



**WATER QUALITY CRITERIA
FOR EUROPEAN FRESHWATER FISH**

Report on chlorine and freshwater fish



**EUROPEAN INLAND FISHERIES ADVISORY COMMISSION
FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS
ROME, 1973**

EUROPEAN INLAND FISHERIES ADVISORY COMMISSION (EIFAC)

EIFAC documents are issued in four series:

EIFAC Report

Report of each session, in English and French.

EIFAC Technical Paper

Selected scientific and technical papers, including some of those contributed as working documents to sessions of the Commission or its sub-commissions. Published in English and French.

EIFAC Occasional Paper

Papers of general interest to the Commission. Published in the language submitted, either English or French.

EIFAC Newsletter

Notes and comments on the activities of EIFAC and its Member Nations, FAO and other organizations: a forum for the exchange of news, ideas and experience. Published in English and French.

Copies of these documents can be obtained from:

Secretary
European Inland Fisheries Advisory Commission
Department of Fisheries
FAO
Via delle Terme di Caracalla
00100 Rome, Italy

WATER QUALITY CRITERIA FOR EUROPEAN FRESHWATER FISH

Report on Chlorine and Freshwater Fish

prepared by

European Inland Fisheries Advisory Commission
Working Party on Water Quality Criteria
for European Freshwater Fish

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS
Rome, 1973

PREPARATION OF THIS DOCUMENT

The background of this paper is described in the Foreword to the report itself. The paper was prepared by the European Inland Fisheries Advisory Commission (EIFAC) Working Party on Water Quality Criteria for European Freshwater Fish. The report is being issued in this series where the first seven documents of the Working Party were published: "Report on finely divided solids and inland fisheries", EIFAC Tech. Pap., (1):21 p., 1964; "Report on extreme pH values and inland fisheries", EIFAC Tech. Pap., (4):24 p., 1968; "Report on water temperature and inland fisheries based mainly on Slavonic literature", EIFAC Tech. Pap., (6):32 p., 1968; "List of literature on the effect of water temperature on fish", EIFAC Tech. Pap., (8):8 p., 1969; "Report on ammonia and inland fisheries", EIFAC Tech. Pap., (11):12 p., 1970; "Report on monohydric phenols and inland fisheries", EIFAC Tech. Pap., (15):18 p., 1972; "Report on dissolved oxygen and inland fisheries", EIFAC Tech. Pap., (19):10 p., 1973.

Distribution:

FAO Department of Fisheries
FAO Regional Fishery Officers
Selector EI/E only

Bibliographic Entry:

EIFAC. Working Party on Water
Quality Criteria for European
Freshwater Fish (1973)
EIFAC Tech. Pap., (20):11 p.
Water quality criteria for European
freshwater fish. Report on chlorine
and freshwater fish

FAO - European Inland Fisheries Advisory
Commission. Report of working party.
Inland water - Europe. Water quality
criteria - chemistry and toxicology
of chlorine. Poisoning, lethal and
sublethal effects on coarse fish and
salmonids - embryo, larvae, fry,
fingerling and adult, behaviour and
spawning. Effects on aquatic inverte-
brates and plants. Effects of environ-
mental factors - dissolved oxygen, pH,
temperature, hardness, salinity.
Selected bibliography.

CONTENTS

	<u>Page</u>
FOREWORD	ii
SUMMARY	vi
1. INTRODUCTION	1
2. CHEMISTRY OF CHLORINE IN WATER	1
2.1 Terminology	3
3. TOXICOLOGY OF CHLORINE IN WATER	4
3.1 Mode of action and symptoms of acute poisoning	4
3.2 Lethal effects on fish	4
3.3 Effects of environmental factors	5
3.4 Sublethal effects on fish	6
3.5 Effects of mixtures of chlorine with other poisons	6
3.6 Effects on aquatic invertebrates and plants	7
4. FIELD OBSERVATIONS	7
5. SUMMARY OF DATA	8
6. TENTATIVE WATER QUALITY CRITERIA	8
7. REFERENCES	9

FOREWORD

This is the eighth technical paper on water quality criteria for European freshwater fish prepared for the European Inland Fisheries Advisory Commission (EIFAC) - an inter-governmental organization with a membership of 23 countries. The Commission has been active in its efforts to establish water quality criteria for European freshwater fish since its Second Session, Paris, 1962, when it took note of a recommendation of the United Nations 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 seven reports on water quality criteria ^{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 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.

-
- ^{1/} See, respectively: EIFAC Report, Second Session, 1962, p. 21-2
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
Report on Extreme pH Values and Inland Fisheries, EIFAC tech.Pap., (4):18 p., 1968
Report on Water Temperature and Inland Fisheries based mainly on Slavonic Literature,
EIFAC tech.Pap., (6):32 p., 1968
List of Literature on the Effect of Water Temperature on Fish, EIFAC tech.Pap., (8):8 p.,
1969
Report on Ammonia and Inland Fisheries, EIFAC tech.Pap., (11):12 p., 1970
Report on Monohydric Phenols and Inland Fisheries, EIFAC Tech.Pap., (15):18 p., 1972
Report on Dissolved Oxygen and Inland Fisheries, EIFAC Tech.Pap., (19):10 p., 1973

This Working Party prepared its first report on finely divided solids and inland fisheries (see footnote 2/) which was submitted to the Commission at its Third Session, Scharfling am Mondsee, 1964, where it was unanimously approved 3/.

The Third Session then suggested that the following studies be considered by the Working Party:

- water temperature (including a review of the effect of heated discharges);
- dissolved oxygen and carbon dioxide; pH; toxic substances including heavy metals, phenols and pesticides and herbicides.

Elevated temperature was given first priority, and a draft on this subject was prepared by the Working Party during the following inter-sessional period. (At the Third Session the work of the Commission was re-organized into three Sub-Commissions, one of which, Sub-Commission III - Fish and Polluted Water - regrouped all the activities of EIFAC in the field of water pollution. The Working Party on Water Quality Criteria for European Freshwater Fish has since functioned under this Sub-Commission.)

