



**WATER QUALITY CRITERIA
FOR EUROPEAN FRESHWATER FISH**

REPORT ON MONOHYDRIC PHENOLS 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, 1972**

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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.

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FOREWORD

This is the sixth 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 five 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.

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/}.

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- ^{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
- ^{3/} EIFAC Report, Third Session, 1964, p. 11

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 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.)

Following the Jablonna Symposium, the Sixth Session of EIFAC, Krakow, 1970, again reviewed the Commission's programme with respect to water quality criteria ^{6/}. 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. ^{7/}

^{4/} EIFAC Report, Fourth Session, 1966, p. 12

^{5/} EIFAC Report, Fifth Session, 1968, pp. 14-5

^{6/} EIFAC Report, Sixth Session, 1970, p. 13

^{7/} Doudoroff, Peter and Dean L. Shumway (1970) Dissolved Oxygen Requirements of Freshwater Fishes. FAO Fish. tech. Pap., (86):291 p.

Since the Sixth Session of EIFAC, the EIFAC Working Party has published the report on ammonia (see footnote 2/) as the fifth review in this EIFAC series of water quality papers; it will be presented to the Seventh Session of EIFAC, 1972. The Working Party has also continued an active literature search on chlorine, copper, zinc and mercury, and is preparing a review of oxygen for European freshwater fishes.

The sixth review, which follows, is the one on water quality criteria for monohydric phenols. For the preparation of this report experts were appointed to the EIFAC Working Party on Water Quality Criteria:

Mr. J.S. Alabaster	(United Kingdom), <u>Convener</u>
Dr. D. Calamari	(Italy)
Mr. M. Grande	(Norway)
Dr. T.B. Hasselrot	(Sweden)
Mr. R. Lloyd	(United Kingdom)
Dr. V. Mitrović	(Yugoslavia)

FAO Secretariat:

Mr. William A. Dill - Secretary to EIFAC
Mr. A. Thorslund - Fishery Officer (Inland Water Pollution)

The preparation of the present report on monohydric phenols and inland fisheries was accomplished largely by Dr. V. Mitrović who prepared the basic manuscript to be reviewed by other members of the Working Party.

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."

This report will be presented to the Seventh Session of EIFAC which is scheduled to be held in Amsterdam, 1972.

SUMMARY

Phenolic wastes can contain monohydric phenols, including phenol, the three cresol isomers, and the six xylenol isomers, together with other substances. They may adversely affect freshwater fisheries by their direct toxicity to fish and fish-food organisms, by their high oxygen demand resulting in oxygen depletion of the receiving water, and by the production of undesirable flavours in the edible flesh of fish.

Laboratory tests show that the toxicity of phenol is increased by decrease in dissolved-oxygen concentration, increase in salinity, and decrease in temperature. Salmonids and newly hatched fish are more sensitive than coarse fish and adults respectively. Cresols, xylenols, and phenols are of similar toxicity, and the toxicity of mixtures of phenols is apparently additive, although the toxicity of phenolic wastes may be greater than expected from chemical analyses, since these may not be equally sensitive to all phenols and may neglect the contribution from other poisons.

Because of difficulties caused by inadequate chemical analysis there are few field observations which can be used to reinforce laboratory findings. For this reason, and also because of gaps in our knowledge of the effect of temperature on toxicity, only tentative criteria can be established, which may have to be modified in the light of further experience.

These criteria are expressed as maximum concentrations which should not be exceeded but it should be appreciated that because of the natural fluctuation in the water quality found in rivers over a period of time, the average concentration will be lower to an extent depending on local circumstances.

Salmonid fish. To ensure long-term survival of salmonids in the presence of phenolic wastes, the concentration of phenol, cresols or xylenols should not exceed 1.0 mg/l, either singly or collectively. Where 2,5-xylenol is the main constituent, the concentration should not exceed 0.5 mg/l. Where the temperature is lower than 5°C, concentrations may have to be halved to ensure the survival of fish.

Coarse fish. Since laboratory data show that coarse fish are more resistant than salmonids to phenols, the concentration of phenol, cresol or xylenol should not exceed 2.0 mg/l, either singly or collectively, provided that oxidation of this concentration does not produce an adverse reduction in the dissolved-oxygen concentration of the water. In the absence of data on the effect of temperature on the toxicity of phenols to coarse fish it is proposed that the reduction in concentration of 50% adopted for salmonids at temperatures below 5°C, should also apply to these species.

Where other poisons are present in addition to phenols due allowance must be made for their contribution to the toxicity, particularly in the case of free chlorine.

Commercial fisheries. There is no laboratory evidence to indicate that levels of phenol and cresols that are safe for fish cause their flesh to become tainted, but xylenols should not exceed 0.5 mg/l. Other phenolic substances, particularly the chlorophenols, are known to cause taint at very low concentrations; strictly these are outside the scope of this report, but the information that has been considered suggests that they should be excluded from waters supporting commercial fisheries.

1. INTRODUCTION

(1) Phenolic wastes arise from the distillation of coal and wood, from oil refineries, chemical plants, livestock dips, and human and animal wastes. They are still one of the main causes of river pollution in several European countries, though in others, for example Czechoslovakia and the United Kingdom, the quantity discharged to flowing waters has been considerably reduced in recent years. Phenols are normally present in purely domestic sewage at low concentrations (0.07 to > 0.1 mg/l) and can also be released into water by aquatic plants and decaying vegetation (Hoak, 1956).

(2) Phenolic wastes can consist of mono-, di-, and poly-hydric phenols, together with aldehydes, ketones, alcohols, organic acids, gases (CO_2 , NH_3) and often cyanide, the proportions of which vary. The monohydric phenol fraction of gas liquors (Blackburn *et al.*, 1954) and coke-oven effluent (Herbert, 1962) consists largely of pure phenol ($\text{C}_6\text{H}_5\text{OH}$) but includes cresols and xylenols, *m*-cresol usually being present in greater quantities than the *o*- and *p*-isomers and the xylenols.

