	Expected Spawning season	Origin ^a
Salmonids	Brown trout	<i>Salmo trutta</i>	Fall	I
(Trout, salmon, whitefish)	Brook trout	<i>Salvelinus fontinalis</i>	Fall	I
	Bull trout	<i>Salvelinus confluentus</i>	Fall	N
	Chinook salmon	<i>Oncorhynchus tshawytscha</i>	Fall	N
	Cutthroat trout	<i>Oncorhynchus clarki</i>	Spring	N
	Rainbow trout	<i>Oncorhynchus mykiss</i>	Spring	N
	Mountain whitefish	<i>Prosopium williamsoni</i>	Fall	N
	Cottids (Sculpins)	Torrent sculpin	<i>Cottus rhotheus</i>	Spring
Catostomids (Suckers)	Bridgelip sucker	<i>Catostomus columbianus</i>	Spring	N
	Largescale sucker	<i>Catostomus macrocheilus</i>	Spring	N
	Longnose sucker	<i>Catostomus catostomus</i>	Spring	N
Cyprinids (Minnows)	Chiselmouth	<i>Acrocheilus alutaceus</i>	Spring	N
	Longnose dace	<i>Rhinichthys cataractae</i>	Spring	N
	Northern pikeminnow (formerly the Northern squawfish)	<i>Ptychocheilus oregonensis</i>	Spring	N
	Redside shiners	<i>Richardsonius balteatus</i>	Spring	N
	Speckled dace	<i>Rhinichthys osculus</i>	Spring	N
Centrarchids	Black crappie	<i>Pomoxis nigromaculatus</i>	Spring	I
(Sunfishes, bass)	Largemouth bass	<i>Micropterus salmoides</i>	Spring	I
	Pumkinseed	<i>Lepomis gibbosus</i>	Spring	I
	Smallmouth bass	<i>Micropterus dolomieu</i>	Spring	I
Percidae (perches)	Yellow perch	<i>Perca flavescens</i>	Spring	I
Ictalurids (Catfishes)	Brown bullhead	<i>Ameiurus nebulosus</i>	Spring	I
	Yellow bullhead	<i>Ameiurus natalis</i>	Spring	I

^a Origin: N- Native – Species indigenous to Idaho, although some populations have been introduced beyond their historical range (e.g. Kokanee and chinook salmon in Coeur d’Alene, Priest, and Pend Orielle lake drainages, rainbow trout in the upper Snake, Spokane, and Pend Orielle drainages); I- Introduced, non-indigenous species. Source – Simpson and Wallace (1982)

Figures 1-4 compare the previous and 1999 updated criteria, and show the relationship between chronic toxicity tests with salmonids used in criteria development with the previous and 1999 ammonia criteria. Results from different studies vary widely, but most results indicate that salmonids would probably be protected by the chronic criterion. Toxicity data are taken from EPA (1999), supplemented by reviews of primary literature, with the exception of the “Genus minimum mean chronic value” (GMCV) which was calculated to get a conservative (low) estimate the central tendency of the chronic salmonid data. The “GMCV” shown here is the geometric mean of highest no-observed-effects-concentrations (NOEC), lowest-observed-effects-concentrations (LOEC), and “less-than” LOECs divided by 2. This estimate is conservative since NOECs were considered “effects” when by definition, they are not adverse effects. A “less-than” LOEC is the biological analog of a “less than detection limit” chemical result. Dividing “less-than” LOECs by 2 is similar to the common practice of dividing chemical “non-detect” values by 2 and including them in statistical summaries.