The Fourth Session of the Commission, Belgrade, 1966, after having studied this first draft of review of literature on the effects of water temperature on aquatic life concluded that such a review required more effort than the resources of the Commission permitted at the time. Meanwhile, it suggested that a water quality report for extreme pH values be prepared for the next Session of EIFAC, and that a report on dissolved oxygen be prepared when funds become available for a full-time consultant 4/.

The report on extreme pH values and inland fisheries (see footnote 2/) was published in 1968, in time for presentation at the Fifth Session of EIFAC, Rome, 1968, where it was unanimously approved 5/.

At its Fifth Session the Commission again reviewed priorities for future studies and decided to undertake critical reviews on the effects of ammonia and phenols on freshwater fishes.

It also recommended that guidance as to its future work in the field of water pollution control, including the development of water quality criteria, be taken from the FAO/EIFAC Symposium on the Nature and Extent of Water Pollution Problems affecting Inland Fisheries in Europe which was later held in Jablonna, Poland, 15-16 May 1970, just before the Sixth Session of EIFAC.

The Fifth Session also approved in draft a report on water temperature and inland fisheries based mainly on Slavonic literature. The report was published in November 1968 as the third in the EIFAC water quality criteria series, and was followed in 1969 by the fourth publication in the series, a list of literature on the effect of water temperature on fish. (See footnote 2/ for both papers.)

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

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

5/ EIFAC Report, Fifth Session, 1968, pp. 14-15

Following the Jablonna Symposium 6/, the Sixth Session of EIFAC, Krakow, 1970, again reviewed the Commission's programme with respect to water quality criteria 7/. Noting that a report on ammonia was almost complete, it approved continuance of work on phenols, and the current work begun by the Working Party on copper, zinc and mercury, and recommended the addition of cyanides, detergents, chlorine and hydrocarbons as items for future reviews. It also recommended eventual resumption of work on water temperature and the preparation of a review based on a critical worldwide report on dissolved oxygen prepared for FAO 8/.

After the Sixth Session of EIFAC, the EIFAC Working Party has published reports on ammonia and monohydric phenols as the fifth and sixth reviews in this EIFAC series of water quality papers 2/ which were presented to the Seventh Session of EIFAC (Amsterdam, 1972 9/) where they were unanimously approved.

Since the Seventh Session, the EIFAC Working Party on Water Quality Criteria has drafted reviews on dissolved oxygen, chlorine and zinc which were studied at its 11th and 12th meetings held in Rome (15-17 January 1973) and Karlsruhe (25 May 1973), respectively. The report on dissolved oxygen has been published as the seventh review of this series 2/ and will be presented to the Eighth Session of EIFAC, which is scheduled to be held in U.K. (Aviemore, Scotland, 6-10 May 1974). The Working Party is continuing an active literature search on mercury and copper, and is finalizing its review on zinc and inland fisheries.

The eighth review, which follows, is the one on chlorine and freshwater fish. For the preparation of this report, the following experts were appointed to the EIFAC Working Party on Water Quality Criteria:

Mr. J.S. Alabaster	(United Kingdom), Convener
Dr. D. Calamari	(Italy)
Dr. M. Grande	(Norway)
Dr. T.B. Hasselrot	(Sweden)
Mr. R. Lloyd	(United Kingdom)
Dr. A.W. Lysak	(Poland)
Dr. W.K. Besch	(Germany, Fed. Rep.)

FAO Secretariat:

Mr. J.-L. Gaudet - Acting Secretary to EIFAC

The preparation of the present report on chlorine and freshwater fish was accomplished largely by the Water Pollution Research Laboratory (Stevenage, U.K.) which prepared the basic manuscript to be reviewed by the members of the Working Party.

-
- 6/ Holden, A.V. and R. Lloyd (1972), Symposium on the Nature and Extent of Water Pollution Problems affecting Inland Fisheries in Europe. Synthesis of National Reports, EIFAC tech.Pap., (16):20 p.
- 7/ EIFAC Report, Sixth Session, 1970, p. 13
- 8/ Doudoroff, Peter and Dean L. Shumway (1970), Dissolved Oxygen Requirements of Freshwater Fishes. FAO Fish.tech.Pap., (86):291 p.
- 9/ EIFAC Report, Seventh Session, 1973, p. 18

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 they prove to be important."

This report will be presented to the Eighth Session of EIFAC (Aviemore, Scotland, United Kingdom).

The Seventh Session of EIFAC (see footnote 2/) suggested as possible future subjects for reviews cadmium and lead.

SUMMARY

Chlorine as hypochlorous acid and chloramines is toxic to aquatic life. Coarse fish species, invertebrate organisms and plants are generally more resistant to chlorine than salmonids, although the production of young *Daphnia* is reduced at a concentration of 0.0035 mg/l (0.0004-0.0014 mg HOCl/l).

From the limited data available, it seems that concentrations of chlorine greater than 0.008 mg HOCl/l could be harmful or lethal within 4 days to both salmonoid and coarse fish, whereas 0.004 mg HOCl/l has been endured by sensitive species of fish for 5 days, although with some decline in the normal activity.

The toxicity of chlorine to fish is increased by a reduction in the concentration of dissolved oxygen, and little changed by increase in salinity up to 50 percent sea water, but there are few or no data available on the effect of temperature, pH, and water hardness.

Avoidance behaviour of rainbow trout under experimental conditions has been slight at a concentration of chlorine of 0.001 mg/l (0.0002-0.0008 mg HOCl/l) and marked at 0.001-0.008 mg HOCl/l.

