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WATER QUALITY CRITERIA FOR EUROPEAN FRESHWATER FISH

Report on cadmium and freshwater fish

with the cooperation of the
United Nations Environment Programme

EUROPEAN INLAND FISHERIES ADVISORY COMMISSION
FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS

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REPORT ON CADMIUM AND FRESHWATER FISH

Prepared by

EIFAC Working Party on Water Quality Criteria

for European Freshwater Fish

with the cooperation of the United Nations Environment Programme (UNEP)

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS
Rome, 1977

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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 with the cooperation of the United Nations Environment Programme (UNEP).

The report is being issued in this series where the first ten 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):19 p., 1972; "Report on dissolved oxygen and inland fisheries", EIFAC Tech. Pap., (19):10 p., 1973; "Report on chlorine and freshwater fish", (20):11 p., 1973; "Report on zinc and freshwater fish", EIFAC Tech.Pap., (21):22 p., 1973; "Report on copper and freshwater fish", EIFAC Tech.Pap., (27):21 p., 1976.

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CONTENTS

FOREWORD

This is the eleventh technical paper on water quality criteria for European freshwater fish 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 ten 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 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/.

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

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
Report on Chlorine and Freshwater Fish, EIFAC Tech.Pap., (20):11 p., 1973
Report on Zinc and Freshwater Fish, EIFAC Tech.Pap., (21):22 p., 1973
Report on Copper and Freshwater Fish, EIFAC Tech.Pap., (27):21 p., 1976

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

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

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 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.

4/ EIFAC Report, Fourth Session, 1966, p. 12
5/ EIFAC Report, Fifth Session, 1968, pp.14-5
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., 1972
7/ EIFAC Report, Sixth Session, 1970, p. 13
8/ Doudoroff, P. and D.L. Shumway (1970), Dissolved Oxygen Requirements of Freshwater Fishes, FAO Tech.Pap., (86):291 p.
9/ EIFAC Report, Seventh Session, 1973, p. 18

After the Seventh Session, the EIFAC Working Party on Water Quality Criteria drafted reviews on dissolved oxygen, chlorine and zinc which were studied at its eleventh and twelfth meetings held in Rome (15-17 January 1973) and Karlsruhe (25 May 1973), respectively. The reports on dissolved oxygen, chlorine and zinc have been published as the seventh, eighth and ninth reviews of this series 2/ and were approved by the Eighth Session of EIFAC (Aviemore, Scotland, 1974) 10/. The Eighth Session gave priority to cadmium as the subject of the next report. It recommended in addition (i) that all completed reports should be updated where necessary and offered to a publisher for printing in a single volume and (ii) that research in the field to provide information essential for the formulation of water quality criteria should be encouraged by EIFAC.

After the Eighth Session, the EIFAC Working Party on Water Quality Criteria drafted reviews on copper and cadmium, which were studied at its fourteenth and fifteenth meetings held in Oslo (20-21 May 1975) and Helsinki (9-10 June 1976), respectively. The report on copper and freshwater fish was published as the tenth review of the series 2/ and approved by the Ninth Session of EIFAC (Helsinki, 9-15 June 1976) 11/.

The eleventh review which follows is the one on cadmium 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 W.K. Besch	(Germany, Fed.Rep.)
Dr D. Calamari	(Italy)
Dr M. Grande	(Norway)
Dr T.B. Hasselrot	(Sweden)
Mr R. Lloyd	(United Kingdom), Rapporteur
Dr A.W. Lysak	(Poland)

FAO Secretariat

Mr J.-L. Gaudet - Secretary of EIFAC

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

> "Water quality criteria for freshwater fish should ideally permit all stages in the life cycles to be successfully completed and, in addition, should not produce conditions in a river water which would either teint 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 Tenth Session of EIFAC (Hamburg, Germany Fed.Rep., June 1978).

10/ EIFAC Report, Eighth Session, 1975, p.11

11/ EIFAC Report, Ninth Session, FAO Fish.Rep., (178):p.7

SUMMARY

Cadium is widely used in industry and small quantities are discharged to surface fresh waters; natural background concentrations are usually below 1 µg/l and higher levels have been found in polluted waters. A substantial proportion of the cadmium in a river water is adsorbed onto solids in suspension but only the soluble forms of cadmium are toxic to fish. The concentrations at which soluble cadmium is present in natural and polluted waters are close to the limits of measurement and this causes difficulties in defining and interpreting field data. Little is known of the toxic action of cadmium to fish. The metal is accumulated predominantly in the gills, liver and kidney, but the significance of the levels found to the functioning of these organs is not clear although there is some evidence that the osmoregulatory role of the gills and kidney may be impaired. Cadmium is slowly lost from the tissues when fish previously exposed to cadmium are returned to clean water, but loading can occur in a short period of time causing death several days later.

Acute and chronic toxicity tests with sensitive species of fish have given conflicting results which may have been caused by the variable and unusual concentration/response curve or errors in measuring concentrations of soluble cadmium. Concentrations lethal after at least 10 days exposure can be up to 100-fold less than those lethal in 2 to 4 days, and if a threshold lethal concentration exists, it is ill defined. Several environmental factors influence the position and shape of the concentration/response curve. A decrease in water hardness and dissolved oxygen and possibly in pH value, produces a lower LC50; changes in temperature and salinity may also affect cadmium toxicity.

The sensitivity of different species of fish is more variable for cadmium than for other common pollutants but comparisons between data are difficult to make because of differences in water quality and exposure times. However, of the few species tested, salmonids are more sensitive than cyprinids (with the possible exception of carp), with pike occupying an intermediate position. Juvenile stages appear to be the more sensitive.

Few sub-lethal effects of cadmium have been observed. Minnows have been shown to develop spinal deformities and in rainbow trout the development of ova can be impaired. Increased activity of male brook trout during spawning in low concentrations of cadmium has led to increased mortality.

Salmonid fish appear to be more sensitive than those other components of the aquatic biota which have been tested. Some species of invertebrates such as *Daphnia magna* and *Gammarus fossarum* appear to be as sensitive as salmonids, but most others are much more resistant. Some species of aquatic plants grow more slowly in concentrations of cadmium which are close to the limits for the survival of fish, but the majority of plants appear to be very resistant.

Few data exist on the status of the fish fauna in surface waters polluted with cadmium, although there is some evidence that brown trout were absent from waters where the cadmium concentration was predicted to be harmful on the basis of laboratory experiments. Minnows were also found at concentrations predicted to be harmless to rainbow trout. However, rivers polluted with cadmium also contain other pollutants, especially heavy metals, and although some of these have been shown to be additive with cadmium in their joint toxic action, there is some evidence that zinc may have an antagonistic effect.

On the basis of a critical examination of the available data (summarized in paras. 77-99), tentative criteria for dissolved cadmium can be proposed as follows:

Table 1

Approximate maximum annual 50 and 95 percentile concentrations of soluble cadmium (μg Cd/l) for freshwater fish. Adjustment should be made for the presence of other harmful substances, low concentration of dissolved oxygen and other species

Water hardness (mg/l as $CaCO_3$)	(a) Rainbow trout		(b) Perch	
	50 percentile	95 percentile	50 percentile	95 percentile
10	0.3	0.6	10	20
50	0.4	0.9	15	30
100	0.5	1.0	19	38
300	0.75	1.5	25	50

Values for common carp should be taken to be the same as those for rainbow trout pending further data on long-term effects. The corresponding values for brown trout and pike appear to be about twice as high as those for rainbow trout while those for the more insensitive non-salmonid fish such as perch (Table 1) and minnow would be about thirty eight times higher.

The values in Table 1 should be decreased to allow for low concentration of dissolved oxygen and for the presence of other poisons.

There is a need for reliable field data from polluted and unpolluted rivers and from semi-artificial experimental aquatic ecosystems, to reinforce these criteria. Such studies are particularly necessary to establish the maximum concentrations associated with flourishing populations of resistant coarse fish species, and the modifying effects of other pollutants, especially zinc, in the water.

The concentration of cadmium in the muscle of fish exposed for long periods to low concentrations of cadmium in the water under either laboratory or field conditions is highly variable and can be between 1 and 1 000 times higher (on a dry weight basis) and 0.1 and 100 times higher (on a wet weight basis) than that in the water, i.e., <1 mg Cd/kg muscle (dry weight) or <0.1 mg Cd/kg muscle (wet weight) of fish from water containing 1 μg Cd/l. The reasons for these wide differences are not known.

