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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**



**EUROPEAN INLAND FISHERIES ADVISORY COMMISSION
FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS
Rome, 1968**

PREPARATION OF THIS PAPER

The background for the preparation of this paper is described in the Foreword of the report.

The paper was prepared by the European Inland Fisheries Advisory Commission (EIFAC) Working Party on Water Quality Criteria for European Freshwater Fish and finalized at the Fifth meeting of the Working Party in London on 23-24 October 1967.

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Second in a series of reports on water quality criteria for European freshwater fish prepared for the European Inland Fisheries Advisory Commission (EIFAC) by the Working Party on Water Quality Criteria. The background of the project is described and reasons for establishing water quality criteria for fish explained. This is followed by a literature survey on effects of acid pH and alkaline pH values. Tentative water quality criteria are suggested as well as the scope for further research.

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Prepared by

European Inland Fisheries Advisory Commission
Working Party on Water Quality Criteria for
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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 A critical review has been made, therefore, of published and unpublished data on both the direct and indirect effects of extreme pH values on fish, with an emphasis on European species; from this review it is clear that the existing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 become 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 the report.

FOREWORD

This is the second of a series of reports on water quality criteria for European freshwater fish prepared for the European Inland Fisheries Advisory Commission (EIFAC) - an intergovernmental organization with a membership of 19 member countries. The Commission, at its Second Session, Paris, 1962, took note of a recommendation of the Conference on Water Pollution Problems in Europe, 1961 that EIFAC take the initiative in drawing up water quality requirements with respect to fisheries^{1/}.

As was stated in its first report^{2/} the Commission "agreed that the proper management of a river system demands that water of suitable quality be provided for each use that is made or intended to be made of it and that the attainment and maintenance of such quality is normally to be sought through the control of pollution. It was necessary therefore to know the standards of quality required for each particular use in order to determine the degree of pollution control necessary and to forecast the probable effect of augmented or new discharges of effluents. It was pointed out that water quality standards for drinking water had been well defined by the World Health Organization (WHO) and that standards for certain agricultural and industrial uses are also well defined. However, water quality criteria for fish have not received the attention that they deserve. All too often, water has been considered quite adequate for fish as long as there has been no obvious mortality which can be ascribed to known pollutants. Degradation of the aquatic habitat through pollution and decrease in the annual production and subsequent harvest of fish have often passed unnoted.

With such reasoning in mind, it was then agreed that the establishment of water quality criteria for European freshwater fish be undertaken by the Commission. This was to be accomplished by a critical examination of the literature, and very possibly experimentation to clear up contradictions and fill in gaps of knowledge, followed by recommendations as to desirable requirements for various aquatic organisms or groups of aquatic organisms with respect to the various qualities of water. The final criteria were to be published and given wide dissemination."

To accomplish this task, the Second Session of the Commission appointed a Working Party of experts selected on the basis of their knowledge of physical, chemical and biological requirements of European freshwater fish in relation to the topics to be studied. This Working Party prepared its first report on finely divided solids and inland fisheries, referred to above, which was submitted to the Commission at its Third Session, Scharfling am Mondsee, 1964, where it was unanimously approved.

^{1/} See, respectively: EIFAC Report, Second Session, 1962, p.21-22.
UN (1961) Conference on Water Pollution Problems in Europe,
held in Geneva from 22 February to 3 March 1961.
Documents submitted to the Conference. Vols. I-III, United
Nations, Geneva, 600 p.

^{2/} Report on Finely Divided Solids and Inland Fisheries, EIFAC tech.Pap., (1):21 p.
1964.

At the same time, the Commission selected the subject of future reports to be prepared by the Working Party, as follows 3/:

- Water temperature (including review of the effect of heated discharges)
- Dissolved oxygen and carbon dioxide
- pH
- Toxic substances including heavy metals, phenols and pesticides and herbicides.

The Commission further suggested that the subject of effluents acting in combination (synergism) to produce deleterious effects on fisheries should be considered.

The Fourth Session of the Commission, Belgrade 1966, after having studied the first draft of the review of literature on the effects of water temperature on aquatic life, gave priority to the preparation of the reports on water quality criteria for pH and for dissolved oxygen. With respect to the latter, it was mentioned that the task would be lengthy and costly and would require the assistance of highly qualified scientists 4/, but that it should be prepared as soon as sufficient funds became available to engage a full-time consultant.