(3) These wastes affect fisheries by their direct toxicity to aquatic life and by tainting the flesh of fish, especially when chlorinated. Being mainly oxidizable they can also contribute to the depletion of the dissolved-oxygen concentration of polluted waters, so making it difficult to assess the direct importance of phenols as poisons simply from an examination of analytical data.

(4) Extensive literature reviews of the effect of phenol on fish include that of Bandt (1958), and more recently that of Lukanenko (1967), which covers Russian literature. This report will deal principally with the effect of mono-hydric phenols, namely phenol ($\text{C}_6\text{H}_5\text{OH}$), *o*-, *m*-, and *p*-cresol ($\text{CH}_3\text{C}_6\text{H}_4\text{OH}$), and the six xylenols, 2,3-xyleneol, 2,4-xyleneol, 2,5-xyleneol, 2,6-xyleneol, 3,4-xyleneol, 3,5-xyleneol ($(\text{CH}_3)_2\text{C}_6\text{H}_3\text{OH}$), but some reference will be made to gas liquors and coke-oven wastes and their components.

(5) Because of the failure in much of the early literature to distinguish between the different isomers, and differences in the nomenclature adopted, particularly for the xylenols, together with the use of analytical methods that measure different proportions of the isomers, polyhydric phenols, and other substances (see Table I), the value of much of the published information has been reduced. To clarify the nomenclature we have chosen to use the term "phenols" only when it is not possible to refer to monohydric phenols, dihydric phenols, polyhydric phenols or to a specific isomer for which data are available, in which case we have used, whenever possible, the system given by the International Union of Pure and Applied Chemistry (1965).

Table I. Relative colour intensity produced by different phenols and aniline

Phenols	Analytical method		
	Aminoantipyrene (Ochynski, 1960)	Folin and Denis (1915)	p-nitroaniline (Nolte, 1933)
<u>Monohydric</u>			
phenol	100	100	100
<u>o</u> -cresol	72	78	147
<u>m</u> -cresol	62	85	120
<u>p</u> -cresol	6	68	21
2,3-xylenol	44		16
2,4-xylenol	22		52
2,5-xylenol	42		92
2,6-xylenol	42		52
3,4-xylenol	4		16
3,5-xylenol	33		52
<u>Dihydric</u>			
pyrocatechol (catechol)	0		
3-methyl catechol	0	148	29
4-methyl catechol	0		
resorcinol	62	117	
2-methyl resorcinol	22		
4-methyl resorcinol	10		
5-methyl resorcinol	28		
hydroquinone (quinol)	0		
guaiacol			165
naphthol			23
aniline		59	

2. DIRECT LETHAL ACTION ON FISH

2.1 Symptoms of poisoning and mode of action

(6) Fish exposed to concentrations of phenol and cresols that are lethal within a few days soon become excited, swimming rapidly and becoming more sensitive to outside stimuli and showing increased respiration (e.g., Veselov, 1957). In addition there may be colour changes (Wuhrmann and Woker, 1950) and increased secretion of mucus (e.g., Greven, 1953). Death may occur quickly or follow after a stage of depressed activity and loss of equilibrium interrupted by occasional convulsions (Lukanenko, 1967). With xylenols, however, Lukanenko did not find increased sensitivity to stimuli in Crucian carp (Carassius carassius), whereas Albersmayer and Erichsen (1959) found the contrary. Acute poisoning by phenol is generally attributed to nervous paralysis, and Lukanenko (1967) has shown that the brain

is involved in the specific reaction of poisoned fish. Halsband and Halsband (1954) found that the threshold concentration for disturbance of trout was 1.3 mg/l phenol.

(7) Fish surviving long-term exposure to low concentrations of phenol show general inflammation and necrosis of the tissues, including the erythrocytes (Waluga, 1966 and 1966a) possibly because of irreversible changes induced in the proteins (see also para. 42). In a detailed study with bream held for seven days in 9 mg/l of phenol, she found haemorrhage and necrotic and degenerative changes in several tissues, including skin, muscle, gills, liver, spleen and kidney. There was also a sharp decrease in the number of erythrocytes in the peripheral blood and leucopenia; the high count of abnormal and juvenile cells was thought to be evidence of damage to the blood-producing tissues. At high concentrations of phenol (> 6 mg/l) the blood cells are destroyed (Andres, 1969). Halsband and Halsband (1963), using trout exposed to 1.5 mg/l for 24 h, found a reduction in number and an increase in surface area of erythrocytes. V.M. Brown and D.G. Shurben (personal communication) studied the effect on rainbow trout (Salmo gairdneri) of concentrations of 1, 2, 3, 4, and 5 mg/l of phenol over a period of 18 weeks and found pronounced histopathological changes in the liver, heart, skin, and spleen, while the intestinal tract, spinal cord, and excretory part of the kidney were similar to those of the control fish.

(8) Mikriakov (1969) found that serum proteins decreased and immunoglobulin formation was inhibited in common carp (Cyprinus carpio) held for two months at 12.5 mg/l of phenol. Reduction in serum proteins of common carp was also observed by Lebedinski and Pomarzenskia (1968) in fish exposed for 30 days to phenol at a concentration of 25 and 10 mg/l, and a very slight reduction at 1 mg/l; changes were also reported in concentrations of metals in various organs, including blood, muscle, and bones, the significance of which is unknown.

(9) Specific sublethal actions are dealt with in Section III, paras 36 to 47.

2.2 Factors affecting lethal levels

2.2.1 Temperature

(10) Several authors (e.g. Bucksteeg et al., 1955) have shown that increase in temperature shortens the time of reaction and period of survival of fish in solutions containing high concentrations of phenols. However, Brown, Jordan and Tiller (1967), using fish which had been previously acclimated for three days to the test temperatures, found that the resistance of rainbow trout to low concentrations of phenol increased with increase in temperature, the concentration lethal to 50 percent of the fish in two days (the 48-h LC50) at 6, 12 and 18°C being approximately 5, 8 and 9.8 mg/l respectively, and a somewhat similar relationship was found with a simulated gas liquor. More recent tests (UK, Ministry of Technology, 1968) carried out with juvenile rainbow trout 3 to 5 cm long at 3 to 4°C and 12 to 13°C after prior acclimation to the test temperature for 3 to 4 days showed that the 48-h LC50 values were about 3 and 5 mg/l respectively.