In cooperation with the Washington Department of Ecology and EPA, the primary literature was searched for ammonia toxicological results that could be used to evaluate the protectiveness of the national recommended criteria to Northwest regional species (with a focus on salmonids and sturgeon). A few substantive papers not available in EPA 1999b were evaluated, these included Linton et al (1999a, b), Wicks et al. (2002a,b), and Meyer and Hansen (2002). Key papers with salmonids used by in EPA (1999b) were also critically reviewed, rather than relying solely on EPA’s (1999b) interpretation. These included Burkhalter and Kaya 1977, Calamari et al 1977, Thurston and Russo 1978, Rankin 1979, Buckley et al. 1979, Rice and Bailey 1980, Arillo et al 1981, Thurston et al 1984, Hermanutz et al 1987, Solbe and Shurben 1989, and Salin and Williot, 1991.

Arillo et al. (1981) were able to measure changes in fish blood chemistry at ammonia concentrations lower than the recommended criteria. However, their results could not be related to effects related to survival or reproductive success of individuals, or population viability. Thus, other than suggesting avenues for further research, conclusions about protectiveness to salmonid individuals or populations could not be drawn from this study. EPA (1999b, pp. 118-121), although not including the Arillo et al. (1981) study, made similar conclusions about sublethal histopathological effects. Noting that some histopathological effects of ammonia on fish were temporary, and occurred at concentrations that did not adversely affect growth, survival, or reproduction, EPA concluded that histopathological effects were not adequate to base criteria upon. Two other major recent studies found that long-term exposure to sublethal ammonia concentrations had neutral or even beneficial effects on rainbow trout (Linton et al. 1999a, b).

Wicks et al (2002a,b) noting that ammonia is unlike other toxicants, in that all organisms produce ammonia and must excrete it to avoid self-intoxication, tested ammonia toxicity under conditions that standard test methods (e.g. EPA or ASTM seek to avoid – feeding and exercise. Ammonia becomes internally elevated in fish under these conditions. Wicks et al. (2002a) tested the acute (96-hour) toxicity to ammonia while forcing coho salmon to swim in a current at 60% of the velocity that results in exhaustion (critical swimming velocity). When tested under these conditions, the LC₅₀ of the coho salmon

(32 mg/L) was similar to the ammonia CMC (36 mg/L) for the tested pH and temperature (pH 6 and 12°C). In contrast, when feeding coho salmon during acute toxicity testing it was evident that feeding protects rainbow trout from ammonia toxicity during the first 24-h of exposure and that fasting exacerbates ammonia toxicity (Wicks 2002b). Standard acute toxicity test methods call for fasting before and during testing. Since fish in the wild both must swim (which can exacerbate ammonia toxicity) and eat (which lessens ammonia toxicity) it is not clear whether together these results suggest ammonia in natural waters would be more or less toxic than in laboratory test waters. Wicks et al. (2002a) also reported that sublethal ammonia exposures at concentrations ≥ 0.04 mg NH_3/L (which at pH 6 is equivalent to about 151 mg N/L using the aqueous ammonia equilibrium calculations from Emerson et al.s (1975).

This review supported the conclusions of EPA (1999b) that the 1999 criteria would probably be protective for salmonids. Most (11 of 13) studies reviewed found that thresholds of adverse effects were higher than criteria (Table 2, Figures 1 and 3). To the extent that any one study can be considered more influential than others, that consideration should be based upon the rigor of the study, rather than their numerical results. The Montana 5-year full life cycle testing with rainbow trout (Thurston et al. 1984) and Minnesota field tests with rainbow trout in experimental streams (Hermanutz et al. 1987) are especially relevant. The Montana 5-year full life cycle test is by far the most ambitious laboratory study completed. The Minnesota tests are especially relevant because of the natural conditions that fish experienced during both winter and summer tests. These two studies indicated that the 1999 ammonia criteria would be protective. Also, taken together, the tests did not suggest consistent species sensitivity differences among the salmonids.