1. INTRODUCTION

1.1 Source of Cadmium

(1) Cadmium is a rare element and is usually found as an impurity in ores of other metals, principally those of zinc. It is obtained as a by-product in the refining of zinc and copper, but small quantities can remain as impurities in these and other metals. It is present in low concentrations in soils, sandstones and shales from which it is leached only very slowly into surface water (Bowen,1966) and is also present in some phosphate fertilizers. Because of its many industrial applications, chief among which is electroplating, it is often present in manufacturing industrial discharges. Other sources of surface water contamination include rainfall with airborne particulate matter (e.g., from the burning of fossil fuels, including emission from vehicle exhausts), corrosion and erosion.

1.2 Chemistry of Cadmium in Freshwater

(2) The chemical properties of cadmium are intermediate between those of zinc and mercury and consequently cadmium compounds are predominantly ionic in character. Cadmium occurs in the moderately electropositive oxidation state two in aqueous solution so that reduction cannot occur in water containing dissolved oxygen. The hydrated ion ($Cd(H_2O)_6^{2+}$) is stable in aqueous solution, is not readily hydrolyzed and is far less amphoteric than the corresponding zinc ion. Organocadmium compounds (i.e., those with metal-carbon bonds) are known but are far less important in the environment than those of mercury and are not stable in aqueous solution.

(3) Cadmium can form a wide variety of soluble complexes. Complexation in freshwater has been estimated from stability constants published by Weber and Posselt (1974) and Elder (1975), and has been studied experimentally using the specific-ion electrode by Gardiner (1974a) and using anodic stripping voltammetry (ASV) by, for example, O'Shea (1972). The humic complex is usually the most important in water containing organic matter (deriving either from decayed vegetation or from sewage effluent) but complexes with the carbonate, sulphate, chloride and hydroxide, and with chelating agents such as ethylene-diamine tetra-acetic acid (EDTA) and nitrilotriacetic acid (NTA),may also be present. However, the free, uncomplexed ion can normally be expected to predominate over cadmium complexes especially in unpolluted soft waters of relatively low pH value (Gardiner, 1974a).

(4) The solubility of cadmium in natural waters and the rate of precipitation have been studied by Weber and Posselt (1974) and Hem (1972). In aerobic natural waters the carbonate is usually the least soluble salt at concentrations greater than 10 µg Cd/l, precipitation may occur within the pH range of approximately 8.5 to 11; where soluble cadmium is present the principal route by which the metal is removed from solution is by adsorption. The tendency of cadmium to be adsorbed on naturally occurring solids has been studied by Gardiner (1974b). Cadmium ions are adsorbed onto solid humic materials to a far greater extent than onto clay or silica particles. The reduction in the dissolved cadmium concentration observed during biological sewage treatment (Oliver and Cosgrove, 1974) is caused by adsorption on solids, and a large proportion of the cadmium transported in rivers is carried on solid particles (Williams, 1973). The distribution of cadmium in an eutrophic lake has been studied by Mathis and Kevern (1975).

1.3 Analytical Methods

(5) The main analytical techniques used routinely for determining cadmium in natural waters are atomic absorption spectrometry (AAS) using conventional flame excitation (Kuwata *et al.*, 1971) and preceded if necessary by solvent extraction and concentration, flameless AAS with graphite furnace (Rattonetti, 1974) and colorimetric methods (e.g., American Public Health Association, 1971). All should be capable of a detection limit of at least 0.1 µg/l under favourable conditions but normally conventional AAS would be used when the cadmium concentration is at least 5 µg/l to avoid preliminary solvent extraction.

Other techniques used have included: ASV (Gardiner and Stiff, 1975) which also has a detection limit of approximately 0.1 µg/l but is operationally difficult; neutron activation analysis; X-ray fluorescence; fluorimetry; flame photometry and optical emission spectrometry.

(6) Concentrations of cadmium found in surveys of European and North American fresh waters uncontaminated by any known point sources of the metal are usually between 0.01 and 0.5 µg/l (Henriksen et al., 1976).

(7) Because of difficulty both in measuring cadmium at the concentrations usually found in water and in identifying the forms relevant to its toxicity to fish and other aquatic organisms, particularly under field conditions, much of the published data on cadmium in water and on other relevant water quality characteristics are inadequate. Comparison between the results of field and laboratory studies must be made with care. In many cases the concentrations used in laboratory tests are well above the solubility and often the nominal concentrations used are not checked by chemical analysis. Also, differences in the interval between making up test solutions and introducing fish in static tests and in the mean retention time in continuous flow tests, could result in differences in the chemical conditions to which the test fish are exposed.

2. ACCUMULATION OF CADMIUM IN FISH TISSUES

2.1 Laboratory Experiments

(8) Mount and Stephan (1967) using bluegill (*Lepomis macrochirus*) found that cadmium accumulated maximally in the kidney, liver, gill and gut, to a lesser extent in the spleen but not significantly in bone or muscle. The uptake curves indicated that within 30 to 60 days equilibria were established between the concentration of cadmium in the water and those in the tissue. Equilibria were also found to occur after about 2 months in bluegill and largemouth bass (*Micropterus salmoides* (Cearley and Coleman, 1974) and in flagfish (*Jordanella floridae*) (Spehar, 1976).

(9) Similar results have been obtained by Kumuda (1972) using rainbow trout (*Salmo gairdneri*). Calamari and Marchetti (in press) exposed rainbow trout to 50 µg Cd/l (water hardness 320 mg/l as $CaCO_3$) for 120 days and found the metal to be accumulated in various organs with equilibrium reached after 80 days. The increase (on a wet weight basis) was about 30-fold in the blood and liver (0.12 to 3.4 mg Cd/kg), 80-fold in the gill and 100-fold in the kidney (0.17 to 16.5 mg Cd/kg). Concentrations found in the muscle were about 0.030 mg Cd/kg. These fish were apparently in good health. When the fish were returned to clean water the concentrations of cadmium fell by 50 percent in the gill after 7 days and in the liver and kidney after 50 days; normal values were reached in all organs after 80 days.

(10) V.M. Brown, D.G. Shurben and W.F. Miller (personal communication) kept rainbow trout for 65 weeks in nominal concentrations of 2, 5 and 8 µg Cd/l and found a minimal degree of accumulation in muscle and no trend with time. Accumulation factors for muscle, liver and kidney (on a dry weight basis) at the end of the period were no more than about 500, 3 000 and 10 000 respectively. The concentration factor in the gills of fish kept for 3 days at 1 mg Cd/l (equivalent to the 4 to 5 day LC50 for rainbow trout) was 20 for rainbow trout and about 3 for roach (*Rutilus rutilus*) and perch (*Perca fluviatilis*) (Department of the Environment, 1973).

2.2 Field Observations

(11) Lucas et al. (1970) studied trace element concentrations in various species of fish from the Great Lakes using neutron activation analysis and found a median value for cadmium of 0.094 mg Cd/kg for whole (wet) body and 0.4 mg/kg for concentrations in the (wet) liver. Uthe and Blight (1971) using atomic absorption spectrophotometry found less than 0.05 mg Cd/kg for whole (wet) body analyses of different species of freshwater fishes with no differences between fish from industrialized and non-industrialized areas.

(12) Fish from New York State contained about 0.02 mg Cd/kg in (wet) eviscerated body, with only a few individuals having levels up to 0.1 mg/kg (Covett et al., 1972).

(13) Comparable surveys have not been carried out in Europe but Jaakkola et al. (1971) found 0.003 mg Cd/kg in the wet muscle of pike (Esox lucius) in a "clean" area and between 0.004 and 0.013 mg/kg in fish from a "polluted" area in Finland. Values for the liver and kidney in these fish were 0.028 to 0.055 mg/kg and 0.153 to 0.232 mg/kg respectively for the clean area and 0.034 to 0.113 mg/kg and 0.169 to 0.339 mg/kg respectively for contaminated areas.