2.2.2 Dissolved oxygen

(11) Low dissolved-oxygen concentration shortens the time of response of fish to monohydric phenols and reduces the concentrations that are lethal (as for example, in tests with p-cresol by Southgate et al., 1933). Tests with rainbow trout in a mixture of phenols (Herbert, 1962) have also demonstrated that a reduction in dissolved oxygen from 100 percent to 50 percent of the air-saturation value reduces the estimated "threshold" * LC50 by about 20 percent, a reduction similar to that found for zinc, copper and lead (Lloyd, 1961).

* The concentration lethal after long-term exposure of the fish

2.2.3 pH value

(12) Within the range of pH values from 6.5 to 8.5 there was little or no difference in toxicity of monohydric phenols to rainbow trout (Herbert, 1962) and similar results have been reported with Crucian carp within the range of pH 4 to 11 (Lukanenko, 1967).

2.2.4 Water hardness

(13) At a total water hardness of 50 mg/l as calcium carbonate the threshold LC50 of monohydric phenols was no lower than at 310 mg/l (Herbert, 1962) but at lower hardnesses toxicity increased slightly; the 48-h LC50 values of phenol for rainbow trout in water having a hardness of 320 and 10 mg/l as calcium carbonate were 6.8 and 5.2 mg/l respectively (UK, Ministry of Technology, 1968). This accords with the results of Pickering and Henderson (1966) for fathead minnow (Pimephales promelas), of Lukanenko (1967) for Crucian carp, and of Leclerc and Devlaminck (1950) for mosquito fish (Gambusia affinis), for which the minimum lethal concentrations of phenol in a hard and in a distilled water were 24 to 28 and 18 to 20 mg/l respectively.

2.2.5 Salinity

(14) Holland et al. (1961) found that young coho salmon (Oncorhynchus kisutch) tested in a crude mixture of cresols (cresylic acids) were about twice as sensitive in sea water as in fresh water, concentrations tolerated for four days being 1.6 to 3.1 and 3 to 5.5 mg cresol/l respectively. A similar effect was reported by Brown, Shurben, and Fawell (1967) for rainbow trout tested in phenol, sensitivity increasing linearly with increase in salinity; at 15°C the 48-h LC50 was 9.3 mg/l in fresh water and 5.2 mg/l in 60 percent sea water, and there was also a decrease in the time of response of fish in sea water. Lukanenko (1967) found that Acipenser stellatus and A. güldenstaedti, both migratory species of sturgeon, were more resistant than the freshwater species, A. rhutenus, when tested in fresh water.

2.2.6 Age of fish

(15) Concentrations of phenol that were lethal to adult Crucian carp, tench (Tinca tinca), and stickleback (Gasterosteus aculeatus) were not apparently harmful to their eggs and sperm (Albersmayer and Erichsen, 1959), the first symptoms of damage to these stages being observed at concentrations greater than 50 mg/l, as judged only from the appearance of the eggs and the mobility of the sperm. No observations were made, however, of the fertilization, development, and hatching of the eggs.

(16) Volodin et al. (1965, 1966) found that resistance to poisoning changes during development, embryos of bream (Abramis brama) and a similar species, A. ballerus, being most sensitive to phenol from the beginning of cleavage to gastrulation and again towards the end of the larval period, although the larvae survived 4 to 11 times longer than the fry at concentrations of 25 to 150 mg/l of phenol. Nevertheless, embryos of A. brama died at a concentration of 50 mg/l phenol and hatching was delayed at 25 mg/l. Eggs and fry of perch (Perca fluviatilis) were more resistant to phenol than 1-year-old fish (Mosevich et al., 1952).

(17) V.M. Brown (personal communication) using brown trout (Salmo trutta) and rainbow trout, found that the 5-day LC50 of phenol was greater than 16 mg/l for pre-eyed eggs (17 days post-fertilization), greater than 40 mg/l for eyed eggs (25 days post-fertilization), and 1-day-old rainbow trout alevins, and greater than 60 mg/l for 3-day-old brown trout alevins, whereas it was less than 10 mg/l for 15-day-old brown trout fry. On the other hand, Albersmayer and Erichsen (1959) reported that "trout" embryos were more sensitive than adult fish to monohydric phenols, but gave no data on developmental state. Lukanenko and Flerov (1966 and 1966a) found that the 24-h LC50 was 11 mg/l for 1-year-old rainbow trout and 7.5 mg/l for 2-3-year-old fish.

2.2.7 Size of fish

(18) Bluegill sunfish (Lepomis macrochirus) 14 cm long were less tolerant of phenol than fish 7 cm long, the 96-h LC50 being 11.5 mg/l and 20 mg/l respectively (Cairns, 1956). Similar results were obtained by Holland et al. (1961) using coho salmon, and by Lukanenko and Flerov (1966 and 1966a) using rainbow trout, who also found that resistance decreased with increase in body weight.

2.2.8 Acclimation to phenol

(19) Some authors report that fish that have overturned in the presence of phenol tend not to recover when transferred to clean water, whereas with cresols and xylenols they do (Embody et al., 1940; Jones, 1951; Albersmayer and Erichsen, 1959; and Holland et al., 1961). Other workers, however, (V.M. Brown and J.F. de L.G. Solbé, personal communication) have found that all rainbow trout overturned on exposure to 20 mg/l phenol apparently recovered when placed in clean water.