The Lost River sucker, *Deltistes luxatus*, a fish endemic to desert drainages in central Oregon was exposed to combinations of low DO concentrations, elevated pH, elevated ammonia concentrations, in subchronic tests (reduced growth, altered whole-body ion content, and reduced swimming performance). Adverse effects occurred only at ammonia concentrations greater than the chronic criterion, even with the additional stress of low DO and elevated pH (Meyer and Hansen 2002). If the sensitivity of the Lost River sucker is similar to that of non-salmonid, Idaho fishes that inhabit desert drainages, then these results would suggest the chronic ammonia criterion would be protective of them as well

Endemic Snake River aquatic snails are also species of special concern, including the Snake River physa, Idaho springsnail, Banbury Springs lanx, Bliss Rapids snail, and the Utah valvata. EPA 1999(b) reported genus mean acute values for *Physa* at 74 mg N/L, well above the corresponding acute ammonia criteria of about 12 mg N/L. *Physa* was ranked 24/34 most sensitive taxa. Another freshwater snail, *Helisoma*, had a genus mean acute value of 94 mg N/L, ranked 26th in sensitivity of 34 species. These data suggest aquatic snails are not among the more sensitive species to ammonia.

Table 3. Summary of selected studies of chronic or sublethal exposure of ammonia to salmonids. Studies are all laboratory studies unless otherwise indicated

Test (Location, species, duration)	Results suggest risk of adverse effects at EPA 1999 criteria concentrations?	Citation
Montana, Cutthroat trout 29d	No	Thurston et al. 1978
Montana, Rainbow trout 5yr	No	Thurston et al. 1984
Montana, Rainbow trout 42d	No	Burkhalter and Kaya 1977
United Kingdom, Rainbow trout 72d	Yes	Solbe and Shurben 1989
Italy, Rainbow trout 72d	Yes	Calamari et al. 1977
British Columbia, Sockeye salmon, 62d	No	Rankin 1979
Minnesota Rainbow trout 237d field	No	Hermanutz et al 1987
Minnesota Rainbow trout 69d field	No	Hermanutz et al 1987
Minnesota Rainbow trout 28d field	No	Hermanutz et al 1987
Alaska, Pink salmon 61d	No	Bailey and Rice 1980
Ontario Rainbow trout 90-d	No	Linton et al. 1999a, 1999b
British Columbia, Coho salmon, swimming performance	No	Wicks et al. 2002a
Washington, Coho salmon 91days	No	Buckley et al. 1979

In summary, the information reviewed indicated that ambient ammonia concentrations up to EPA's 1999 recommended criteria concentrations would be unlikely to adversely affect indigenous aquatic life communities, including salmonid fishes.

Figure 1. Criteria vs. temperature: Comparison of 1984 chronic ammonia criteria, 1999 criteria, and chronic toxicity tests with salmonids at pH 8.