(14) A sample of 10 brown trout (Salmo trutta) from the River Churnet, England, where the median and 95 percentile values for cadmium in membrane-filtered samples of water taken over a 44-month period were 3 and 6 μg Cd/l, contained average values of 1.4, 4.0, 6.3 and 17.7 mg Cd/kg dry weight in the muscle, liver, kidney and spleen respectively (J.F. de L.G. Solbé, personal communication). Somewhat similar results (0.1, 1.1, 15.4 and 15.7 mg Cd/kg dry weight respectively) have been reported by R. Huddart and H.A. Hawkes (personal communication) for rainbow trout kept for 3 months in an outdoor channel containing river water in which the 50 percentile and 95 percentile concentrations of cadmium were 2 and and 4 μg Cd/l respectively. The concentration factor for the cadmium in the muscle on a dry weight basis is thus about 470 for the brown trout and 50 for the rainbow trout in these two studies.

(15) In Lake Ringvatnet, Norway, where the median and 95 percentile values of cadmium were 0.6 and 1.4 μg Cd/l, the concentration of cadmium in the muscle of char (Salvelinus alpinus) and brown trout was about 0.03 and 0.075 mg/kg dry weight respectively (M. Grande and K.W. Jensen, personal communication), i.e., a concentration factor of about 50 and 125 respectively.

(16) In the River Elsenz, Federal Republic of Germany, where the average reported concentration of cadmium over 2 months' period was 0.5 μg Cd/l, the concentration of cadmium in the wet muscle was 0.04 mg/kg for a one-year-old rainbow trout and 0.05 mg/kg for two six-year-old roach; where the concentration in the water was 0.9 μg Cd/l, the concentration of cadmium in the whole (wet) body of two 3-spined stickleback (Gasterosteus aculeatus) was about 0.1 μg/kg (Prosi, 1976). Much higher concentrations were present in the kidney and liver.

(17) In no case has a positive correlation been noted between cadmium concentration and size or age of the fish.

3. LETHAL EFFECTS ON FISH

3.1 Mode of Action

(18) Calamari and Marchetti (in press) suggested that the toxic effect of cadmium cannot be attributed to one or another of the different chemical forms of the metal in solution but that probably all the "soluble" chemical forms are of similar toxicity (i.e., that passing through a filter having a porosity of 0.45 μm).

(19) Hyperplasia and necrosis of the epithelium of the secondary lamellae of the gill occurred in rainbow trout exposed to 10 mg Cd/l, but gill damage was less evident at 0.01 mg Cd/l (Ministry of Technology, 1970). Bilinski and Jonas (1973) observed extensive degeneration of gill structure in this species after exposure to 1.12 mg Cd/l for 24 h in very soft water (4 mg/l as $CaCO_3$). They found detachment of the epithelial layer, hypertrophy and hyperplasia of the interlamellar epithelium and also a significant (60 percent) depression of lactate oxidation in excised gill filaments from surviving fish. Exposure to a lower concentration (11 μg Cd/l which caused a 75 percent mortality in 96 h) did not result in detectable reduction in the oxidative activity.

(20) The liver, heart and brain can also be affected by cadmium (Ministry of Technology, 1970, 1973). Gardner and Yevich (1970) found pathological changes in kidney and intestinal tract and a rapid increase of eosinophil levels in the blood of mummichog (or killifish) (Fundulus heteroclitus) exposed to cadmium, and suggested that death was caused by impairment of respiratory and extrarenal function through reduction in respiratory surface.

(21) Changes in the activity of some liver enzymes of this species were observed by Jackim et al. (1970). In vitro, the alkaline phosphatase (ALP) activity was the most sensitive to cadmium, but in vivo this was not different from that of the control; on the other hand, the in vivo activity of acid phosphatase, xanthine oxidase and catalase was significantly depressed in fish surviving short exposure to the 96 h LC50. In vitro, cadmium is also able to interrupt energy production in the liver mitochondria of bluegill by blocking oxygen uptake at a concentration of 0.37 mg Cd/l (Hiltibran, 1971). Much higher levels (420 to 1 000 mg/l) are required to induce inhibition of plasma lactate dehydrogenase (PLDH) and plasma glutamic oxalacetic transaminase (PGOT) in white sucker (Catostomus commersoni) (Christensen, 1971). However, the same author found a statistically significant decrease in weight, an increase in protein content, and an increase in activity of acetylcholinesterase (ACH) in alevins of brook trout (Salvelinus fontinalis) held in 0.7 and 3.4 µg Cd/l in soft water; at the higher concentration he found an increase in activity of PGOT and ALP (Christensen, 1975).

(22) Larsson et al. (1976) exposed flounder (Platichthys flesus) for 15 days to sub-lethal concentrations of cadmium and found a reduction in the size of the liver, anaemia, alteration in carbohydrate metabolism (increased blood sugar and liver glycogen and reduced blood lactate and muscle glycogen) and increased plasma Na^+, Cl^-, and Mg^{2+} and reduced plasma K^+ and Ca^{2+}. Increased concentrations of calcium and zinc and reduced concentrations of copper in the liver and reduced concentrations of calcium in the bone were found in several rainbow trout after exposure to 8 µg Cd/l for 80 weeks (V.M. Brown, D.G. Shurben and W.F. Miller, personal communication); changes in the calcium concentrations suggest an alteration of calcium metabolism which might explain the suppression of maturation found in the females (Water Research Centre, 1975). Cadmium-induced ionic imbalance could also explain neuromuscular disturbances, hyperexcitability, convulsions and tetany observed in fish by various authors (Cearley and Coleman, 1974; Eaton, 1974; Benoit et al., 1976; Spehar, 1976) and also perhaps the degeneration of muscle fibre (Department of the Environment, 1973) and lesions in the spinal cord (Bengtsson et al., 1975). The latter authors attribute the high (30 percent) incidence of spinal damage in minnow (Phoxinus phoxinus) to the continuous tension of opposing muscles brought about by prolongation of the muscle action potential caused by cadmium. Spinal deformities have also been described in a large proportion of fish ("Tribolodon") that died after nearly 15 months exposure to 5 µg Cd/l (Nakamura, 1974).

(23) Inflammation of the pancreas has been found in roach surviving exposure to 9.0 mg Cd/l for 50 days (Department of the Environment, 1973), and changes in carbohydrate metabolism in flounder were attributed to pancreatic disorders (Larsson, 1975). Histological changes have been demonstrated in blood-forming tissues of rainbow trout (spleen) (Ministry of Technology, 1970) and mummichogs (head of kidney) (Gardner and Yevich, 1970). Sangalang and O'Halloran (1972) found testicular damage with extensive haemorrhagic necrosis and a reduction in in vitro synthesis of androgen (11 ketosterone) in brook trout.

(24) Irreversible lethal effects appear to have been caused in rainbow trout within 24 h when exposed to the 48-h LC50 value and within 48 h when exposed to the 6-day LC50 (paragraph (25)).

(25) Cadmium has been found in fish tissues in laboratory experiments with fish exposed to known aqueous concentrations (paragraphs 8 to 10) and in fish caught in polluted waters (paragraphs 13 to 14) but little is known of its significance in causing disorders or impairment in function in organs though concentrations there may be much higher than in normal tissues.

(26) It appears that damage to the ion-regulating mechanisms by cadmium is more likely to be the cause of death than respiratory impairment or damage to the nervous system (Cearley and Coleman, 1974), but the precise toxicology of the metal to various species of fish, and the cause of the wide variation in species sensitivity have yet to be clarified. Further information is given in paragraphs (53) to (56).

3.2 Factors Affecting Lethal Levels

(27) Ball (1967) found that the relationship between the logarithm of the median period of survival of rainbow trout and the logarithm of the cadmium concentration was described by a sloping straight line over the range 1 to 64 mg Cd/l, and by a horizontal line over the range 0.01 to 1.0 mg Cd/l. Later investigation showed that the linear relation in the latter range had a slight slope, survival time being highest at low concentrations (Department of the Environment, 1972); the slope varies with environmental factors such as water hardness, dissolved oxygen concentration (Calamari and Marchetti, in press) and temperature (M. Grande, personal communication) and with different species of fish; with goldfish (*Carassius carassius*) for example, the slope is such that the 2, 4 and 10 day LC50 values are quite similar to each other (A.H. Houston and C. McCarty, personal communication). The flatness of the toxicity curve for rainbow trout, also found in another test (Ministry of Technology, 1968), may contribute to poor replication of test results. However, additional problems of defining the amount of readily available toxic material in test aquaria are caused by the low solubility of cadmium in moderately hard waters of high pH value (see paragraph (25)). The median asymptotic value (or median threshold concentration) for cadmium is difficult to estimate for some species because it may not be evident until after several months of exposure have elapsed. Concentrations lethal in a few days may be up to 100-fold higher than those causing mortality in long-term experiments.