(20) Perch kept for 7 days in 6 mg/l of phenol (Bucksteeg et al., 1955), and bitterling (Rhodeus sericeus amarus) kept for 4 days in 4 mg/l (Malacea, 1968) took at least twice as long to react to higher concentrations than unacclimated fish. Similar results were obtained by Volodin et al. (1965 and 1966) with embryos of bream kept in 5 mg/l, and by Lukanenko (1967) with Crucian carp held in 1 to 5 mg/l for 25 to 40 days; this could perhaps be explained by diminished excitability of the fish. On the other hand, Crucian carp kept for 60 days at 1 to 5 mg/l were more sensitive than controls. However, none of these experiments indicated that any alterations of the threshold concentrations had occurred.

2.3 Summary of toxicity data

2.3.1 Phenol

(21) A wide range of phenol concentrations (0.08-1900 mg/l) has been reported as harmful to fish, thus reflecting differences in the sensitivity of the different species used, in the ways of expressing toxicity, in the conditions of exposure, and in the duration of the tests. The lowest values, however, are often misquoted. Those of Symons and Simpson (1938), for example, relate to North American species of "minnow" killed in 30 minutes in samples of river water containing not only 0.08 mg/l of phenol but a variety of other wastes in addition; these authors also found that 10 mg/l of phenol did not kill (common) carp within 6 hours. Furthermore, data from older references (e.g., Weigelt et al., 1885) have occasionally been quoted ten times lower than the original. It is also noteworthy that the response of individual fish to phenol not only varies widely but also involves the elapse of a long time interval between overturning and death; for example, the survival time of Crucian carp ranged from 21 to 171 hours in 25 mg/l of phenol, and from 3 to 148 hours in 50 mg/l (Lukanenko, 1967), and similar results have been found by other authors (e.g., Mitrović et al., 1968). Taking reliable figures for median lethal concentrations for periods between 6 and 96 hours, the range is between 4 and 56 mg/l, the most frequent values for adult fish in well-aerated fresh water being 9-25 mg/l.

(i) Coarse fish

(22) One of the most resistant coarse fish appears to be goldfish (Carassius auratus), the 48-h LC50 at 25°C being 44.5 mg/l according to Pickering and Henderson (1966), and Bach (1929) (in Southgate et al., 1933) reported that this species survived 3 months in 4.2 mg/l at 16.5-23°C and 7-12 mg/l dissolved oxygen. For Crucian carp the 129-h LC50 at 12 to 14°C has been reported as 25 mg/l (Lukanenko and Flerov, 1963), and the same concentration has been given as the 24-h LC50 at 18°C (Albersmayer and Erichsen, 1959). The 48-h LC50 for gudgeon (Gobio gobio) at 10°C is approximately 25 mg/l (unpublished work at the Water Pollution Research Laboratory, UK). The minimum lethal concentration for the bitterling is given as 20 mg/l by Malacea et al. (1967). For roach (Rutilus rutilus) the 24-h LC50 at

18°C is 14.5 mg/l and for tench 17 mg/l (Albersmayer and Erichsen, 1959). Some work (UK, Ministry of Technology, 1969) indicates that although the 24-h LC50 values for roach and perch at 18°C are approximately 25 and 15 mg/l respectively, the median threshold concentration for both is close to 12 mg/l; and more recent tests (UK, Ministry of Technology, 1971) have shown that while perch, pike (Esox lucius), and rainbow trout all responded more quickly than common carp, rudd (Scardinius erythrophthalmus) and eel (Anguilla anguilla) at any given concentration, the 7-day LC50 was similar (8-11 mg/l) for all these species except in the case of carp (15 mg/l).

(ii) Salmonids

(23) The concentrations of phenol reported as lethal to rainbow trout are generally lower than the corresponding values for coarse fish; the 24-h LC50 varies from 5 mg/l at 18°C (Albersmayer and Erichsen, 1959) for embryos to 11 and 7.5 mg/l for 1- and 3-year-old fish at 12 to 14°C (Lukanenko and Flerov, 1966); the 48-h LC50 was 9.8 mg/l at 17°C (Herbert and Vandyke, 1967) and 9.3 mg/l at 15°C (Brown, Shurben, and Fawell, 1967). Coho salmon are possibly slightly more sensitive, the 72-h LC50 being 3.2 to 5.6 mg/l at 6 to 11°C (Holland et al., 1961). M. Grande (personal communication) has found that the 5-day LC50 for Atlantic salmon fry (Salmo salar) at 10°C was about 5 mg/l.

(24) V.M. Brown and D.G. Shurben (personal communication) kept batches of 25 rainbow trout at concentrations of 1, 2, 3, 4, and 5 mg/l at 14 to 18°C over a period of 18 weeks. There was a 75% mortality at the highest concentration and 28% at 3 mg/l, and the 18-week LC50 was estimated as approximately 4.0 mg/l.

2.3.2 Cresols

(25) Cresols have been studied to a lesser extent than phenol. Of the three isomers the least toxic is m-cresol, while reports for the relative toxicity of o- and p-cresol are inconsistent.

(26) Lethal concentrations of cresols and phenol are usually within a two-fold range, but differences are not consistent between species. Comparable data on the acute toxicity of phenol and the three isomers of cresol are given by Albersmayer and Erichsen (1959) for several species over a range of temperatures of 13 to 19°C (see Table II). Bucksteeg et al. (1955) found that the threshold concentrations for loss of coordinated movement in perch were 6 mg/l for phenol and 10 mg/l for the cresols. Pickering and Henderson (1966) give the 96-h LC50 of o-cresol for goldfish as 17 to 31 mg/l at 25°C.