Chlorine is too reactive to persist for long in most streams and therefore the upper limit for fish survival might be set closer to the lethal levels than might otherwise be the case, especially as avoidance behaviour is likely to afford additional protection to the fish from regions of high concentration. Consequently it is tentatively suggested that an acceptable upper limit would be 0.004 mg HOCl/l, because it should result in little or no mortality of fish, perhaps have only a minor effect on fish behaviour and not be high enough to be damaging to the majority of fish food organisms. The amount of total chlorine corresponding to this concentration varies according to the temperature and pH value of the water, as shown in the following table:

Temperature (°C)	pH			
	6	7	8	9
5	0.004	0.005	0.011	0.075
25	0.004	0.005	0.016	0.121

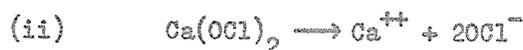
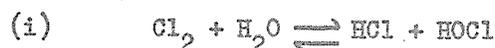
Since chlorine may react with thiocyanide to produce lethal concentrations of hydrogen cyanide and/or cyanogen chlorine and concentrations of chlorine as low as 0.001 mg/l in the presence of phenols are likely to produce taints in the flesh of fish, an upper limit of less than 0.004 mg HOCl/l might be necessary in the presence of these other poisons.

1. INTRODUCTION

(1) Chlorination (by elemental chlorine (Cl_2), hypochlorites, or chloramines) is used in disinfecting and removing unwanted tastes and odours from drinking water. Sufficient chlorine (defined in para. 7) is added to give a small excess for the destruction of pathogenic bacteria, but this excess can make municipal tap waters unsuitable for fish-keeping purposes. Chlorination is also used in the textile and paper-pulp industries for bleaching and slimicidal purposes, and in sewage treatment to reduce either odour, the density of 'ponding' algae on filter beds, or the numbers of bacteria in effluents discharged to surface waters. The amount of chlorine added to sewage is insufficient to oxidize the waste completely (i.e., the chlorine 'demand' is not fully satisfied) and there is no excess chlorine to impair the biological processes essential for treatment, or the life in the waters to which the effluent is discharged. Chlorine is also added to cooling waters, and other industrial waste waters, to reduce or eliminate growths of algal or bacterial 'slimes' in cooling towers and associated systems, and to swimming pools for the purpose of disinfection. Literature on the effects of chlorine on fish has been summarized previously by Southgate (1948), Doudoroff and Katz (1950), Liebmann (1960), McKee and Wolf (1963), Jones (1964) and Zillich (1972), and that on freshwater organisms other than bacteria by Ewins (1972).

2. CHEMISTRY OF CHLORINE IN WATER

(2) When elemental chlorine or hypochlorite compounds, e.g., calcium hypochlorite, are added to water at pH values above about 5, reactions rapidly occur, resulting in the formation of hypochlorous acid (HOCl) in equilibrium with hypochlorite ions (OCl^-) as shown by the following two sets of equations:



(The presence of the extremely fugitive elemental chlorine (Cl_2) can be ignored for the purpose of the present review.)

(3) Since the toxic chemical species in solution in chlorine poisoning is probably hypochlorous acid, a weak acid, the toxicity of any solution containing chlorine will depend on the pH of the solution, because it markedly influences the degree of dissociation. Ionization constants (pK_a) for temperatures between 0°C and 30°C are given in Table I, and the proportions of HOCl and OCl^- in solution at 5°C and 25°C at pH values between 5 and 9 shown in Fig. 1.

Table I

Ionization constants (pK_a) for hypochlorous acid at temperatures between 0°C and 30°C (Sillén and Martell, 1964)

Temp. ($^\circ\text{C}$)	0	5	10	15	20	25	30
pK_a	7.83	7.75	7.69	7.63	7.58	7.54	7.50

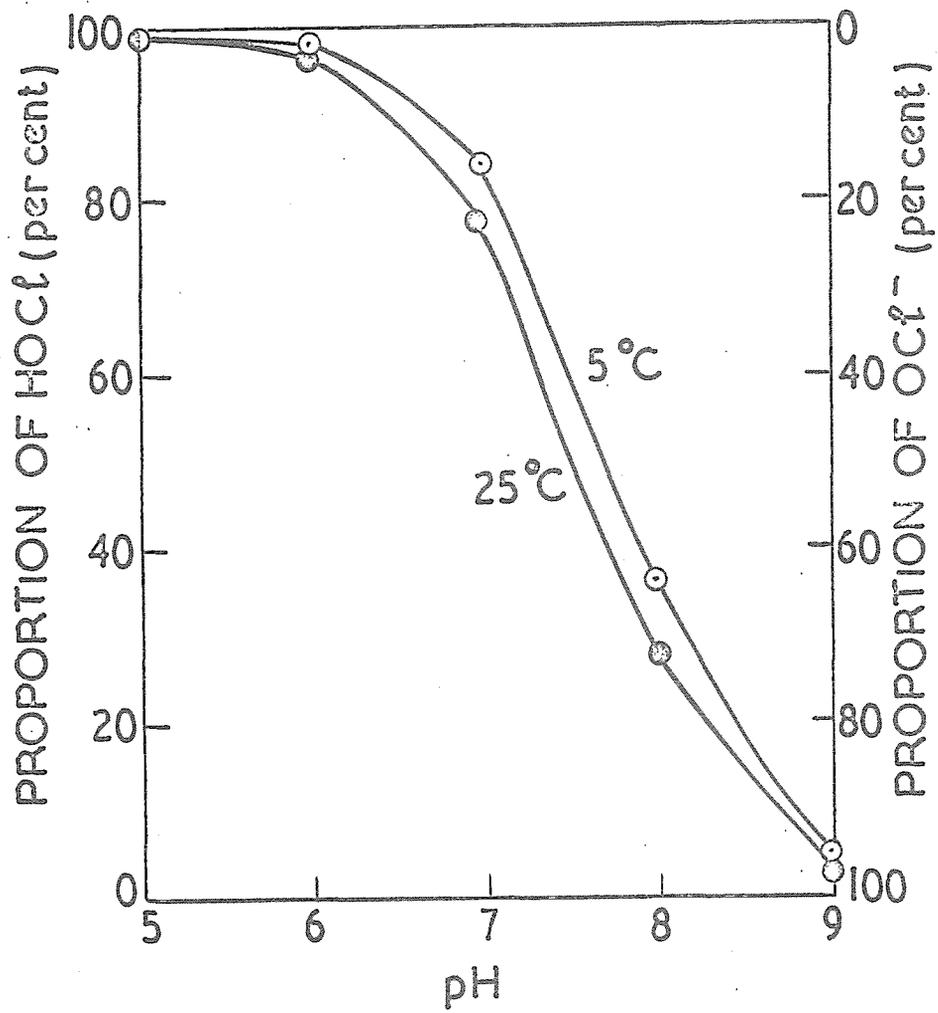
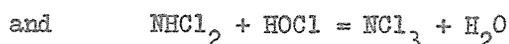
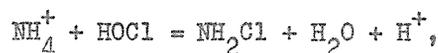