(a) Temperature

(28) There are few data available on the effects of temperature on the toxicity of cadmium; with Atlantic salmon (*Salmo salar*) M. Grande (personal communication) found that the 5-day LC50 at 4°C and 10°C in a soft water was about 1 000 µg Cd/l and 50 µg Cd/l respectively although the corresponding 24-h LC50 values were virtually identical. Greater toxicity at high temperature has also been found by Eisler (1971) (paragraph 34).

(b) Dissolved oxygen

(29) Calamari and Marchetti (in press) used rainbow trout acclimated for one week to dissolved oxygen at 40 percent of the air saturation value and found a decrease in survival time in comparison with fish held at the same cadmium concentration at 100 percent air saturation, and a slight reduction of about one third for the LC50 values at 4 to 40 days.

(30) On the other hand, Voyer (1975) found that the 24-h and 96-h LC50 of cadmium to mummichog were not significantly different at levels of dissolved oxygen between 4 mg/l and the air saturation value, to which the fish were acclimated for less than 2 h.

(c) pH value

(31) There is no information published on the effect of pH on the toxicity of cadmium but Pickering and Gast (1972) report a personal communication of R.W. Andrew who found that cadmium had the highest acute toxicity at high pH value despite the fact that in hard water with alkaline pH values cadmium is precipitated from solution (Pickering and Gast, 1972; Eaton, 1974) (see paragraph (4)). On the other hand, preliminary studies (V.M. Brown and D.G. Shurben, personal communication) have shown that a concentration of 4 mg Cd/l is not lethal to rainbow trout within 10 days at a pH of 8.4 but is lethal with a few days at pH 7.2 in water having a hardness of about 280 mg/l as $CaCO_3$.

(d) Hardness

(32) Brown (1968) produced a curve showing a positive relation between the logarithm of the 48-h LC50 of cadmium to rainbow trout and the logarithm of the water hardness. Calamari and Marchetti (in press) confirmed the relationship with alevins acclimated to the test water hardness, the 48-h LC50 being about 0.12, 0.44 and 3.8 mg Cd/l at a water hardness of 20, 80 and 320 mg/l as $CaCO_3$ respectively. This is in reasonable accord with the 75 percent mortality of rainbow trout in 4 days at 11 µg/l observed by Bilinski and Jonas (1976) at a hardness of 4 mg/l as $CaCO_3$.

(33) Recent investigations have shown that the long-term toxicity of cadmium to rainbow trout increases with decrease in hardness of the water; at a total hardness of 14 mg/l (as $CaCO_3$) the 42-day LC50 was 6 µg Cd/l compared with 15 µg Cd/l at a total hardness of 250 mg/l (as $CaCO_3$) (Department of the Environment, 1976). A marked effect of hardness on the toxicity of cadmium to goldfish has also been demonstrated by L. McCarty and A.H. Houston (personal communication) using a static test procedure; the 10-day LC50 values were 1.78 and 40.2 mg Cd/l in waters having a hardness (expressed as $CaCO_3$) of about 21 and at least 100 mg/l respectively.

(e) Salinity

(34) Mummichog, acclimated to different salinities, were more susceptible to cadmium at 5 percent than at 15, 25 or 35 percent salinity (Eisler, 1971), the 8-day LC50 being about 15 mg Cd/l at 5 percent and about 30 mg Cd/l at 35 percent at $20^\circ C$. At lower temperature ($5^\circ C$) the lethal values were about 30 and 50 mg Cd/l respectively for the two extreme salinities. Apparently, fish held at 15 percent were generally more resistant than those acclimated at higher and lower salinities, a phenomenon also observed for other poisons which Herbert and Wakeford (1964) suggested occurs when the blood of fish is approximately isotonic with the surrounding medium.

(f) Suspended solids

(35) It has been determined that cadmium is as toxic in hard water (240 mg/l as $CaCO_3$) at pH 8.0 without organic solids as it is in the presence of 25 mg/l humus solids (containing low levels of metals and detergents) obtained from a percolating filter effluent (Department of the Environment, 1972).

(g) Intermittent exposure to potentially lethal concentrations

(36) Rainbow trout exposed to the 48-h LC50 of cadmium for only 24 h exhibited similar mortalities (50 percent) after 9 days as fish continuously exposed to this concentration (Ministry of Technology, 1969), showing that irreversible lethal effects had occurred within the 24-h exposure period. Calamari and Marchetti (in press) found that about 50 percent of each batch of rainbow trout were killed by the 6-day LC50 of cadmium, whether the fish were exposed to the poison for an uninterrupted 144-h or for 3 successive 48-h periods separated by intervals of 12, 24, 48, 72 or 96 h in clean water.

(h) Acclimation to cadmium

(37) The range of aqueous concentrations of cadmium, represented by the highest concentration at which the standing crop of fish (proportion of fish surviving multiplied by their weight) was not significantly different from the controls, and the lowest concentration at which it was significantly different, have been calculated by Eaton et al. (in press) for two groups of brown trout acclimated to cadmium for different periods. Lower figures (1.1 to 3.7 µg Cd/l compared with 3.8 to 11.7 µg Cd/l) were obtained for brown trout whose exposure started only at the late eyed stage, and therefore involved only 2 days' exposure as embryos compared with 50 days' for the other group exposed as fertilized eggs. Similar results were found with coho salmon (*Onchorhynchus kisutch*). This suggests that acclimation to cadmium occurred during the embryonic stage. Spehar (1976) has found similar increased resistance of flagfish larvae which had been first exposed to cadmium as embryos.

(i) Fish behaviour

(38) Larsson *et al.* (1976) exposed flounder to 10 mg Cd/l and observed increased activity among the fish after 9 to 10 days and the death of a single individual (out of a batch of 8) after 13 days. Benoit *et al.* (1976) found that males of brook trout when exposed to solutions containing cadmium, were more excitable and suffered greater mortality than did the females during spawning. Hyperactivity has also been reported for bluegill (Cearley and Coleman, 1974; Eaton, 1974), for largemouth bass (Cearley and Coleman, 1974) and for flagfish (Spehar, 1976) though there were no differences in this respect between the sexes. Ellgaard *et al.* (in press) have also described an increase in the locomotor activity of bluegill at concentrations of cadmium of 0.1 and 0.25 mg Cd/l, which were not lethal to the fish within 2 weeks; at 0.5 mg Cd/l there was reduced activity and 30 percent mortality. Benoit *et al.* (1976) also quote R.A. Drummond who isolated 28 yearling brook trout from each other and exposed them to 40 µg Cd/l for 144 h and found only 14 percent mortality, suggesting that interaction between individuals in a test container can increase the apparent toxicity of cadmium to fish.

(j) Joint effect of cadmium and other poisons

(39) Eisler and Gardner (1973) found increased mortality of mummichog when non-lethal concentrations of cadmium were present with lethal concentrations of copper and zinc in saline waters. On the other hand, Eaton (1973) found that the 96-h LC50 for fathead minnow (*Pimephales promelas*) in hard water was only 0.8 of that predicted for a mixture containing mainly copper and zinc with cadmium comprising only 4 percent of the total. Tests with rainbow trout in hardwater (J.F. de L.G. Solbé and V.A. Cooper, personal communication) have shown that the 48-h LC50 for zinc was about 3.8 mg Zn/l in the presence of cadmium at concentrations of up to 2 mg Cd/l and that at lower concentrations of zinc down to 0.5 mg Zn/l, times of survival were accountable by the concentration of cadmium alone. Furthermore, in another experiment in which rainbow trout yearlings were exposed for four weeks to mixtures of either 30 or 40 µg Cd/l and zinc at concentrations of up to 500 µg Zn/l in a hard water (245 mg/l as $CaCO_3$) at pH values of about 7.8 there was a tendency for mortality to be least at intermediate concentrations of zinc suggesting some antagonism between the two metals.