Table II. Approximate 24-h LC50 of phenols to fish (mg/l) (from Albersmayer and Erichsen, 1959)

Phenols	Crucian carp	Roach	Tench	"Trout" embryos
Phenol	25	15	17	5
<u>o</u> -cresol	30	16	15	2
<u>m</u> -cresol	25	23	21	7
<u>p</u> -cresol	21	17	16	4
2, 4-xyleneol	30	-	13	28
2, 5-xyleneol	10	10	9	2
3, 4-xyleneol	21	16	18	7
3, 5-xyleneol	53	-	51	50

2.3.3 Xylenols

(27) Of the monohydric phenols, xylenols are the least studied and no work has been carried out specifically on 2,3-xyleneol or 2,6-xyleneol. A mixture of xylenols used by Pickering and Henderson (1966) was intermediate between phenol and o-cresol in its toxicity to goldfish, fathead minnow, and the guppy (*Lebistes reticulatus*). Based on 24-h LC50 values for Crucian carp and tench, 2,5-xyleneol is roughly twice as toxic, and 3,5-xyleneol about half as toxic, as 2,4-xyleneol and 3,4-xyleneol (Albersmayer and Erichsen, 1959) and phenol (Table II). The comparatively low toxicity of 3,5-xyleneol to coarse fish is confirmed by the concentrations reported as "having no toxic effect" in 3 to 5 days (Bandt, 1958), being 15, 18, and 20 mg/l for perch, roach, and bream respectively, while the corresponding values for 2,4-xyleneol were 8, 8, and 10 mg/l respectively. Rainbow trout embryos appear to be as resistant as adult carp to 2,4-xyleneol and 3,5-xyleneol (Albersmayer and Erichsen, 1959).

2.3.4 Other components of phenolic wastes

(28) Some polyhydric phenols, including hydroquinone, 8-oxyquinolin, and naphthols were reported more toxic than phenol (0.1-4.0 mg/l) by Sollmann (1949) and Bandt (1958) but these are usually present in only small quantities in phenolic wastes.

2.3.5 Mixtures of phenols and other substances

(29) Where the toxicity of phenol or individual cresols and xylenols have been investigated, the concentrations are given in terms of weight of substance used. With mixtures of unknown composition, however, the concentration may be determined by colorimetric analysis and the colour produced compared with that given by pure phenol. For example, in Herbert's (1962) experiments with a simulated gas liquor, one part by weight of gas liquor phenols was colorimetrically equivalent to 0.72 parts phenol by analysis. For rainbow trout at 9°C, the median threshold concentration of this prepared mixture was 6.1 mg/l by weight and 4.4 mg/l by analysis. The close agreement with the data obtained for phenol alone at this temperature indicates that the cresols, which composed 38% of the mixture by weight, did not markedly affect the toxicity of the phenol present (54% by weight).

(30) Liepolt (1954) found that a gas liquor killed rainbow trout in 12 hours at a concentration equivalent to 4.3 mg/l of phenol, and other authors have reported toxic concentrations of phenol in the range 3 to 5 mg/l in water polluted by phenolic wastes (Ebeling, 1940; Mann, 1951; Bandt, 1958).

(31) When tar is removed from coal-processing wastes, the main components remaining are monohydric phenols, ammonia, cyanide, sulphide, thiosulphate, and thiocyanate, of which the first three contribute most to short-term toxicity (Herbert, 1962). Studies with mixtures of ammonia and phenol (Herbert, 1962), phenol and zinc (Herbert and Vandyke, 1967), ammonia, phenol and zinc (Brown, Jordan, and Tiller, 1969), and copper and phenol, and also copper, zinc and phenol (Brown and Dalton, 1970) have shown that the toxicity of the mixture is approximately additive in terms of the fractions of the median lethal concentrations of the individual poisons at 2 or 3 days (which are often close to the median threshold concentrations of these poisons); the mixture kills 50% of the fish at 2 or 3 days when the sum of the fractions equals unity. Using this procedure, the predicted toxicities of samples of effluents and polluted river waters (Lloyd and Jordan, 1963, 1964; Herbert *et al.*, 1965; and Brown, Shurben, and Shaw, 1970) which contained monohydric phenols, ammonia, cyanide, zinc, and copper, were close to the observed values, although some samples were more toxic than predicted, perhaps because of the presence of other poisons. Again, it must be emphasized that the addition of chlorine to phenolic wastes can produce highly toxic chlorinated phenols.

2.3.6 Field observations of fish kills

(32) There are very few cases where fish kills or adverse effects on natural fish populations can be clearly attributed solely to phenols. Again, one of the main problems is that

of analysis, since the identities and proportions of the various monohydric phenols in the water are rarely, if ever, determined, and the analytical results can include other phenols. It is very difficult, therefore, to correlate field data with results from laboratory tests with individual phenols.

(33) Muller and Anwand (1967) could attribute only 3 out of 19 recorded fish kills to phenol, which is perhaps to be expected since phenol pollution is almost always accompanied by reduced dissolved oxygen and the presence of other poisons. Liepolt (1954) ascribed a kill of trout and grayling (Thymallus thymallus) in the River Murtz to a discharge of concentrated gas liquor. Lüdemann (1954), who studied Berlin waters, was of the opinion that fish would be killed when the phenol concentration was more than 3 to 5 mg/l. Kalabina (1935) did not find fish in parts of a river containing 0.3 mg/l phenol, and found an abundant and diversified fish fauna where it was 0.02 mg/l. Perhaps the most interesting data have been given by Krombach and Barthel (1964) for a small stream in Luxembourg which was chronically polluted by phenolic wastes and had a concentration of phenols of about 1 mg/l and yet supported fish, including salmonids. After a sudden increased discharge in August all animal life was destroyed within a 9 km stretch where the phenol concentration exceeded 10 mg/l and the dissolved oxygen was 0 to 10% of the air-saturation value. Further downstream where the phenol concentration was 3 to 10 mg/l and the dissolved-oxygen concentration 10 to 50% of the air-saturation value, salmonids were killed, while in a length where the phenol was less than 3 mg/l there were no fish kills.

(34) A more recent observation on the River Péstan in Yugoslavia, also chronically polluted by phenolic wastes (V. Mitrović and J.S. Alabaster, personal communication), showed that good populations of chub (Leuciscus cephalus) and gudgeon, together with smaller numbers of barbel (Barbus spp) occurred where the concentration of phenols ranged from zero to 4.4 mg/l, but that fish were absent where it was between 3.2 and 130 mg/l.