Fig. 1 Proportion of HOCl and OCl⁻ in solution at temperatures of 5° and 25° C and pH values between 5 and 9

(4) Below pH 7.5, therefore, at all temperatures at which the majority of European fish species are likely to be found, the greater part of any chlorine present will be in a toxic form. When chlorine (as HOCl) is added to water containing ammonia it will, in the absence of other oxidizable substances, initially form monochloramine (NH_2Cl), dichloramine (NHCl_2), trichloramine or nitrogen trichloride (NCl_3), or a mixture of these compounds. Formation of the more highly substituted derivatives is favoured by increased acidity of solution and increased gravimetric ratio of chlorine to ammoniacal nitrogen according to Palin (1950) who describes the following reactions as taking place:



(5) In non-acidic waters further addition of chlorine gives as main products probably chloride ion and elemental nitrogen. The concentration at which any particular compound will be present is difficult to predict, although probably at the normal pH values of natural waters only relatively small amounts of nitrogen trichloride (a poison known to have chronic systemic effects) are formed. However, it appears that chloramines slowly reach equilibrium with a small concentration of hypochlorous acid which possibly accounts for their toxicity to fish.

(6) Since sewage effluents almost always contain ammonia the effects of chlorine should not be considered without taking into account the effects of chloramines, which though less toxic than chlorine are more persistent. Hypochlorous acid and hypochlorite ion decompose slowly in solution forming chloride ion and oxygen, a process accelerated in the presence of sunlight, and they are more readily removed by organic matter than chlorine and chloramines.

2.1 Terminology

(7) When chlorine is present in water in a form in which it is available to act as an oxidant it may be described in the literature as "free-", "available-", "active-", or "residual-" chlorine, or by some combination of these adjectives. When present as chloramines it may also be referred to as "bound-" chlorine. These forms can conveniently be classified as:

- (a) Free available chlorine, that present as an equilibrium mixture of hypochlorite ions (OCl^-) and hypochlorous acid (HOCl),
- (b) Combined available chlorine, that present in chloramines or other compounds with an N-Cl link, and
- (c) Total available chlorine, essentially the sum of (a) and (b).

(8) For brevity in this report the term "chlorine" is used to refer to the total available chlorine when this cannot be, or does not need to be, more closely defined. It does not, however, include elemental chlorine (Cl_2). Specific compounds are named whenever possible. It should be noted that some of these, e.g., dichloroisocyanurates (used for the disinfection of swimming-bath waters) may react as free available chlorine in commonly used methods of chemical analysis.

(9) Where possible the concentration at which hypochlorous acid may be present has been estimated, but this cannot always be done because many reports fail to give adequate details of the chlorine source and of temperature and pH of the solutions.

3. TOXICOLOGY OF CHLORINE IN WATER

3.1 Mode of action and symptoms of acute poisoning

(10) Various authors have described how fish exposed to chlorine solution become restless before losing equilibrium and dying. No direct information on the chemical basis of chlorine toxicity to fish is available, but enzymes within the cell contain sulphhydryl (-SH) groups essential to their activity and these become oxidized almost immediately by chlorine in both animals and plants, enzymatic activity being irreversibly abolished (Green and Stumpf, 1946) because of the strength of the covalent bond formed (Albert, 1965). This may explain why once equilibrium has been lost, the fish do not recover when placed in clean water (Taylor and James, 1928; Panikkar, 1960; Pike, 1971).

3.2 Lethal effects on fish

(i) Embryos, larvae and fry

(11) Blake (1930) showed that eyed ova of brown trout (Salmo trutta) incubated at 3-5°C and exposed to 10 mg/l of chlorine for 30 min showed a slight increase in mortality on hatching (1.2 percent compared with 0.6 percent among controls).

(12) In general, newly hatched larvae are more susceptible than eggs. Grande (1966) reported that in a very soft water (14 mg/l as CaCO₃) at 9°C and a pH of 6.4 a chlorine concentration of 0.07 mg/l was not lethal within 3 days to salmon (Salmo salar) fry exposed immediately after completion of absorption of the yolk. At 0.1 mg/l, however, the mean period of survival was 1.2 days, at 0.13 mg/l it was 8 h, and 0.3 mg/l only 3 h. (The maximum concentration of HOCl under these conditions would be about 94 percent of the given chlorine concentration.) Scheuring and Stetter (1950/51) also report that trout died in 16-24 h at a concentration of 0.1 mg/l at 10-12°C.

(13) M. Grande (personal communication) also reported mortality of fry of brown trout, rainbow trout (Salmo gairdneri), Arctic char (Salvelinus alpinus), and Atlantic salmon in chlorinated tap water at about 0.1 mg/l of chlorine (equivalent to about 0.09 mg/l of HOCl) over a period of several days. "Trout" fry were killed in 48 h by 0.05-0.06 mg/l of "chlorine" but 0.01 mg/l did not prove fatal over a period of two weeks (Coventry et al., 1935).