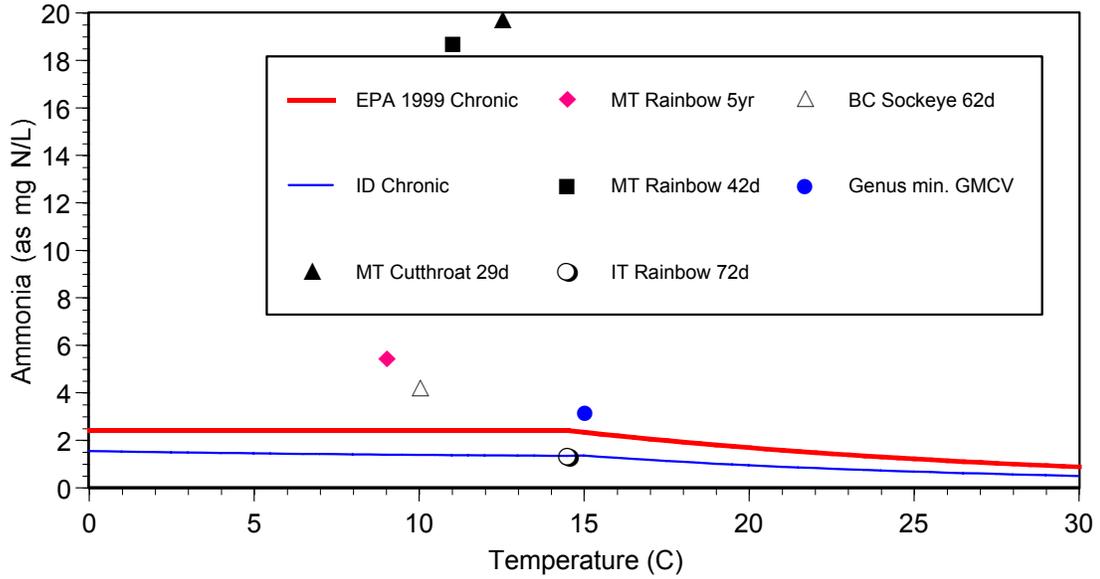


Figure 2. Comparison of 1984 chronic ammonia criteria, 1999 criteria, at (a) pH 8 and at (b) pH 7.5

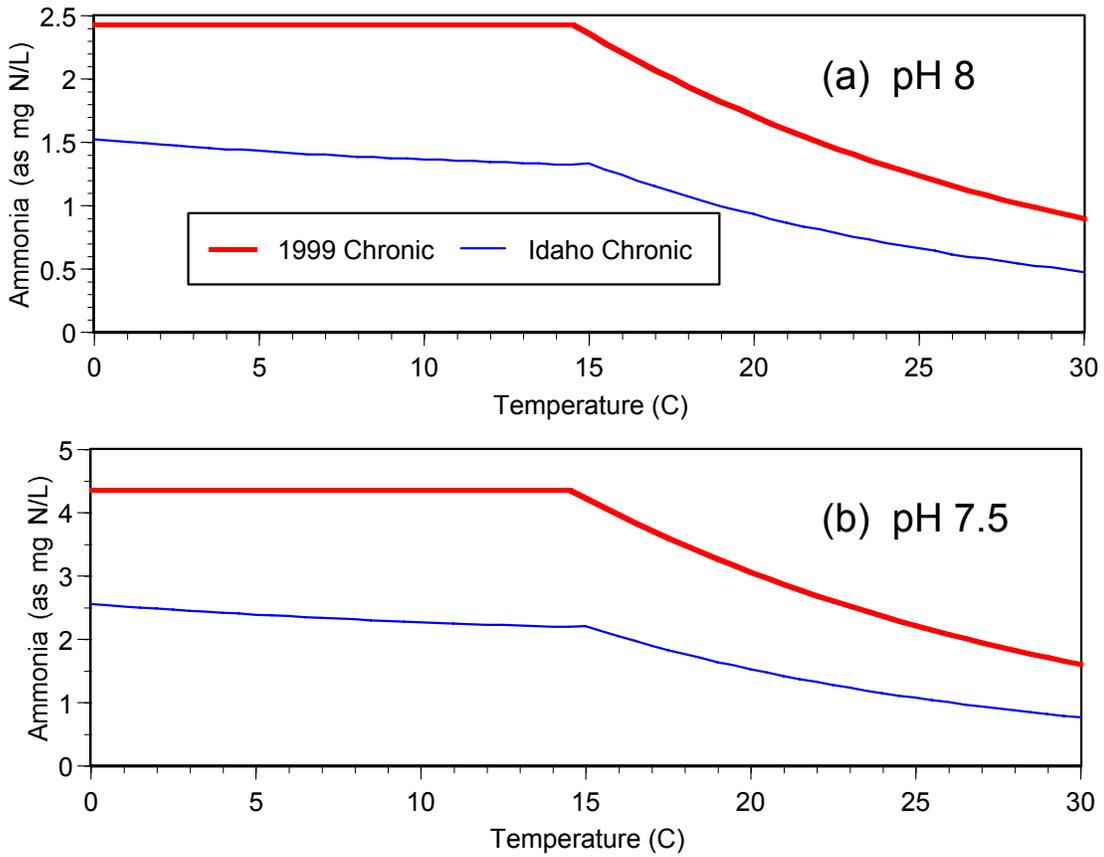


Figure 3. Criteria vs pH: comparison of 1984 chronic ammonia criteria, 1999 criteria, and chronic toxicity thresholds with salmonids at 14°C. See text for chronic toxicity threshold explanations.