(35) These data corroborate those from laboratory tests insofar as there are no recorded instances of fish living at a concentration of phenols higher than that found toxic under experimental conditions.

3. SUBLETHAL ACTION ON FISH

3.1 Growth

(36) Mikriakov (1969) observed a loss in weight of common carp exposed for 2 months to 12.5 mg/l phenol. Stepanov and Flerov (1969) reported that guppies kept for a year in 12.5 mg/l phenol first spawned at the age of 5 months compared with 10 months for the controls, but there was no reduction in growth. There was, however, decreased sexual activity in this species (Flerov, 1969) as well as alteration of reflexes at this concentration and at 6.3 mg/l, but not at 3.1 mg/l (Matay, 1969).

(37) V.M. Brown and D.G. Shurben (personal communication) studied the effect on rainbow trout of concentrations of 1, 2, 3, 4, and 5 mg/l of phenol over a period of 18 weeks and found that there was a 20% reduction in growth at 1 mg/l and greater reductions at higher concentrations.

3.2 Resistance to disease

(38) Some reports suggest that fish that are exposed to relatively high concentrations of phenols are subsequently more susceptible to attack by Saprolegnia or Ichthyophthirius (Lukanenko, 1967; Lammering and Burbank, 1960), but to what extent this may be important in harming fish in polluted waters is not known.

3.3 Avoidance reactions

(39) Hasler and Wisby (1949) showed that the bluntnose minnow (Pimephales notatus) could be trained to detect phenol at concentrations below 0.01 mg/l (some individuals being capable

of detecting as little as 0.0005 mg/l) and to distinguish between phenol and *o*-chlorophenol. Yet, when given the choice of clean water or water containing phenol in a small horizontal tube, minnows (*Phoxinus phoxinus*) did not choose clean water in preference to either 400 mg/l or 4 mg/l or phenol (Jones, 1951), and rainbow trout did not avoid the lower concentrations (0.001 to 10 mg/l) that were used by Sprague and Drury (1969). Minnows avoided 400 mg/l of *p*-cresol and *o*-cresol but not lower concentrations (Jones, 1951), a behaviour pattern that is paralleled by that of *Lepomis cyanellus*, the green sunfish (Sommerfelt and Lewis, 1967). On the other hand Ishio (1965) using a different kind of apparatus, presented a very brief summary of pooled data for several species, including carp and goldfish, showing that the median position occupied by the fish in his gradient channel coincided with concentrations of phenol (15 mg/l) and cresol (47 mg/l) that were only slightly lower than the "lowest lethal levels", and stated later (1969) that the minnow (*Maracco steindachneri*) avoided "phenol from cresote oil" in concentrations lower than 0.1 mg/l.

(40) Evidence of avoidance of phenolic wastes under field conditions is also conflicting. Kalabina (1935) reported that fish would leave parts of a river containing 0.2 to 10 mg/l of phenol, whereas Shelford (1917) said that they would tend to enter and remain in portions of a stream polluted with gas liquor.

(41) Definite conclusions cannot be drawn about avoidance reactions of fish in phenol from this conflicting and sparse evidence, together with that given in paragraph 34 on the distribution of fish in the River Pēstan, but it seems that if there is avoidance of polluted waters containing low concentrations of phenol, it is unlikely to be caused by the phenol alone.

3.4 Uptake and loss of phenol

(42) Phenols in both free and conjugated forms are normally found in mammalian tissues, but few observations have been made on fish; Reichenbach-Klinke (1965) usually found less than 0.3 mg phenol per kg in *Alburnus punctatus* and roach from the unpolluted River Isar, whereas there was up to 3.2 mg/kg in bream and barbel (*Barbus barbus*) from polluted parts of the Elbe and Rhine that contained 0.2 to 0.7 mg/l phenol, values almost as high as in roach kept in 6 mg/l phenol for 14 days. In the American brown bullhead (*Ictalurus nebulosus*) kept 4 days in 5 mg/l phenol, Mann (1953) found 10 mg/kg in viscera and 6 mg/kg in muscle; he also showed that accumulation in common carp held for 5 days in 10 mg/l phenol was increased by the addition of 2 mg/l of dodecylbenzol sulphonate (Mann, 1962). Common carp held for 3 days in 10 mg/l phenol (Schultze, 1961) had the highest concentration in liver (19 mg/kg) and progressively lower concentrations in gill, kidney, testis, muscle, and intestine (7 mg/kg). Waluga (1966 and 1966a) obtained similar results with bream held for seven days in 9 mg/l phenol, concentrations being high in the blood and body cavity fluid and low in the cerebral fluid and brain. Concentrations in rainbow trout killed by 10 mg/l phenol were also highest in skin as well as spleen, liver, kidney, and gill (11 to 25 mg/kg), and lowest in muscle (3.2 mg/kg) (Kariya *et al.*, 1968). In fish killed and then held for 5 hours in 10 mg/l phenol, phenols were detected only in skin, muscle, and gill at 5.7, 2.8, and 6.5 mg/kg respectively.

(43) Although Mackiel *et al.*, (1958) (in Brodie *et al.*, 1958) reported that goldfish and perch were not able to detoxify phenol by the otherwise ubiquitous formation of conjugation products with glucuronides and sulphates, Hoar and Randall (1968) have stated that these processes do occur in fish.

(44) Kariya *et al.*, (1968) found a lower concentration of phenol (2.0 mg/kg) in goldfish which survived exposure to the 48-h LC50 and were then kept for 24 h in tap water, than in fish killed by the same concentration and washed afterwards in tap water for 24 h (9.4 mg/kg). R. Lloyd (personal communication) has found a normal urinary excretion rate in rainbow trout of 0.7 mg monohydric phenols per kg per day, and about 8 mg total phenols per kg per day, and that these rates are increased as a graded response in fish exposed to phenol in the range 1.5 to 6 mg/l; the data indicate that phenol concentrations less than 1.0 mg/l are unlikely

to lead to an increased phenol excretion rate.