For the preparation of the report on water quality criteria for pH the following experts were appointed to the EIFAC Working Party on Water Quality Criteria:

| | |
|--|-----------------------------------|
| Mr. J.S. Alabaster | (United Kingdom), <u>Convener</u> |
| Dr. Torsten B. Hasselrot | (Sweden) |
| Mr. A.V. Holden | (United Kingdom) |
| Mr. R. Lloyd | (United Kingdom) |
| Prof. R. Marchetti | (Italy) |
| Prof. H. Reichenbach-Klinke | (Fed. Rep. of Germany) |
| Dr. Tadeusz Backiel | (Poland), FAO Consultant |
| <u>FAO Secretariat:</u> Mr. William A. Dill - Secretary to EIFAC | |
| Mr. Jean L. Gaudet - Assistant Secretary to EIFAC | |

The Working Party used the same general basis for their work on which they had agreed for the preparation of their first report that:

"Water quality criteria for freshwater fish should ideally permit all stages in the life cycles to be successfully completed and, in addition should not produce conditions in a river water which would either taint the flesh of the fish or cause them to avoid a stretch of river where they would otherwise be present, or give rise to accumulation of deleterious substances in fish to such a degree that they are potentially harmful when consumed. Indirect factors like those affecting fish-food organisms must also be considered should these prove to be important."

3/ EIFAC Report, Third Session, 1964, p.10-11

4/ EIFAC Report, Fourth Session, 1966, p.12

The preparation of the present 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 as well as a few experts from outside the region, notably:

- Dr. Peter Doudoroff, Oregon State University (U.S.A.)
- Dr. William A. Spoor, University of Cincinnati (U.S.A.)
- Dr. André Coche, UNDP expert at Chilanga, Lusaka, Zambia.

This report will be presented to the Fifth Session of EIFAC which is scheduled to be held in Rome, on 20-24 May 1968.

1. INTRODUCTION

(1) 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 to 9.0 with the majority of water-courses being within the range 6.7 to 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.

(2) During the past 18 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 between 4 and 10, the safe range was 5 to 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 to 9 has been generally 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.

(3) 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 effect 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.

(4) 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 observations of mortalities where the pH value of the water was 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. LITERATURE SURVEY ON EFFECTS OF ACID pH VALUES

Direct Lethal Action:

2.1 Laboratory Data

Variables Affecting the Lethal Levels

(a) Concentration of free carbon dioxide

(5) 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 ppm for rainbow trout (*Salmo gairdnerii*) (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 ppm 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 ppm 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.

(b) Total hardness

(6) 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 ppm as CaCO_3 respectively (Lloyd and Jordan, 1964), and this variable is, therefore, of little importance when comparing published data on lethal levels.

(c) Size and age of fish

(7) In tests using blue-gill sunfish (*Lepomis macrochirus*) of different size groups, Cairns and Scheier (1958) found that the median lethal pH value for 4 days' exposure was 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 months old fish survived more than three times as long as those four months old, although the increase in resistance, in terms of the lethal pH value for these two age groups, was only 0.3 of a pH unit.

(d) Acclimation pH value

(8) 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. 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 slowly to a progressive decrease in the pH value of the water towards that normally considered to be lethal.

(e) Other factors

- (9) There are no reliable data for the effect of low dissolved oxygen concentration or of temperature on lethal acid pH values.

Summary of Toxicity Data

(a) Salmonids

(10) 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 to 6.2 in two-day tests, but since the water was acidified with free carbon dioxide, it is not clear whether dissolved carbon dioxide or hydrogen-ion in concentration was the main toxic agent. Dahl, K. (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 between 4.7 to 5.4, and 10 per cent died in the range 5.1 to 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 to 14 hours at a pH value of 3.3 and survived a pH value of 4.1 for 7 days (M. Grande, pers.comm.). 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 hours respectively; however, it is possible that more than 20 ppm 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.

(11) Grande, M. (pers.comm.) 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 brown trout ova 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.

(b) Other species

(12) Using a soft water acidified with nitric acid, Carpenter (1927) found that the survival time of minnows (Phoxinus phoxinus) was 28 hours at a pH value of 5.0, whereas a pH value of 5.2 had no effect in three days. Under similar conditions, but using hydrochloric acid, sticklebacks (Gasterosteus aculeatus) survived for about 5 1/2 days at a pH value of 4.8 and lived for as long as the control fish (10 days) at a pH value of 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.