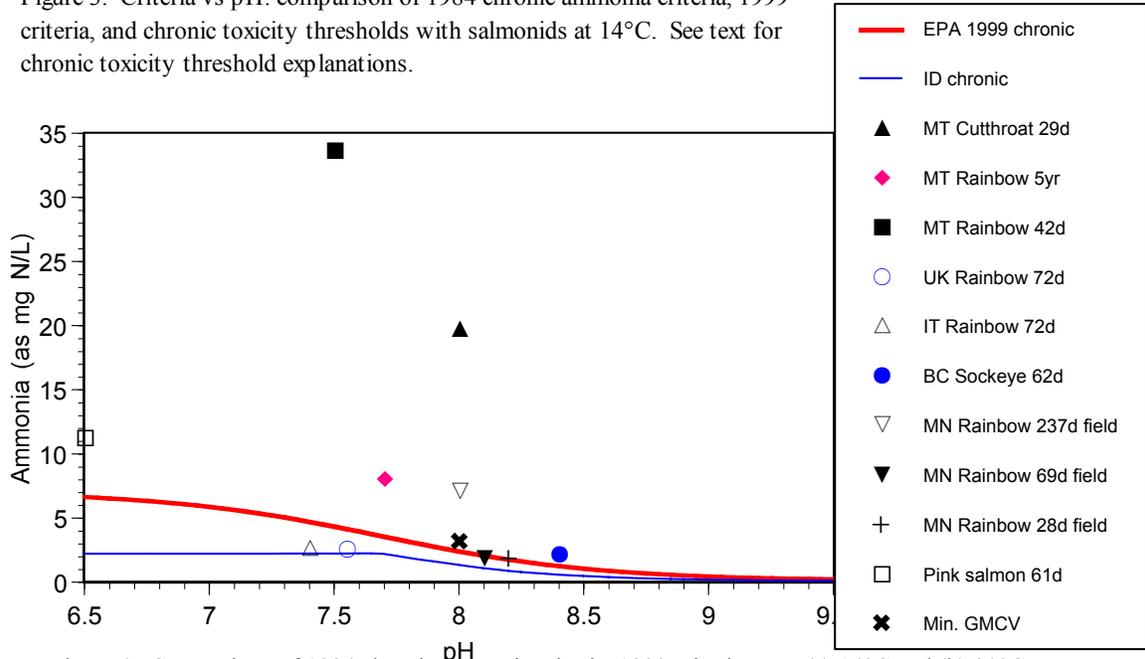
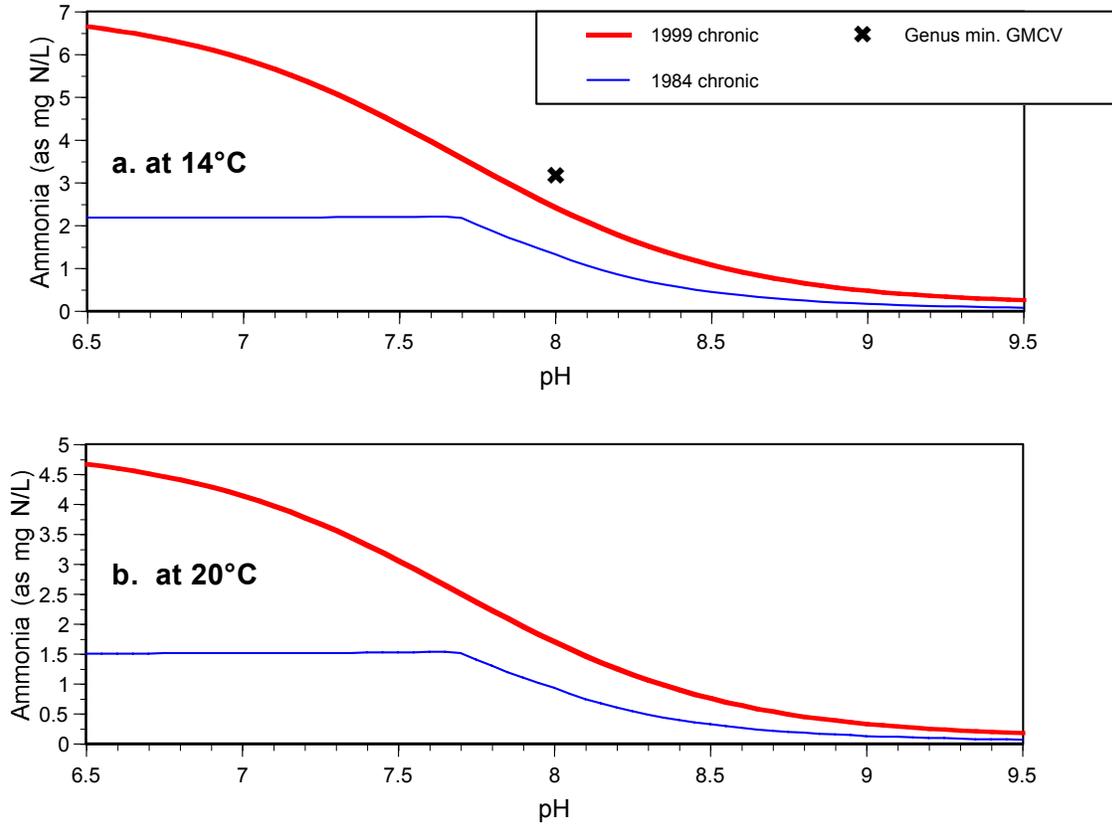