(ii) Fingerling and adult salmonids

(14) Rainbow trout fingerlings and yearlings died in 2 h at 0.3 mg/l and in 4-5 h at 0.25 mg/l (Taylor and James, 1928). At a dissolved oxygen concentration of 10-11 mg/l, temperature of 15°C, and pH of either 6.3 or 7.0, a mixture of HOCl, NH₂Cl and NHCl₂ in which the former predominated, was more toxic than one in which either NH₂Cl or a mixture of mono- and dichloramines predominated, the concentration at which the mixture containing predominantly HOCl killed rainbow trout in a given time interval being about one third of that in which NH₂Cl predominated. The 7-d LC50 of a solution containing chlorine mainly as NH₂Cl was 0.08 mg/l (Merkens, 1958). Studies with 4-month old silver salmon (Oncorhynchus kisutch) showed that 76 percent of the fish were killed at pH 7.6 by 0.2 mg/l chlorine (= 0.1 mg/l HOCl) in about 19 h (Department of Fisheries, Washington, 1960). Pike (1971) found that brown trout (12.5-18 cm long) were all killed within 24 h by exposure for only 2 min to chlorine concentrations greater than 0.04 mg/l at 11°C. With continuous exposure the median period of survival at 0.03 mg/l was less than 7.5 h, at 0.02 mg/l less than 10.5 h, and at 0.01 mg/l (0.008 mg HOCl/l) less than 45.5 h. Dandy (1972) showed that at 0.35, 0.08, and 0.04 mg/l chlorine (0.0034 mg HOCl/l) survival times of brook trout (Salvelinus fontinalis) were 9, 18, and 48 h respectively, while at 0.005 mg/l (0.004 mg HOCl/l) the fish survived at least 7 days.

(iii) Fingerling and adult coarse fish

(15) Zimmerman and Berg (1934) observed that goldfish (Carassius auratus) were killed within 8 h by exposure to water containing 1.0 to 1.5 mg/l of chlorine and replaced at a rate of

4 l/min; at a pH of 7.9, a temperature of 25°C, and a concentration of 2 mg/l (0.64 mg HOCl/l) they were killed within 17-48 h. Wakabayashi and Imaoka (1968) reported that goldfish were killed by unrenewed solutions having initial concentrations of 0.6 to 0.7 mg/l chlorine. At 1 mg/l chlorine (0.32 mg HOCl/l) some were killed in 96 h (Ellis, 1937), and at 0.1-0.2 mg/l chlorine they survived for an "extended" period (Schaut, 1939). Taylor and James (1928) also report that they were not affected in 42 h by 0.25 mg/l.

(16) Ebeling (1931) observed the mortality of six species of fish over a period of 4 days in ponds having a temperature of 4.5-7°C, pH of 7.2-7.3, and a nominal concentration of chlorine of about 1.0 mg/l (0.7 mg HOCl/l), the dissolved oxygen concentration being "constant"; pike (Esox lucius) died within 30 h, rainbow trout within 37-40 h, rudd (Scardinius erythrophthalmus) within 41-82 h, and about 80 percent of the common carp (Cyprinus carpio), 20 percent of the tench (Tinca tinca), and one of the eels (Anguilla anguilla) died after 100 h. Zimmerman and Berg (1934) also observed that 1.2 mg/l killed large common carp. Scheuring and Stetter (1950/1) report that at constant concentration of 0.15 mg/l trout were killed within 14 days, whereas tench, common carp, crucian carp (Carassius carassius), pike and pike perch (Lucioperca lucioperca) survived between 6 and 37 days without apparent harm.

(17) Thus coarse fish appear to be much more resistant to high concentrations of chlorine than salmonids.

3.3 Effects of environmental factors

(i) Dissolved oxygen

(18) The median period of survival of rainbow trout in a given concentration of chlorine (added as sodium hypochlorite) was found to be shorter at low concentrations of dissolved oxygen than it was at high (Department of Scientific and Industrial Research, 1958). Trout in solutions at pH 7.4 containing about 0.1 mg/l chlorine (the lowest concentration tested, and equivalent to a maximum HOCl concentration of about 0.06 mg/l) were killed in 1 000 min at a dissolved-oxygen concentration of 90 percent of the air saturation value (ASV) compared with 80 min at 40 percent ASV. At pH 6.3 (when the concentration would be about 0.09 mg HOCl/l) the respective survival times were 700 and 53 min. (Some of the chlorine may have reacted with ammonia excreted by the trout and been present as chloramines.)

(ii) pH

(19) No information is available on the effects of pH on the toxicity to fish of a given concentration of molecular HOCl, but the data of Merckens (1958) on the toxicity of mixtures of chlorine and chloramines to rainbow trout suggest that there is no effect.

(iii) Temperature

(20) No information is available on the effect of temperature on the toxicity of chlorine, but there is a suggestion that toxicity might be greatest at low temperatures (Ebeling, 1931).

(iv) Hardness

(21) There is no information on the effect of hardness on the toxicity of chlorine to fish.

(v) Salinity

(22) At a concentration of total halogen (some of which would be bromine displaced by chlorine) of 1.34 mg/l total chlorine and 0.95 mg/l "free chlorine" (0.19 mg HOCl/l) rainbow trout in 50 percent sea water (salinity 33.34 g/1 000 g) at a pH of 8.3 had a median period of survival of 52 min (Department of Scientific and Industrial Research, 1958). It was concluded that the toxicity of the halogens resulting from the addition of chlorine to "sea water" was only slightly less than that of chlorine in fresh water. "Critical"

(presumably lethal) levels of chlorine in sea water were found to be 0.05 mg/l for chinook salmon (Oncorhynchus tshawytscha) and pink salmon (O. gorbuscha), while 0.09 mg/l killed silver salmon within 216 h (Department of Fisheries, Washington, 1960).

3.4 Sublethal effects on fish

(i) Behaviour

(23) Fish may avoid or be attracted to waters containing low concentrations of chlorine; Sprague and Drury (1969) found that rainbow trout showed a slight degree of avoidance of water containing chlorine at a concentration of 0.001 mg/l but that this reaction became more marked at 0.01 mg/l (12-d LC50), and strong at 1 mg/l (4-h LC50); however, at 0.1 mg/l (4-d LC50) preference was shown for the chlorinated water. Since the reported variation in pH of the test solutions was from 7.0 to 8.4, the percentage of HOCl present could have been between 80 and 20 percent of the nominal chlorine concentration. The reason for this behaviour is unknown, but Dandy (1972), who measured the activity of brook trout in the presence of chlorine, found that activity increased at 0.35 mg/l (9-h LC50) and 0.08 mg/l (18-h LC50), and suggested this would increase the possibility of fish moving randomly into fresh water given the choice, whereas at 0.04 mg/l (0.034 mg HOCl/l) (2-d LC50) activity was depressed, which would reduce the chances of movement into clean water. There was also a greater decline in activity than found in controls in fish kept at 0.005 mg/l (0.004 mg HOCl/l) (not lethal to fish at 7 days) for more than 5 days.