(13) Although roach (Rutilus rutilus) 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 those 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 3.5 cm common carp (Cyprinus carpio) were killed within 4 hours at a pH value of 4.9, but the level of dissolved oxygen was low (2.4 ppm) 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).

(14) Volodin (1960) showed that the resistance of the various developmental stages of burbot (Lota lota) embryos to acid water varied, and successful development could only take place 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.

2.2 Field Observations

(a) Natural populations

(15) 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) found that the Eastern brook trout (Salvelinus fontinalis) was found in waters with a pH value of 4.1. However, although older fish might tolerate these low values, a survey by the Norsk Institutt for Vannforskning (Grande, M. pers.comm.) showed that, in Norway, salmonids were absent in waters where the pH value fell below the range 4.6 to 4.8; this may be the result of the susceptibility of the eggs and fry to these values (para.11).

(16) Vallin (1953) reports that in Lake Blamissus (northern Sweden) the water has a pH value of 2.8 to 3.1 and an iron content of 6 to 7 ppm Fe. in the surface waters; the flora and fauna are poor and no fish have been reported there. The water from this lake flows into Lake Sladen which has a pH value of 3.7 to 3.8, an iron content of 0.3 to 1.2 ppm Fe., and a slightly more abundant flora and fauna including roach, perch (Perca fluviatilis) and pike (Esox lucius) together with bream (Abramis brama) during the breeding season. However, in the spring, the pH falls to 3.5 to 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 (para.13) and it is possible that some long-term acclimation has taken place. In Lake 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 to 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 to 3.8 without adverse effect, although these values adversely affect carp.

(17) It would appear from these field observations that some species of fish can become acclimated to pH values lower than those found to be lethal in laboratory experiments.

(b) Fish kills

(18) 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 pH values which were actually responsible for the mortality.

(19) 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 to 4.4 containing between 1.2 to 10.5 ppm Fe.. Larsen and Olsen (1948) found that fish kills occurred in a trout hatchery when the pH value of the water was 6.2 to 7.0 and the water contained from 1.5 to 20 ppm Fe.; 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 ppm Fe. 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 (EIFAC 1964), 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 (Lepomis cyanellus) and largemouth bass (Micropterus salmoides) found that high concentrations of precipitated ferric hydroxide (up to 27 ppm Fe.) 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 to 4.7. There are, to our knowledge, no controlled laboratory experiments on the toxicity of ferric hydroxide suspensions to fish.

(20) 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 ppm) 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.

(21) Vallin (1962) stated that when the River Morrum in southern Sweden (pH value 6.0) was polluted by an increased discharge from a sulphite cellulose factory, the pH value fell to between 4.0 and 4.5 and mortalities of tench, roach and bream were recorded, whereas perch and pike were more resistant. Neutralisation 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.

(22) 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 Mode of Toxic Action

(23) 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 the complete destruction of the gill epithelium, a rather rapid degeneration since this pH value has been found to be the 96-hour median tolerance limit (Ellis, 1937).

(24) Lloyd and Jordan (1964) found no evidence of gill tissue damage or precipitated mucus in rainbow trout taken at death after a 7½-hour exposure to a solution of pH value 3.4. Dahl, K. (1927) found that salmon held at a pH value of 4.7 to 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 hours 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 of 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 ppm free carbon dioxide (Lloyd and Jordan, 1964). These authors were of the opinion that, in the rainbow trout, the cause of death is acidaemia.

(25) There are few data on the sub-lethal 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.

(26) The life cycles of some fish parasites are affected by pH value. Ichthyophthirius can reproduce normally within the pH range 7.2-8.7, and can only become attached to the host fish 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 to 8.0.

2.4 Avoidance Reactions

(27) 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.

(28) Jones (1948) found that sticklebacks definitely avoided acid waters with pH value 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 to 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.

(29) Höglund also found that pH values in the range 5.6 to 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 to 6.6) and from an alkaline lake (pH values 8.4 to 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.

(30) 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.

(31) 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.

2.5 Effect on Growth

(32) It is well known that the growth rate of fish in acid waters is usually less than that under alkaline conditions. There is no evidence to suggest that this follows from a direct effect of hydrogen-ion concentration on the growth rate. 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 Pentelov (1944). From data supplied by the Department of Agriculture and Fisheries of Eire (Twomey, E., pers.comm.), 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.