Figure 4. Comparison of 1984 chronic ammonia criteria, 1999 criteria, at (a) 14°C and (b) 20°C.



References

- Arillo, A., C. Margiocco, F. Melodia, P. Mensi, G. Schenone. 1981. Biochemical aspects of water quality criteria: the case of ammonia pollution. *Environmental Technology Letters*. V.2, pp. 285-292.
- Buckley, J.A., C. M. Whitmore, and B.D. Liming. 1979. Effects of prolonged exposure to ammonia on the blood and liver glycogen of coho salmon (*Oncorhynchus kisutch*). *Comp. Biochem. Physiol.* 63:297-303
- Burkhalter, D.E. and C.M. Kaya. 1977. Effects of prolonged exposure to ammonia on fertilized eggs and sac fry of rainbow trout (*Salmo gairdneri*). *Transactions of the American Fisheries Society* 106 (5):470-475
- Calamari, D.R., R. Marchetti, and G. Vailati. 1977. Effects of prolonged treatments with ammonia on the developmental stages of rainbow trout (*Salmo gairdneri*). *Nuovi Ann. Ig. Microbiol.* 28:333-345. (English translation)
- Emerson, K., R. C. Russo, R. E. Lund, and R. V. Thurston. 1975. Aqueous ammonia equilibrium calculations: effect of pH and temperature. *Journal of the Fisheries Research Board of Canada* 32:2379:2383.
- EPA. 1985. Ambient water quality criteria for ammonia - 1984. EPA 440/5-85-001. U.S. Environmental Protection Agency, Washington, D.C.
- EPA. 1999a. Water quality criteria; notice of availability 1999 update of Ambient water quality criteria for ammonia. Federal Register Volume 64(245) pp. 71973-71980, December 22, 1999.
- EPA. 1999b. 1999 update of Ambient water quality criteria for ammonia. EPA 822/R-99-014. U.S. Environmental Protection Agency, Washington, D.C.
- Grafe, C. S., C.A. Mebane, M.J. McIntyre, D.A. Essig, D.H. Brandt, and D.T. Mosier. 2002. The Idaho Department of Environmental Quality Water Body Assessment Guidance, Second Edition. Idaho Department of Environmental Quality, Boise. 230 pp.
- Hermanutz, R.O., S.F. Hedkte, J.W. Arthur, R.W. Andrew, and K.N. Allen. 1987. Ammonia effects on microinvertebrates and fish in outdoor experimental streams. *Environmental Pollution*. 47:249-283
- Linton, T.K. S.D. Reid, and C.M. Wood. 1999. Effects of a restricted ration on the growth and energetics of juvenile rainbow trout exposed to a summer of simulated warming and sublethal ammonia. *Transactions of the American Fisheries Society* 128:758-763
- Linton, T.K. S.D. Reid, and C.M. Wood. 1999. The metabolic costs and physiological consequences to juvenile rainbow trout of a simulated winter warming scenario in the presence of absence of sublethal ammonia. *Transactions of the American Fisheries Society* 128:611-619.