(ii) Spawning

(24) The only precise data on the effects of chlorine on spawning are the unpublished results of Arthur and Eaton (quoted by Zillich, 1972) who found that chloramines at concentrations as low as 0.085 mg/l nearly eliminated spawning of the fathead minnow (Pimephales promelas) and that at 0.043 mg/l the number of spawnings per female and the number of eggs per spawning were reduced.

(iii) Taste and odour

(25) There is no evidence that the presence of chlorine on its own can produce taints in the flesh of fish, but when present with phenols the resulting chlorinated phenols can produce taints at concentrations as low as 0.001 mg/l (EIFAC, 1972).

3.5 Effects of mixtures of chlorine with other poisons

(26) Schaut (1939) found that following chlorination of solutions containing potassium thiocyanide at a concentration of 6 mg/l "minnows" were affected the same as by 3.6 mg/l of sodium cyanide, and considered this to be a consequence of hydrogen cyanide production:



Allen, Blezard and Wheatland (1948) studied the same phenomenon and concluded that the poison was more likely to be cyanogen chloride:



(27) Both investigations showed, however, that fish which had lost equilibrium in such mixtures recovered in poison-free water, which suggests that the effect was not produced by chlorine, which typically has an irreversible reaction (para. 10) but rather by cyanide (a poison whose reaction is reversible).

(28) There is no information on the effect of chlorine in the presence of other poisons with which it does not react chemically.

3.6 Effects on aquatic invertebrates and plants

(29) Much of the information available on invertebrates will not be quoted because it relates to organisms that are not important as food for fish and to nominal concentrations that are rapidly lethal (Ewins, 1972).

(30) Among the crustacea, Cyclops sp. were stunned but recovered after 24 h exposure to 1 mg/l chloramines (Phillips, 1966) and in soft water Daphnia magna was killed in 72 h at 0.5 mg/l chlorine (Ellis, 1937). For Gammarus pseudolimnaeus exposed to chlorine for a period of 15 weeks at 23°C, pH between 7.2 and 8.6, dissolved oxygen concentration between 5.2 and 10.4 mg/l, and total hardness of 44 to 48 mg/l, there was marked reduction in survival and no production of young at 0.035 mg/l and reduction in the number of young produced per female at 0.0035 mg/l (0.0004-0.0014 mg HOCl/l) (Arthur and Eaton, 1971). Asellus sp. were stunned but recovered after 24 h exposure to 2 mg/l chloramine yet were apparently unaffected by exposure for this period to 2 mg/l free chlorine (Phillips, 1966). Copulation of A. aquaticus was inhibited by 0.5 mg/l (Holland, 1956). 'Crayfish' were killed by 1.2 mg/l chloramines (Coventry, Shelford and Miller, 1935).

(31) There was an 85 percent kill of Chironomus spp. larvae in 24 h at a concentration of chlorine of 0.65 mg/l (Buchmann, 1932).

(32) Among the molluscs, Potamopyrgus jenkinsi appeared dead after exposure to 100 mg/l for 24 h, but some recovered when transferred to fresh water (English, 1958).

(33) Little information is available on the effects of chlorine on higher plants on which fish may feed, but Zimmerman and Berg (1934) reported that Gabomba caroliniana and Elodea canadensis became slightly chlorotic after 6 days' exposure to a chlorine concentration of 3 mg/l (but not at lower concentrations). However, the concentrations fell to as little as 5 percent of the nominal values within 3 h of preparation, suggesting that the plants may be more susceptible than these tests indicate. Initial concentrations of 0.25-0.3 mg/l of chlorine have controlled the growth of algae (McKee and Wolf, 1963).

(34) It is therefore clear that the resistance of most species of invertebrates and some plants to acutely lethal levels of chlorine is greater than that of fish.

4. FIELD OBSERVATIONS

(35) Chlorine was reported to have caused the deaths of many fish in the River Spree (Ebeling and Schröder, 1929) and was strongly implicated in the elimination of populations of most species in rivers immediately downstream of outfalls of chlorinated effluent containing about 1 mg/l chlorine (Tsai, 1968).

(36) Barsch et al. (1971) described the lethal effects on caged rainbow trout of chlorinated effluents from municipal waste water treatment plants serving small human populations (and presumably, therefore, largely domestic in origin). Without chlorination no deaths occurred over a test period of 4-5 days, but with chlorination there was more than 60 percent mortality within this period, 90 to 100 percent being killed in one stream where the average chlorine concentration was 0.07 mg/l, and 55 percent where the average was 0.014 mg/l; however all survived an average of 0.002 mg/l. The estimated 90-h LC50 values in two of the streams were 0.014 mg/l and 0.029 mg/l respectively (although these findings conflict with the data presented which apparently contain errors). Similar experiments (J.S. Alabaster, personal communication) with this species in the chlorinated effluent from synthetic resin manufacture gave an estimated 24-h LC50 of 0.07 mg/l (0.05 mg HOCl/l).

(37) No data are available on the effects of chlorine or chlorinated effluents on fisheries (potential, catchability, or yields) in areas where such wastes are discharged except that, as indicated earlier, fishery sites may be lost or displaced very locally.

5. SUMMARY OF DATA

(38) Chlorine as hypochlorous acid and chloramines is toxic to aquatic animals and, in contrast to some other poisons, for example HCN, once fish have lost their equilibrium they do not recover when placed in clean water (para. 10).