3.3 Summary of Toxicity Data

(40) The majority of the concentrations reported to be lethal to fish are in the range 10 to >10 000 µg Cd/l. The differences can be attributed mainly to duration of the experiments (paragraphs (26) and (27)) and the shape of the concentration/response curve which causes difficulty in defining a median lethal threshold concentration even after months of exposure, water hardness (paragraphs (32) and (33)), temperature (paragraph (28)) and species of fish (paragraph (32)). Differences attributable to pH (paragraph (31)), and stage in life cycle (paragraph (41)) are less clearly defined.

(a) Acutely lethal values

(i) Salmonid alevins and fry

(41) The 5-day LC50 of cadmium to 14-day alevins of brown trout at 320 mg $CaCO_3$/l hardness and 10° to 12°C is about 30 µg Cd/l (Ministry of Technology, 1967). Alevins of rainbow trout are also quite sensitive, a mortality of 50 percent and 33 percent having been found during a 48-h exposure to 120 and 25 µg Cd/l respectively in soft water (20 mg/l as $CaCO_3$) (Calamari and Marchetti, in press). Similar findings are reported for swim-up fry of chinook salmon (*Oncorhynchus tshawytscha*) in soft water; the 8-day LC50 was 1.6 µg Cd/l (Environmental Protection Agency, 1975), while in a 19-week test with eggs through to fry there was 27 and 18 percent mortality at 1.9 and 1.3 µg Cd/l, suggesting the possibility of some acclimation having occurred in the egg stage (see paragraph (35)). Alevins of both chinook salmon and steelhead trout (*Salmo gairdneri*) are markedly more resistant to cadmium than are the swim-up fry, the 8-day LC50 for both species being greater than 26 µg Cd/l for alevins and about 1.4 µg Cd/l for swim-up fry in water at about 12°C and having a hardness of about 25 mg/l as $CaCO_3$ (G.A. Chapman, personal communication).

(ii) Salmonid juveniles and adults

(42) In very soft water (4 mg/l as $CaCO_3$) there was a 75 percent mortality of rainbow trout in 96 h at 11 µg Cd/l (Bilinski and Jonas, 1973). In some experiments in hard water (290 to 320 mg/l as $CaCO_3$) the 96-h LC50 was between 2 and 3 mg Cd/l (Ball, 1967; Calamari and Marchetti, in press) and in others (240 mg/l as $CaCO_3$) as low as 50 g Cd/l for fry and adults (Ministry of Technology, 1969) or 30 g Cd/l (Department of the Environment, 1972). The reasons for these differences are not clear but they might be attributable to differences in pH value and in the equilibrium between Cd^{++} and other forms of cadmium in the test solutions.

(43) The resistance (8-day LC50) of parr and smolt of both chinook salmon and steelhead trout to cadmium (0.9 to 2.3 µg Cd/l) is similar to that of swim-up fry (1.4 µg Cd/l) at about 12°C in water having a hardness of about 25 mg/l as $CaCO_3$ (G.A. Chapman, personal communication) but appears to be lower than that of adult male steelhead which had a 17-day LC50 of 4.8 µg Cd/l at a temperature of about 10°C in water having a hardness of about 44 mg/l as $CaCO_3$ (G.A. Chapman and D.G. Stevens, personal communication).

(44) Grande (1972) has carried out short-term tests with Atlantic salmon under-yearlings (4-5 cm in length) and found a 6-day LC50 of 45 µg/l in a soft water (hardness 9.6 mg/l as $CaCO_3$) and at a temperature of 9°C. This suggests that salmon may be slightly more resistant than rainbow trout to acutely lethal concentrations. However, at 4°C the 25-day LC50 for salmon was about 5 µg Cd/l with no indication of a threshold concentration for survival at this time (M. Grande, personal communication). No significant difference in survival between under-yearling brown trout and rainbow trout was found over the range 10 to 1 000 µg Cd/l in hard water (250 mg/l as $CaCO_3$) at pH 7.5 and a temperature of 11°C, the median lethal threshold concentration (at 10 days) being about 10 µg Cd/l for both species (D.G. Shurben, personal communication).

(iii) Non-salmonid fish

(45) Rehwoldt et al. (1972) reported the 96-h LC50 for common carp (*Cyprinus carpio*) to be 240 µg Cd/l in water having a hardness of 55 mg/l as $CaCO_3$.

(b) Long-term lethal values

(i) Salmonid fish

(46) The range of concentrations of cadmium, represented by the highest concentration at which the standing crop of fish (proportion of fish surviving multiplied by their weight) was not significantly different from that of the controls, and the lowest concentration at which it was significantly different, have been calculated by Eaton et al. (in press) for several salmonid species exposed to cadmium in a soft water (45 mg/l as $CaCO_3$) at pH 7.2 to 7.8 and at temperatures of about 10°C during their embryonic stage and for at least 60 days during their subsequent larval stage; the ranges were 4.4 to 12.3 µg Cd/l for lake trout (*Salvelinus namaycush*), 3.8 to 11.7 for brown trout and 1.1 to 3.8 for brook trout.

(47) The 50-day LC50 for rainbow trout was found to be 10 µg/l in water having a hardness of 240 mg/l as $CaCO_3$ at a pH of about 8.0 (Department of the Environment, 1972). On the other hand, Calamari and Marchetti (in press) using a somewhat harder water (320 mg/l as $CaCO_3$) obtained a threshold of 100 µg/l for yearlings of the same species in a 40-day experiment, and observed almost complete survival of adults (200 g in weight) during a 120-day period of exposure to 50 µg/l under the same environmental conditions. The reasons for this difference in results with rainbow trout are not clear.

(ii) Non-salmonid fish

(48) The range of concentrations of cadmium, represented by the highest concentration at which the standing crop of fish (proportion of fish surviving multiplied by their weight) was not significantly different from that of the controls, and the lowest concentration at which it was significantly different have been calculated by Eaton et al. (1976) for pike exposed to cadmium in soft water (45 mg/l as $CaCO_3$) at pH 7.2 to 7.8 at a temperature of about 16°C for 7 days as embryos and subsequently for 28 days as larvae; the range was 4.2 to 12.9 µg Cd/l which is similar to that for brown trout (paragraph (46)).

(49) No other data are reported on young stages and few are available for the adults of European species of coarse fish. The 60-day LC50 for stone loach (Noemacheilus barbatulus) in a hard water (240 mg/l as $CaCO_3$) at about 12°C was approximately 2 mg Cd/l (Solbé and Flook, 1975); the 7-day LC50 for stone loach was also about 2 mg Cd/l which is much higher than the corresponding value of about 0.01 mg Cd/l found for rainbow trout by Ball (1967) under comparable conditions.

(50) Bream (Abramis brama) all survived for 6 weeks at 5 mg Cd/l or for 10 weeks at 0.5 mg Cd/l, though pathological changes occurred inthe latter test, necrosis of the liver being particularly evident (Department of the Environment, 1971). The 50-day LC50 for perch in hard water (250 mg/l as $CaCO_3$) was about 0.5 mg Cd/l, and for roach >9 mg Cd/l (Department of the Environment, 1973); although all the roach survived 50 days at 0.5 mg Cd/l, every fish showed degeneration of muscle fibres.

(51) Bengtsson et al. (1975) kept minnow for 70 days in a water having an alkalinity of 40 mg/l as $CaCO_3$, and a salinity of 6.7 percent, at pH 7.8 to 8.0 in the presence of cadmium. The 70-day LC50 was 0.4 mg Cd/l (95 percent confidence limits of 0.15 and 1.16 mg Cd/l) and there was about 30 percent mortality at 34 µg Cd/l and about 20 percent at 7.5 µg Cd/l and in the controls (up to 1 µg Cd/l). A small proportion (<5 percent) of those surviving at about 7.5 µg Cd/l showed signs of spinal deformity compared with none in the controls and about 15 percent in those surviving 34 µg Cd/l.

4. SUB-LETHAL EFFECTS ON FISH

(52) Some sub-lethal effects have already been mentioned in paragraphs (21) to (23) and (25) in relation to the mode of action of cadmium.