- Meyer, J.S. and J.A. Hansen. 2002. Subchronic Toxicity of Low Dissolved Oxygen Concentrations, Elevated pH, and Elevated Ammonia Concentrations to Lost River Suckers. *Transactions of the American Fisheries Society* 131:656–666
- Rankin, D.P. 1979. The influence of un-ionized ammonia on the long-term survival of sockeye salmon eggs. (Canadian) Fisheries and Marine Service Technical Report 912
- Rice, S.D. and J.E. Bailey. 1980. Survival, size, and emergence of pink salmon, *Oncorhynchus gorbuscha*, alevins after short and long-term exposure to ammonia. *Fishery Bulletin* 78:641-648
- Russo, R.C. 1985. Ammonia, nitrite, and nitrate. in Rand, G.M. and S.R. Petrocelli (eds). *Fundamentals of aquatic toxicology*. Hemisphere Publishing. pp. 455-474.
- Salin C. and P. Williot. 1991. Acute toxicity of ammonia to Siberian sturgeon. Williot, P. (ed). pp. 153-167 in *Acipenser*, Cemagref Publishers
- Simpson, J. C., and R. L. Wallace. 1982. *Fishes of Idaho*. University of Idaho Press, Moscow, Idaho.
- Solbe, J.F. De L.G. and D.G. Shurben. 1989. Toxicity of ammonia to early life stages of rainbow trout (*Salmo gairdneri*). *Water Research*. 23:127-129.
- Stephan, C. E., and coauthors. 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. U.S. Environmental Protection Agency, PB85 227049, Duluth, Narragansett, and Corvallis.
- Thurston, R.V. and R.C. Russo. 1978. Acute toxicity of ammonia and nitrite to cutthroat trout fry. *Transactions of the American Fisheries Society* 107:361-368
- Thurston, R.V., R.C. Russo, R.J. Luedtke, C.E. Smith, E.L. Meyn, C. Chakoumakos, K.C. Wang, and C.J.D. Brown. 1984. Chronic toxicity of ammonia to rainbow trout. *Transactions of the American Fisheries Society* 113:56-73.1984
- Wicks, B. J., R. Joensen, Q. Tang, and D. J. Randall. 2002. Swimming and ammonia toxicity in salmonids: the effect of sub lethal ammonia exposure on the swimming performance of coho salmon and the acute toxicity of ammonia in swimming and resting rainbow trout. *Aquatic Toxicology* 59:55-69.
- Wicks, B. J., and D. J. Randall. 2002. The effect of feeding and fasting on ammonia toxicity in juvenile rainbow trout, *Oncorhynchus mykiss*. *Aquatic Toxicology* 59:71-82.