(39) The lowest concentration of chlorine reported as lethal to trout is 0.01 mg/l (0.008 mg HOCl/l) under laboratory conditions (para. 3) and 0.014 mg/l in the field (para. 5), while the highest non-lethal concentrations having no apparent adverse effect on sensitive species of fish within 5 days are 0.005 mg/l (0.004 mg HOCl/l) for brook trout in the laboratory (para. 14), though there was some decline in normal activity at this concentration (para. 23), and 0.002 mg/l for brown trout under field conditions (para. 36). Field data are, however, very scant.

(40) Acutely lethal levels of chlorine are reduced by reduction in the concentration of dissolved oxygen, little changed by increase in salinity up to 50 percent sea water, but there is little or no information available on the effect of temperature, pH, and water hardness.

(41) Slight avoidance behaviour of rainbow trout under experimental conditions has been found at a concentration of chlorine of 0.001 mg/l (0.0002-0.0008 mg HOCl/l).

(42) Coarse fish species (paras. 15 and 16), fish food invertebrate organisms (paras. 30-32), and plants (para. 33) are generally more resistant to chlorine than salmonids, although the production of young Daphnia was reduced at a concentration of 0.0035 mg/l (0.004-0.0014 mg HOCl/l) (para. 30).

(43) Chlorine may react with thiocyanide to produce lethal concentrations of hydrogen cyanide and/or cyanogen chloride (para. 26).

(44) Concentrations of chlorine as low as 0.001 mg/l in the presence of phenols are likely to produce taints in the flesh of fish (para. 25).

6. TENTATIVE WATER QUALITY CRITERIA

(45) From the limited data available, it seems that concentrations of chlorine greater than 0.008 mg HOCl/l could be harmful or lethal within 4 days to salmonids and that a concentration as low as 0.001-0.008 mg HOCl/l can produce marked avoidance reactions.

(46) On the other hand a concentration of 0.004 mg HOCl/l has been endured by sensitive species of fish for 5 days, though there was some decline in the normal activity.

(47) Chlorine is too reactive to persist for long in most streams and therefore the upper limit for fish survival might be set closer to the lethal levels than might otherwise be the case, especially as avoidance behaviour is likely to afford additional protection to the fish from regions of high concentration. Consequently it is tentatively suggested that an upper limit might be set at 0.004 mg HOCl/l, which should result in little or no mortality, perhaps have only a minor effect on behaviour, and not be low enough to be damaging to the majority of fish food organisms.

(48) The amount of total chlorine corresponding to a concentration of 0.004 mg HOCl/l varies according to the temperature and pH value of the water, as shown in Table II.

Table II

Approximate total concentration of chlorine corresponding to 0.004 mg HOCl/l (mg/l)

Temperature (°C)	pH			
	6	7	8	9
5	0.004	0.005	0.011	0.075
25	0.004	0.005	0.016	0.121

7. REFERENCES

- Albert, A., Selective toxicity. London, Methuen. Surveyor and Municipal City Engineer, 1965 pp. 105, 298
- Allen, L.A., N. Blezard and A.B. Wheatland, Formation of cyanogen chloride during chlorination of certain liquids; toxicity of such liquids to fish. J.Hyg., 46:184-93 1948
- Arthur, J.W. and J.G. Eaton, Chloramine toxicity to the amphipod Gammarus pseudolimnaeus and the fathead minnow (Pimephales promelas). J.Fish.Res.Board Can., 28:1841-5 1971
- Barsch, R.E. et al., Chlorinated municipal waste toxicities to rainbow trout and fathead minnows. Environmental Protection Agency. Washington DC, U.S. Government Printing Office, Water Pollut.Control Res.Ser., (19050 G22, 10/71):49 p. 1971
- Blake, I., The external disinfection of fish ova with reference to prophylaxis of furunculosis. Rep.Fish.Board Scotl.Salm.Fish., (11):10 p. 1930
- Buchmann, W., Chironomus control in bathing establishments, swimming pools and water supplies by means of chlorine and copper. Z.Gesundheitstech.Städtehyg., 24:235-42 (in German) (abstr. in J.Am.Water Works Assoc., 25:1317) 1932
- Coventry, F.L., V.E. Shelford and L.F. Miller, The conditioning of a chloramine treated water supply for biological purposes. Ecology, 16:60-6 1935
- Dandy, J.W.T., Activity response to chlorine in the brook trout Salvelinus fontinalis (Mitchill). Can.J.Zool., 50:405-10 1972
- Department of Fisheries, Washington, Toxic effects of organic and inorganic pollutants on young salmon and trout. Res.Bull.State Wash., (5) 1960
- Department of Scientific and Industrial Research, Water pollution research 1957. London, 1958 HMSO, p. 25
- Doudoroff, P. and M. Kats, Critical review of literature on the toxicity of industrial wastes and their components to fish. 1. Alkalies, acids, and inorganic gases. Sewage Ind.Wastes, 22:1432-58 1950
- Ebeling, G., Einfluss der abwasserchlorung auf Fischgewasser. Vom Wasser, 5:201-12 1931