(53) Kumada et al. (1972) found no significant mortality, and no effect on growth of rainbow trout exposed to a concentration of 5 µg Cd/l over a period of 30 weeks; the hardness of the water was not stated but from the low 10-day LC50 values it might have been very low. Long-term constant-flow tests have been carried out on under-yearling rainbow trout over a period of 65 weeks in hard water (250 mg/l as $CaCO_3$) at nominal concentrations of cadmium of 0, 2, 5 and 8 µg Cd/l (V.M. Brown, D.G. Shurben and W.F. Miller, personal communication). All of the fish survived and their growth was apparently not affected by the cadmium, but the development of ova, the hatchability of artificially-stripped eggs and the survival of the larvae were all adversely affected at levels down to 2 µg Cd/l. Spermatogenesis was adversely affected in only a single male kept at 8 µg Cd/l. The fish at this concentration were exposed for a further 15 weeks without any mortality or development of ova. The observed concentration related suppression of female maturity was confirmed by histological examination; ovaries from fish exposed to 8 µg Cd/l contained only immature oocytes at an early stage of development. All control fish were easily stripped of eggs, but only 3 out of 4 fish at 2 µg Cd/l, 2 out of 4 at 5 µg Cd/l and none at 8 µg Cd/l could be treated in this way. The mortality of eggs was 75 percent in the controls at 7 weeks and 100 percent at 2 µg Cd/l after 5 weeks and at 5 µg Cd/l after one week. The hatch of control eggs and the survival of control larvae subsequently exposed to cadmium was not affected by levels up to 8 µg Cd/l. The in vitro respiration of liver mitochondria of fish exposed to cadmium for 33 weeks (B.N. Zaba and E.J. Harris, personal communication) was not inhibited (cf. paragraph (21)), but concentrations of cadmium and copper were lowest in mitochondria from fish exposed to the highest concentrations of cadmium (see paragraph (22)). The diffusing capacity (a measure of

respiratory function) of the gills of the fish after exposure to cadmium for 7 months was examined by Hughes (1976); the results indicate a reduction in diffusing capacity at all concentrations (V.M. Brown, G. Knowles and G.M. Hughes, personal communication). The concentration of cadmium in the control water was about 0.4 μg Cd/l.

(54) A preliminary constant-flow test in a hard water (240 mg/l as $CaCO_3$) using batches of 10 yearling brown trout 10 weeks before the onset of sexual maturity at ambient temperatures of 7 to 19°C showed that 20 percent of the fish became mature at nominal concentrations of 3 μg Cd/l, 9 μg Cd/l, and in the controls although at 27 μg Cd/l 10 percent had died and none matured. Fourteen months after the beginning of the experiment 80 percent were sexually mature in the controls and in those at 3 μg Cd/l and 9 μg Cd/l; at 27 μg Cd/l 60 percent had died and 3 of the 4 remaining fish were sexually mature (V.M. Brown and D.G. Shurben, personal communication). These findings suggest that brown trout may be less sensitive to cadmium than rainbow trout.

(55) Peterson (1976) found that juvenile Atlantic salmon acclimated to 15°C in a soft water (13 mg/l as $CaCO_3$) selected this temperature in a horizontal gradient tank and tended to select a slightly lower value (14°C) in the presence of 2 μg Cd/l, although this preference was not statistically different from that of the controls.

(56) Weis and Weis (1966) found that initial healing and formation of the blastema of amputated fins of killifish was inhibited at a concentration of 10 μg Cd/l which was not lethal to the fish in 14 days.

5. FIELD OBSERVATIONS ON FISH

(57) Downstream of a sewage effluent outfall in the River Arrow, England, where concentrations of soluble cadmium ranged from 8 to 25 μg Cd/l and averaged 19 μg Cd/l, other poisons being present at 0.1 of the combined 48-h LC50 values for rainbow trout, the median period of survival of caged rainbow trout was 8 days which is close to the results found in laboratory experiments (paragraph (42)). Some non-salmonid fish were resident upstream of the outfall, however, where the mean concentration of cadmium was only about 0.8 μg/l (0.08 of the 10-day LC50 value) (Ministry of Technology, 1970).

(58) It has been shown that brown trout were present upstream of an effluent outfall in the River Tean, England (hardness 210 mg/l as $CaCO_3$) where the median and 95 percentile concentrations of "soluble" cadmium over a 44-month period were 2.6 and 6.4 μg Cd/l respectively, but were absent downstream of the outfall where the corresponding values were 7 and 19 μg Cd/l (V.A. Cooper and J.F. de L.G. Solbé, personal communication). The latter figure is lower than the 8-month LC50 for brown trout (30 μg Cd/l); only small concentrations of other poisons, principally copper and zinc were also present which, on average, were equivalent to only 0.06 and 0.04 of the respective predicted 48-h LC50 values to rainbow trout. Other species which were present under these conditions were bullhead (<u>Cottus gobio</u>), 3-spined stickleback and minnow (Department of the Environment, 1973).

(59) Similar observations (V.A. Cooper and J.F. de L.G. Solbé, personal communication) have been made in the head waters of the River Churnet, England, where the median pH value was 7.2, the median hardness was 104 mg/l as $CaCO_3$ and the 50 and 95 percentile values of soluble cadmium, where brown trout and bullhead were present, were 3 and 6 μg Cd/l; median and 95 percentile values of copper and zinc were equivalent to 0.11 and 0.28 respectively of their combined predicted 48-h LC50 values to rainbow trout.

(60) Recent studies in Norway (M. Grande and K.W. Jensen, personal communication) have shown that good brown trout fisheries were present in soft water streams (average hardness between 17 and 20 mg/l as $CaCO_3$) where the median and 95 percentile values of soluble cadmium over the period March-August were about 0.3 and 0.6 μg Cd/l respectively. Good char fisheries were also present in two lakes of similar hardness into which the streams discharged: Lake Ringvatnet, where the corresponding percentile values were about 0.6 and 1.4 μg Cd/l

respectively and L. Hostovatnet, where they were about 0.5 and 1.2 g Cd/l respectively. Average concentrations of zinc in the water were up to 35 µg Zn/l in the streams and up to 88 µg Zn/l in the lakes; the corresponding values for copper were up to 43 µg Cu/l for both streams and lakes.

6. AQUATIC INVERTEBRATES

6.1 Laboratory Tests

(61) Brkovic-Popovic and Popovic (in press) carried out tests with Tubifex tubifex at 20°C and found 48-h LC50 values of about 2.8, 31, 45 and 720 µg Cd/l in water having a total hardness of 0.1, 34.2 (without phosphate buffer), 34.2 (with phosphate buffer) and 261 mg/l expressed as $CaCO_3$. These authors report (personal communication) similar results for Daphnia magna. Thus it seems that water hardness has a marked effect on the acute toxicity of cadmium to these species, just as it has on the toxicity of cadmium to fish.

(62) Some freshwater crustaceans, such as Daphnia magna have been shown to be among the aquatic invertebrates most sensitive to cadmium. Cebejszek and Stasiak (1960) found that the 48, 96 and 120-h LC50 values for this species in a hard water (275 to 290 mg/l as $CaCO_3$) at 20 to 22°C were 620, 470 and 370 µg Cd/l for cadmium sulphate and slightly higher for the chloride salt. Bringmann and Kühn (1959) found a much lower 48-h LC50 of 100 µg Cd/l for the juvenile stages in a somewhat softer water (hardness 215 mg/l as $CaCO_3$) at 23°C, while Biesinger and Christensen (1972) obtained a 48-h LC50 of 65 µg Cd/l for unfed young in a much softer water (hardness 44 to 53 mg/l as $CaCO_3$) at 11 to 19°C. Thus the young appear to be somewhat more sensitive than the adults.

(63) However, immobilization of this organism has been observed after 64 h at 2.6 µg Cd/l in water having a hardness of 100 mg/l as $CaCO_3$ and a temperature of 25°C (Anderson, 1948). Also Biesinger and Christensen (1972) found that the 21-day LC50 was only 5 µg Cd/l. Furthermore, they showed that there was a 7 percent lower weight at the end of this period at 1 µg Cd/l than in the controls and that a 50 percent and 16 percent impairment of reproduction was caused at 0.7 and 0.17 µg Cd/l respectively. Boutet and Chaisemartin (1973) found a 50 percent impairment of reproduction in the crustaceans Orconectes limosus and Austropotamobius pallipes at 50 and 40 µg Cd/l respectively (hardness not stated).