(33) 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, pers.comm.). Parsons (1952) reports "amazing growth" of blue-gill sunfish in a pool at a pH value of 4.5.

(34) 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 River Liffey compared with alkaline reaches further downstream. There are no reports of experiments to measure the growth of batches of fish fed the same amount of food but kept in waters of widely different pH values.

2.6 Effect on Food Supply

(35) 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).

(36) 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 (Nees, 1949 - ORSANC0, 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 to 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.

(37) 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 with a pH value of 2.3, 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 specialised flora and fauna developed below 5.0 to at least as low as 2.9; Robeck (1962) 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).

2.7 Toxicity of Other Poisons

(38) 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 ionised and an unionised 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 Pentelov, 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 being 6.4 and 21.8 ppm Zn, respectively in water of total hardness of 100 ppm 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.

(39) 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).

(40) 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). Sub-lethal 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 sub-lethal levels of free carbon dioxide increases the sensitivity of fish to other dissolved poisons.

(41) 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 I.

(42) 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.

3. LITERATURE SURVEY ON EFFECTS OF ALKALINE pH VALUES

Direct Lethal Action

3.1 Laboratory Data

Variables Affecting the Lethal Levels

(a) Effect of size

(43) Using sodium hydroxide, Cairns and Scheier (1958) found that the 4-day median tolerance limits of pH value for blue-gill sunfish were 10.5, 10.5 and 9.9 for fish with mean lengths of 3.9, 6.1 and 14.2 cm 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.

(b) Acclimation pH value

(44) 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 24-hour 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.

(c) Dissolved oxygen concentration

(45) 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 blue-gill sunfish showed distress, and some died, in water of pH value 9.6 and a dissolved oxygen of 5 ppm, but were unaffected by a pH value of 9.5 and a dissolved oxygen concentration of 10 ppm. 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 the concentration of dissolved oxygen 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.

(d) Other factors

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

Summary of Toxicity Data

(a) Salmonids

(47) 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 solutions; a pH value of 9.6 gave a median lethal period of 20 hours, 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 1½ 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).

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

(b) Other species

(49) Bandt (1936), in experiments similar to that in para.(47), 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 to be 9.2-9.6. Sanborn (1945), using sodium hydroxide, found that goldfish died within 3-20 hours 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 minnows (Phoxinus phoxinus) were slightly more sensitive than brown trout to the alkaline effluent described in paragraph (47).

(50) 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).

3.2 Field Observations

(a) Fish kills

(51) 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 river 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 (para.45). 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.

(52) 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 Lake Lyngby (Denmark) where the pH value rose to between 10.3 and 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 (Lucioperca lucioperca) occurred in Lake Ronninge (south of Stockholm) in 1966 when the pH value of the water rose to between 8.4 and 9.5 (Hasselrot, T., pers. comm.); it is thought, however, that toxins from the accompanying algal bloom may have contributed to the death of the fish.

(b) Natural populations

(53) 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 (Reichenbach-Klinke, H., pers. comm.).

(54) 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.

3.3 Mode of Toxic Action

(55) According to several authors (i.e., Kuhn and Koecke, 1956 - Bandt, 1936 - Schäperclaus, 1956) a toxic action of hydroxyl-ions is to destroy the gill and skin epithelium. Eicher (1946) reported that trout found dying at a pH value of 10.2 (para. 52) 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.

3.4 Avoidance Reactions

(56) Jones (1948) showed that sticklebacks avoided solutions of sodium hydroxide with a pH value above 11.0 but the range 7 to 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 in paragraph 30 are pertinent here also.

3.5 Effect on Growth

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

3.6 Effect on Food Supply

(58) 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 (para. 54).

3.7 Toxicity of Other Poisons

(59) 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 ionisation. 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.

(60) In summary, it appears that 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, 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 super-saturated 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.

4. CONCLUSIONS

4.1 Tentative Water Quality Criteria

(61) 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.

(62) 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 summarised in Table I; 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.

4.2 Scope For Further Research

(63) 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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TABLE I. SUMMARY OF THE EFFECT 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, in the long term, persistence of these values will be detrimental to such fisheries. 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 ppm, or the water contains iron salts which are precipitated as ferric hydroxide, the precise toxicity of which is not known. |
| 6.0 - 6.5 | Unlikely to be harmful to fish unless free carbon dioxide is present in excess of 100 ppm. |
| 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.

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