3.5 Taste and odour

(45) Short-term exposure of fish to 25 mg/l phenol (Ebeling, 1940) or for up to four days at 2.5 mg/l (Krishnaswami and Kupchanko, 1969) did not impair the flavour of the flesh, while 10 mg/l cresol induced only a slight taint (Albersmayer and Erichsen, 1959). On the other hand, xylenols and some other constituents of phenolic wastes, including naphthols and quinols, tainted bream and common carp at concentrations between 0.5 and 5.0 mg/l (Bandt, 1955, 1958), while *p*-chlorophenol and *o*-chlorophenol produced an undesirable taint in common carp at concentrations of 0.06 and 0.015 mg/l respectively (Schulze, 1961); the latter substance at a concentration of 0.001 mg/l also tainted the flesh of eels (Boetius, 1954). Thus it is possible that substances such as these were responsible for the taste reported in fish caught in the Rhine when 0.02 to 0.03 mg/l phenols were present (Ebeling, 1940) and in the Elbe containing 0.02 mg/l (Bandt, 1958).

(46) Phenolic flavour may be acquired by fish flesh not only directly from the water but also by the fish eating contaminated food, for example tubifex worms that have been kept in water containing phenol (Mann, 1951). This author and Muller (1962) have both also shown that flavour can be acquired by other animals fed upon tainted fish.

(47) Some phenolic taints may persist in fish flesh for several weeks when fish are kept in clean water (Mann, 1960 and 1960a; Boetius, 1962) unlike some taints, for example those produced by sub-lethal exposure of fish to the herbicide 2,4-D (J. S. Alabaster, personal communication) or by actinomycetes (Thaysen and Pentelow, 1936) which may be lost within 24 h under these conditions.

4. SUMMARY OF DATA ON INVERTEBRATES AND ALGAE

4.1 Phenols

(48) Generally it has been found that bacteria, algae, protozoa, crustacea and mollusca are 10 to 100 times more resistant than fish to phenols (e.g., Anderson *et al.*, 1948; Beer, 1954; Greven, 1956; Bandt, 1958; and Albersmayer and Erichsen, 1959). However, the cladoceran, *Daphnia* sp. appears to be somewhat more sensitive than most other invertebrates (Anderson *et al.*, 1948; Bruun, 1948; Ellis, 1937; Bringmann and Kuhn, 1959 and 1959a; and Patrick, Cairns, and Scheier, 1968); the threshold concentration for *D. magna* is 7 mg/l (Anderson *et al.*, 1948), but with the young (Dowden and Bennett, 1965) and also breeding adults (Mosevich *et al.*, 1952) being most sensitive. There are, however, few laboratory data for other groups, although it has been reported (UK, Ministry of Transport and Ministry of Agriculture, 1936) that freshwater shrimps, snails, and larvae of caddis flies (*Trichoptera*) and mayflies (*Ephemeroptera*) were unaffected at 10 mg/l of either phenol or *o*-cresol in 26 h.

(49) The interpretation of field observations is complicated by low dissolved-oxygen concentrations being associated with high concentrations of phenol, but it has been observed (Beer, 1954) that algae reappeared in the River Plaise where the oxygen concentration had increased to 5.3 mg/l and the phenol concentration had decreased to 4.3 mg/l. In the River Péstan, Mitrović (1963) found tubificids where the dissolved-oxygen concentration was 0.1 to 3.1 mg/l and the phenol concentration 17 mg/l, shrimp, larvae of some chironomids, caddis flies, and mayflies where the water was well aerated and phenol concentrations 1 to 2.5 mg/l, and a diversified and abundant invertebrate community where the maximum concentration of phenol was 1 to 1.5 mg/l.

4.2 Cresols

(50) Comparative studies of all three isomers and phenol with *Microregma heterostoma* (a ciliate) and *Daphnia magna* (Bringmann and Kuhn, 1959 and 1959a) and of *m*-cresol and phenol with the larvae of the mosquito *Culex pipiens* and the phantom midge *Chaoborus cristalinus*,

as well as with the copepod Cyclops strenuus, the ostracod Pionocyprus vidua and Daphnia pulex (Albersmayer and Erichsen, 1959) show that these invertebrates, like fish, are somewhat less resistant to cresols than to phenol and that m-cresol is the least toxic and p-cresol the most toxic isomer. However, the ciliate Paramecium caudatum seems to be much more resistant to a mixture of cresols than to phenol (Halsband and Halsband, 1954) and there is an isolated report (Ellis, 1937) suggesting, contrary to the results of Admas (1927), that the lethal concentration of a mixture of cresols to Daphnia magna is much lower (0.01 mg/l) than it is for phenol (8 mg/l).

(51) With a mixture of cresols, as with phenol, there is some evidence that immature organisms are more sensitive than adults; the 48-h LC50 values for immature Asellus militaris (an isopod) and Gammarus fasciatus (an amphipod) were 33 and 8.6 mg/l respectively and the corresponding values for the adults were 2 to 3 times higher (Emery, 1970).

4.3 Xylenols

(52) There are few data on the toxicity of xylenols to invertebrates. Meissner (in Bandt, 1958) apparently found that the 2,4-isomer was more toxic than either phenol or o-cresol to protozoa, rotatoria, crustacea and mollusca, with little difference between groups, although the type of response measured is not known. Bringmann and Kuhn (1959 and 1959a) using young Daphnia found that, as with fish, 2,5-xyleneol was more toxic than the "m-isomer" (which could include 2,4-, 2,6-, and 3,5-xyleneol), the 24-h LC50 being 10 and 24 mg/l respectively. With the ciliate Microregma the same authors found that food intake was inhibited by various isomers at 10 to 50 mg/l, while the effective concentration for phenol was 30 mg/l. Albersmayer and Erichsen (1959) found that although 2,5-xyleneol was more toxic than phenol to various invertebrates it was not as toxic to these organisms as it was to fish.