- Egeling, G. and T. Schrader, Free active chlorine in water and its effect on fish and other water organisms. Z.Fisch., 27:417, 457
1929
- EIFAC, Report on monohydric phenols and inland fisheries. EIFAC Tech.Pap., (15):18 p.
1972
- Ellis, M.M., Detection and measurement of stream pollution (related principally to fish life). Fish.Bull.U.S.Bur.Fish., 48:365-437
1937
- English, E., Biological problems in distribution systems; infestations of mains water. Proc.Soc.Water Treatm.Exam., 7:127
1958
- Evins, C., The toxicity of chlorine to freshwater organisms other than bacteria. Water Res. Assoc.ILR, (223):22 p.
1972
- Grande, M., Om bruk av klorert vann i fiskeanlegg (Use of chlorinated water in fish hatcheries). Jakt-Fiske Friluftsliv., 95:507-8
1966
- Green, D.E. and P.K. Stumpf, The mode of action of chlorine. J.Am.Water Works Assoc., 38:1301-5
1946
- Holland, G.J., The eradication of Asellus aquaticus from water supply mains. J.Inst.Water Eng., 10:221-41
1956
- Jones, J.R.E., Fish and river pollution. London, Butterworths, 203 p.
1964
- Liebmann, H., Handbuch der Frischwasser- und Abwasser- biologie. 2. München, 1146 p.
1960
- McKee, J.E. and H.W. Wolf, Water quality criteria. Cal.State Water Qual.Control Board Publ., (3-A):548 p.
1963
- Merkens, J.C., Studies on the toxicity of chlorines and chloramines to the rainbow trout. Water Waste Treatm., 7:150
1958
- Palin, A.T., A study of the chloro-derivatives of ammonia and related compounds with special reference to their formation in the chlorination of natural or polluted waters. Paper presented to the Public Works Municipal Services Congress, 1950
1950
Pap. 18
- Panikkar, B.M., Low concentrations of calcium hypochlorite as a fish and tadpole poison applicable for use in partly drained ponds and other small bodies of water. Prog.Fish-Cult., 22:117-20
1960
- Phillips, J.H., The discovery and control of live organisms in the Great Yarmouth water supply. J.Inst.Water.Eng., 20:207
1966
- Pike, D.J., Toxicity of chlorine to brown trout Salmo trutta Linn. N.Z.Wildl., 1971(33):4 p.
1971
- Schaut, G.G., Fish catastrophes during droughts. J.Am.Water Works Assoc., 31:771-822
1939

- Scheuring, L. and H. Stetter, Versuche über die Wirkung von Chlor auf Fische und andere
1950-51 Wassertiere. Vom Wasser, 18
- Sillén, L.G. and A.E. Martell, Stability constants. Spec.Publ.Chem.Soc., Lond., (17)
1964
- Southgate, B.A., Treatment and disposal of industrial waste waters. London, HMSO
1948
- Sprague, J.B. and D.E. Drury, Avoidance reactions of salmonid fish to representative
1969 pollutants. Adv.Water Pollut.Res., 2(1):169-79
- Taylor, R.S. and M.C. James, Treatment for removal of chlorine from city water for use in
1928 aquaria. U.S. Bureau of Fisheries, Doc. No. 1045. Rep.U.S.Comm.Fish., App. 7:
322-7
- Tsai, C., Effects of chlorinated sewage effluents on fish in the upper Patuxent River,
1968 Maryland. Chesapeake Sci., 9:83-93
- Wakabayashi, T. and M. Imaoka, Effect of residual chlorine in tap-water on goldfish.
1968 Yamanashi Daigaku Kogakubu Kepkyu, (19):118-22
- Zillich, J.A., Toxicity of combined chlorine residuals to freshwater fish. J.Water Pollut.
1972 Control Fed., 44:212-20
- Zimmerman, P.W. and R.O. Berg, Effects of chlorinated water on land plants, aquatic plants,
1934 and goldfish. Contrib.Boyce Thompson Inst., (6):39-49

Papers issued in this series

- EIFAC/T1 Water quality criteria for European freshwater fish. Report on finely divided solids and inland fisheries (1964).
- EIFAC/T2 Fish Diseases. Technical Notes submitted to EIFAC Third Session by Messrs. J. Heyl, H. Mann, C.J. Rasmussen, and A. van der Struik (Austria, 1964).
- EIFAC/T3 Feeding in Trout and Salmon Culture. Papers submitted to a Symposium, EIFAC Fourth Session (Belgrade, 1966).
- EIFAC/T4 Water quality criteria for European freshwater fish. Report on extreme pH values and inland fisheries (1968).
- EIFAC/T5 Organization of inland fisheries administration in Europe, by Jean-Louis Gaudet (Rome, 1968).
- EIFAC/T6 Water quality criteria for European freshwater fish. Report on water temperature and inland fisheries based mainly on Slavonic literature (1968).
- EIFAC/T7 Economic evaluation of inland sport fishing, by Ingemar Norling (Sweden, 1968).
- EIFAC/T8 Water quality criteria for European freshwater fish. List of literature on the effect of water temperature on fish (1969).
- EIFAC/T9 New developments in carp and trout nutrition. Papers submitted to a Symposium, EIFAC Fifth Session (Rome, 1968).
- EIFAC/T10 Comparative study of laws and regulations governing the international traffic in live fish and fish eggs, by F.B. Zenny, FAO Legislation Branch (Rome, 1969).
- EIFAC/T11 Water quality criteria for European freshwater fish. Report on ammonia and inland fisheries (1970).
- EIFAC/T12 Salmon and trout feeds and feeding (1971).
- EIFAC/T13 Elements of the theory of age determination of fish according to scales. The problem of validity (1971).
- EIFAC/T14 EIFAC consultation on eel fishing gear and techniques (Rome, 1971).
- EIFAC/T15 Water quality criteria for European freshwater fish. Report on monohydric phenols and inland fisheries (1972).
- EIFAC/T16 Symposium on the nature and extent of water pollution problems affecting inland fisheries in Europe. Synthesis of national reports (1972).
- EIFAC/T17 Symposium on the major communicable fish diseases in Europe and their control. Report (1972).
- EIFAC/T17
Suppl. 1 The major communicable fish diseases of Europe and North America. A review of national and international measures for their control, by P.E. Thompson, W.A. Dill & G. Moore (1973).
- EIFAC/T17
Suppl. 2 Symposium on the major communicable fish diseases in Europe and their control. Panel reviews and relevant papers (1973).
- EIFAC/T18 The role of administrative action as a tool in water pollution control, by G.K. Moore, FAO Legislation Branch (Rome, 1973).
- EIFAC/T19 Water quality criteria for European freshwater fish. Report on dissolved oxygen and inland fisheries (1973).
- EIFAC/T20 Water quality criteria for European freshwater fish. Report on chlorine and freshwater fish (1973).
- EIFAC/T21 Water quality criteria for European freshwater fish. Report on zinc and freshwater fish (1973).