(64) Another sensitive organism appears to be Gammarus fossarum which was killed within 7 days at a concentration of 10 µg Cd/l (as chloride) in a hard water (hardness 320 mg/l as $CaCO_3$) and a temperature of 18 to 20°C (I. Schreiber and W.K. Besch, personal communciation).

(65) Other invertebrates examined are either similar to Daphnia in their sensitivity to acutely lethal concentrations of cadmium or are more resistant. The 10-day LC50 for the chironomid (Tanytarsus dissimilis) was 3.4 µg Cd/l while the 28-day LC50 for the snail (Physa integra) was 8.2 µg Cd/l and for the mayfly (Ephemerella sp.), 1.7 µg Cd/l, but no significant mortality was observed for the caddisfly (Hydropsyche betteni) and the stonefly (Pteronarcys dorsata) (Environmental Protection Agency, 1975). Schweiger (1957) found that Carinogammarus roeseli was not injured in 7 days at 30 µg Cd/l but was killed at 400 µg Cd/l in a water having a hardness of 260 mg/l as $CaCO_3$, and that the corresponding values for Tubifex tubifex were 0.3 mg and 5 mg respectively. Thorp and Lake (1974) tested Australian freshwater crustacea in a soft water (hardness, 10 mg/l as $CaCO_3$) at 15°C and found 96-h LC50 values of 10 µg Cd/l for Austrochiltonia subtenuis, and 60 and 180 µg Cd/l for the shrimp Paratya tasmaniensis for animals collected in the summer and spring respectively.

(66) The 63-h LC50 of the snail Biomphalaria glabrata has been reported as 100 µg Cd/l in a soft water (hardness at about 25 mg/l as $CaCO_3$) at pH 8 and a temperature of 20°C (Ravera et al., 1974) but reproduction was impaired at 10 µg Cd/l.

(67) The 96-h LC50 at 18 to 20°C of the larvae of the mayfly Athalophebia australis in a soft water (hardness 40 mg/l as $CaCO_3$) was 0.84 mg Cd/l (Thorp and Lake, 1974) and for Ephemerella subvaria in water of similar hardness (44 mg/l as $CaCO_3$) it was 2 mg Cd/l (Warnick and Bell, 1969). These latter authors also found that the 4-day LC50 of the larvae

of the stonefly Acroneuria lycorias and the 11-day LC50 of the larvae of the caddisfly Hydropsyche betteni, tested under the same conditions, were both 32 mg Cd/l (cf. paragraph (64) W.K. Besch (personal communication) has found that the structure of nets by larvae of Hydropsyche was appraently normal at concentrations of cadmium in the water falling from about 2 to 0.02 mg Cd/l every 34 h in a hard water (320 mg/l as $CaCO_3$). Median lethal concentrations of the same order of magnitude for larvae of several species of Diptera and Plecoptera, Ephemerella grandis and the caddis Brachycentrus americanus were found by Clubb et al. (1975b)) in a hard water (240 mg/l as $CaCO_3$); the 96-h LC50 of small immature specimens of E. grandis was about 0.2 of that of mature adults. Chironomus thummi survived 50 mg Cd/l for 7 days but was killed at 150 mg Cd/l (Schweiger, 1957).

(68) Other species are even more resistant. The 96-h LC50 for the damselfly nymph Ischnura heterostica is 230 mg Cd/l and for larvae of leptocerid caddisflies is as high as 2 g Cd/l even when deprived of their cases (Thorp and Lake, 1974); the eruciform caddisfly larva of Anabolia nervosa is of similar sensitivity (Schweiger, 1957).

(69) In one study with several species of insects (Clubb et al., 1975a) a higher mortality was found at high concentrations of dissolved oxygen (6 to 7.6 mg/l) than at low concentrations (3 to 4.9 mg/l), and since concentrations of cadmium in the insects also increased with increase in dissolved oxygen concentration it was suggested that the increased toxicity was attributable to increase in metabolic rate at higher dissolved oxygen levels.

(70) Laboratory tests (W.K. Besch, personal communication) in a soft water (hardness about 30 mg/l as $CaCO_3$) showed that when the larvae of Chironomus lepperi were exposed to a concentration of 1 mg Cd/l only 10 percent survived to the adult stage but that in the presence of mud they developed to this stage even when the mud contained a concentration of 22 mg Cd/l wet weight although development appeared more successful when the mud contained only 10 mg Cd/l.

6.2 Field Studies

(71) In the South Esk River, Tasmania, which is heavily polluted by mining wastes and contains about 40 µg Cd/l together with 150 µg Zn/l and 30 µg Cu/l, crustacea, molluscs and larvae of Odonata and Plecoptera were eliminated and mayflies, beetles and caddisflies were severely affected. Further downstream, where concentrations of heavy metals were between 20 percent and 30 percent lower, nearly all taxa were present and crustaceans and campodeiform caddisfly larvae were even more abundant than upstream of the source of pollution (Thorp and Lake, 1974).

(72) In an outdoor channel supplied with river water containing 75 percent sewage works effluent in which the median and 95 percentile concentrations of cadmium over a three-month period were 6.8 and 9.3 µg Cd/l respectively, the pH value about 7, the hardness 254 mg/l as $CaCO_3$, and the mortality of rainbow trout was 32 percent, commonly occurring invertebrates were, in descending order of numerical dominance, Asellus aquaticus, Limnaea pereger, Anatopynia notata, Pentaneura lentiginosa, Tubifex tubifex, Microspectra astrofasciatus and Simulium ornatum (D. Balloch and H.A. Hawkes, personal communication).

(73) These results from the field and simulated stream ecosystems show differences in sensitivity between different species of aquatic invertebrates and fish similar to those observed under laboratory conditions and suggest that where fish faunas are adversely affected by cadmium the direct effects on fish themselves are likely to be more important than indirect effects caused by a reduction in the numbers of fish-food organisms.

7. AQUATIC ALGAE AND MACROPHYTES

(74) Cadmium interferes with photosynthesis of terrestrial plants, partly by reducing the total concentration of chlorophyll pigments and altering their ratios (Bazzaz and Govindjee, 1974), thereby reducing growth rates and crop yields (Haghiri, 1973; Turner, 1973). Few data are available, however, for aquatic plants particularly under field conditions.

(75) A concentration of 300 μg Cd/l in water of low hardness (15 mg/l as $CaCO_3$), was lethal to a culture of the green alga Selenastrum capricornutum, and 50 μg Cd/l inhibited growth (Bartlett et al., 1974). However, subsequent experiments with mixtures of heavy metals suggested that cadmium inhibited the toxicity of copper to this species. Bumbu and Mokryak (1973) found that the addition of $CdCl_2$ to cultures of Scenedesmus quadricauda at concentrations of 50 to 500 μg Cd/l severely reduced growth rates. Klass et al. (1974) found significant reductions in growth of this species at 6.1 μg Cd/l and severe inhibition at 61 μg Cd/l in a hard water (about 270 mg/l as $CaCO_3$).

(76) In laboratory experiments with water milfoil (Myriophyllum spicatum) Stanley (1974) found 50 percent reduction of root weight at 7.4 mg Cd/l and of shoot weight at 14.6 mg Cd/l, of root length at 20.8 mg Cd/l and of shoot length at 809 mg Cd/l, but gave no indication of the threshold concentrations for growth inhibition. Hutchinson and Czyrska (1972) found that at 10 μg Cd/l and 50 μg Cd/l the percentage inhibition of growth of Lemna valvidiana was about 25 percent and 80 percent respectively and that of Salvinia natans, 50 percent and 90 percent respectively; however, cadmium was more toxic to L. valvidiana when grown with S. natans than without it and the latter was able to grow more rapidly and cadmium accumulation was less in the presence of L. valvidiana than in its absence.

8. SUMMARY AND CONCLUSIONS

(77) Cadmium occurs naturally in the environment at geochemically low levels, usually with other metals, principally zinc, and is also present with metals and other chemicals in industrial waste discharges and receiving waters (paragraphs (1) and (57)). This makes it difficult to distinguish the effects of cadmium per se in the aquatic environment.