5. CONCLUSIONS

(53) Phenolic wastes can contain monohydric phenols, including phenol, the three cresol isomers, and the six xyleneol isomers, together with other substances. They may adversely affect freshwater fisheries by their direct toxicity to fish and fish-food organisms, by their high oxygen demand resulting in oxygen depletion of the receiving water, and by the production of undesirable flavours in the edible flesh of fish.

(54) Of the various phenolic substances, phenol has been the most studied under laboratory conditions. Measurements of the effects of various environmental factors have shown that the toxicity of phenol (48-h LC50) to rainbow trout is increased by a decrease in dissolved-oxygen content (para. 11), an increase in water salinity (para. 14), and a decrease in temperature (para. 10), but is not markedly affected by variations in pH value (para. 12) or water hardness (para. 13); similar effects of salinity, pH value, and hardness have been observed with coarse fish species, but there are no data available on the effects of dissolved oxygen and temperature.

(55) Salmonids are more sensitive to phenol poisoning than coarse fish such as carp (paras 22 and 23), and newly hatched fish are generally more sensitive than adults (paras 15 to 17). The concentrations which have been found lethal within a few days lie within the range 4 to 25 mg/l.

(56) Concentrations of phenol of 1 to 2 mg/l maintained for several months are likely to cause slight mortality of part of a trout population as well as reduced growth of the remainder (paras 24 and 37) and there is some physiological evidence (paras 44 and 8) and histopathological evidence (para. 7) to suggest that stress occurs at concentrations greater than 1.0 mg/l. These results were obtained at temperatures greater than 12°C and it is not known whether at lower temperatures these effects would be produced by lower concentrations.

(57) From the few data which exist on cresols and xylenols, it appears that their acute toxicity to fish is of the same order of magnitude as that of phenol (paras 25 to 27), but there is no information on long-term effects.

(58) Work with mixtures of phenols indicates that the individual toxicities of the components are additive (para. 29); however, the toxicity of phenolic wastes such as gas liquor may be greater than expected if the method of chemical analysis used underestimates the concentrations of cresols and xylenols present.

(59) In natural waters, the reported phenols concentration usually represents most of the monohydric phenols of phenolic wastes, but may exclude part of the cresols, especially the *p*-isomer and the xylenols, and include some other phenolic compounds (para. 5). Salmonids have been recorded in natural waters where the phenols level is about 1 mg/l, although killed (in the same stream) at 3 mg/l (para. 33). Chub, gudgeon and barbel have been recorded where the phenols concentration has reached 4.4 mg/l (para. 34) but there have also been frequent kills of fish associated with a phenols concentration of 3 to 5 mg/l or more. Unfortunately, it is not possible to say what any of these concentrations represent in terms of phenols, cresols, xylenols and other substances, and therefore the field observations cannot be used to substantiate the results of the laboratory experiments described here.

(60) There is no strong evidence that fish avoid low concentrations of phenol in laboratory tests (paras 39 to 41); avoidance reactions reported in the field could result from the reaction of fish either to components of phenolic wastes or to low dissolved oxygen, or to both.

(61) Some phenols impair the taste of fish only at relatively high concentrations, but other constituents of phenolic wastes, and chlorinated phenols, which taint the fish flesh at extremely low concentrations may account for the presence of taints in fish from rivers containing such wastes and where the concentrations of total phenols by analysis were in excess of 0.02 mg/l (para. 45).

(62) Those aquatic invertebrates which have been studied in the laboratory are more resistant than fish to phenol poisoning (paras 48 to 52), but there is a dearth of information on the resistance of organisms characteristic of trout streams. However, some field observations have shown that abundant and diversified invertebrate communities exist where the phenols concentration has not exceeded 1.5 mg/l (para. 48).

6. TENTATIVE WATER QUALITY CRITERIA

(63) Although there are extensive data on the toxicity of the monohydric phenols to fish under laboratory conditions, there are few field observations which can be used to reinforce these. One of the main difficulties is that of analytical techniques, in that the levels of cresols and xylenols in rivers may be underestimated. For this reason, only tentative criteria can be established which may have to be modified in the light of further experience especially when more data on the effect of temperature become available. These criteria are expressed as maximum concentrations which should not be exceeded; it should be appreciated that because of the natural fluctuation in the water quality found in rivers over a period of time, the average concentration will be lower to an extent depending on local circumstances.

(64) Salmonid fish. To ensure long-term survival of salmonids in the presence of phenolic wastes, the concentration of phenol, cresols or xylenols should not exceed 1.0 mg/l, either singly or collectively. Where 2,5-xylenol is the main constituent, the concentration should not exceed 0.5 mg/l. Where the temperature is lower than 5°C, concentrations may have to be halved to ensure the survival of fish. Where other poisons are present due allowance must be made for their contribution to the toxicity, particularly in the case of free chlorine.

(65) Coarse fish. Since laboratory data show that coarse fish are more resistant than salmonids to phenols, the concentration of phenol, cresol or xylenol should not exceed 2.0 mg/l, either singly or collectively, provided that oxidation of this concentration does not produce an adverse reduction in the dissolved-oxygen concentration of the water. In the absence of data on the effect of temperature on the toxicity of phenols to coarse fish it is proposed that the reduction in concentration of 50 percent adopted for salmonids at temperatures below 5°C, should also apply to these species. Where other poisons are present due allowance must be made for their contribution to the toxicity, particularly in the case of free chlorine.

(66) Commercial fisheries. There is no laboratory evidence to indicate that levels of phenol and cresols that are safe for fish cause their flesh to become tainted, but xylenols should not exceed 0.5 mg/l (para. 45). Other phenolic substances, particularly the chloro-phenols, are known to cause taint at very low concentrations; strictly these are outside the scope of this report, but the information that has been considered suggested that they should be excluded from waters supporting commercial fisheries.

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