(78) Concentrations of cadmium in fresh waters uncontaminated by known sources of the metal are usually between 0.01 and 0.5 μg Cd/l (paragraph (6)). These concentrations are difficult to measure (paragraphs (2) and (5)) as are the higher levels which adversely affect sensitive aquatic organisms; it is also difficult to measure concentrations of dissolved forms of cadmium which are believed to be mainly responsible for the toxicity. Concentrations of cadmium in natural waters vary and the 95 percentile value over a period of a year or so has been found to be between 2.0 and 2.7 times the 50 percentile value (paragraphs (6), (58) and (59)). Cadmium can form a wide variety of complexes with humic material, inorganic ions, and organic chelating agents but under aerobic aqueous conditions uncomplexed ionic cadmium occurs predominantly, especially in unpolluted soft water of relatively low pH value (paragraph 3). Cadmium carbonate normally precipitates at pH values greater than about 8.5 but cadmium compounds may also be adsorbed, especially by humic material (paragraph (4)). For these reasons and also because data on factors affecting toxicity (paragraphs (28) and (35)) are often lacking, much of the literature is difficult to interpret.

(79) Cadmium has been found to accumulate in the tissues of aquatic organisms exposed to known aqueous concentrations but little is known of its toxicological significance (paragraphs (8) and (14)). It appears, however, that damage to ion-regulating mechanisms is more likely to be a cause of death than respiratory impairment or damage to the nervous system (paragraphs (25) and (26)).

(80) The concentration of cadmium in the muscle of fish exposed for long periods to low concentrations of cadmium in the water under either laboratory (paragraph (10)) or field conditions (paragraphs (14) and (15)) is usually < 1 000 and < 100 times higher (on a dry weight and wet weight basis respectively) than that in the water (paragraphs 9 and 14b), i.e., < 1 mg Cd/kg muscle (dry weight) or < 0.1 mg Cd/kg muscle (wet weight) in fish from water containing 1 μg Cd/l. There is no clear correlation between concentrations of cadmium in the muscle and those in the water to which the fish were exposed.

(81) The relationship between the logarithm of median period of survival of fish and the logarithm of concentration of cadmium is unusual in that the slope of the line is shallow. Moreover the position of the line varies considerably between experiments (paragraph (27)), possibly because the test solutions have not come to the same chemical equilibrium, different

amounts of ionic cadmium being present according to the retention time in the apparatus at the particular pH, temperature and hardness of the water used. It is also possible that the sensitivity of fish to cadmium toxicity may vary with different experimental conditions.

(82) The acute toxicity of cadmium to fish is increased by increase in temperature (paragraphs (28) and (34)) and by reduction in dissolved oxygen (paragraph (29)) in water hardness (paragraphs (32) and (33)) and in pH (paragraph (31)). With hardness the effect is much more marked over a period of 2 to 6 days than it is at 40 to 50 days at which time there may be a clear indication of asymptotic concentrations (paragraphs (32) and (33)). There are no data on the effect of salinity on the toxicity of cadmium to European freshwater fish but toxicity might be least at salinities approximately isotonic with the blood of the fish (paragraph (33)). Toxicity is not apparently affected by the presence of suspended humus solids at a concentration of 25 mg/l (paragraph (34)). Acclimation to cadmium may occur in the egg stage (paragraph (46)). Lethal effects may be increased by factors which increase activity such as spawning and testing of fish in batches rather than singly (paragraph (38)).

(83) Irreversible lethal effects may occur at high concentrations of cadmium; in rainbow trout they occur within 24 h on exposure to the 48-h LC50 and within 48 h on exposure to the 6-day LC50 (paragraph (36)). There is some evidence that the presence of low concentrations of cadmium, which are not lethal on their own, reduce the time of survival of fish at lethal concentrations of copper and zinc (paragraph (39)). On the other hand, the lethal effect of low concentrations of cadmium seem to be reduced by the presence of sub-lethal concentrations of zinc (paragraph (39)).

(84) Species differ in their sensitivity to cadmium. Of the species of fish found in Europe and tested to date, the most sensitive appears to be the rainbow trout, long-term experiments on which have shown that adverse effects on reproduction occur at concentrations of cadmium as low as about 2 μg Cd/l (paragraph (54)). The "no effect" concentration has not been measured but probably lies between 0.5 and 2 μg Cd/l.

(85) Adult brown trout appear to be similar to rainbow trout in their resistance to the acute lethal effects of cadmium although as alevins they appear to be slightly more sensitive than rainbow trout (paragraph (41)); and the threshold concentration for median survival is about 10 μg Cd/l and 30 μg Cd/l for the rainbow and brown trout respectively in hard water (paragraph (44)). Moreover, sexual maturity in brown trout has been observed to occur at concentrations as high as 27 μg Cd/l under laboratory conditions (paragraph (55)).

(86) There are few data on non-salmonid fish and none relate to experiments carried out at more than one hardness for a given species. However, common carp appear to be comparable to rainbow trout (paragraph (45)), whereas goldfish are much less sensitive to acutely lethal concentrations (paragraph (33)), while the long term (40-70 days) lethal values for minnow (paragraph (51)), stone loach (paragraph (49)) and perch, bream and roach (paragraph (50)) are much higher than those of trout. With minnows, however, the lowest concentration at which a significant mortality and spinal deformity occurred was 7.5 μg Cd/l (paragraph (51)) in a soft water (40 mg/l as $CaCO_3$). Embryos and larvae of pike and brown trout are comparable in their sensitivity to cadmium (paragraph 48).

(87) Field data on the effects of cadmium on fish are scarce. Brown trout have been observed in the River Tean in which the median and 95 percentile concentrations of cadmium were 2.6 and 6.4 μg Cd/l respectively and also in the River Churnet where the corresponding concentrations were 3 and 6 μg Cd/l (paragraph (58)). This is consistent with laboratory findings on the ability of this species to survive and become sexually mature in the presence of 27 μg Cd/l (paragraph (54)).

(88) Non-salmonid fish (bullhead, stickleback and minnow) occurred in the River Tean where brown trout were absent and the 50 and 95 percentile concentrations of total "soluble" cadmium were 7 and 19 μg Cd/l; for the minnow this is consistent with the laboratory data (paragraph (51)) bearing in mind the higher water hardness in the River Tean (210 mg/l as $CaCO_3$).

(89) There are almost no data available on the effects of sub-lethal concentrations of cadmium on the behaviour of fish. Hyperactivity has been observed in several species and is associated, especially in males, with increased mortality at spawning time (paragraph (38)).

(90) Aquatic invertebrates are generally more resistant than fish to cadmium posioning (paragraphs (64) to (70)), although Daphnia and Gammarus appear to be particularly sensitive (paragraphs (62) and (64)). Aquatic plants do not appear to be particularly sensitive to cadmium (paragraph (75)) although the absence of data on water hardness generally prevents a comparison to be made with other organisms (paragraphs (74) and (76)). Thus it is likely that the direct effects of cadmium on fish would be more important than those caused indirectly through reduction in numbers of fish food organisms.

(91) There is need for the development of sensitive methods for measuring soluble cadmium particularly in its ionic forms at the low levels ($\mu g/l$) at which it appears to exert its toxic effects on the most sensitive organisms. Relevant environmental variables should also be measured when carrying out laboratory toxicity tests and field studies, the latter being particularly important in developing water quality criteria.

9. TENTATIVE WATER QUALITY CRITERIA

(92) The data on the toxicity of cadmium to aquatic organisms are not very extensive. Fish, particularly the rainbow trout, have received most attention and the threshold concentrations for median survival at different hardnesses of water and the threshold concentrations for reproductive success in a hard water have been established under laboratory conditions. However, different workers obtain different results under apparently similar conditions. Effects of other environmental variables, especially pH value and temperature, are not yet thoroughly worked out. Moreover, the measurement of cadmium, particularly in the dissolved states at concentrations which adversely affect aquatic organisms, has generally been unsatisfactory.

(93) Salmon are similar to rainbow trout in their response to acutely lethal concentrations of cadmium in soft water while brown trout appear to be more resistant to adverse effects on reproduction in a hard water. Pike and brown trout appear to be similar in their sensitivity to cadmium at the embryonic and larval stages. Non-salmonid fish are more resistant than salmonid fish to long-term lethal effects in hard water and minnows are more resistant than salmonids to adverse effects on growth in soft water.

(94) Field data on all species are few and relate mainly to brown trout.

(95) Thus, any water quality criteria that are developed for cadmium must remain very tentative until further observations are available.

(96) Concentrations of cadmium in fresh water fluctuate seasonally and within shorter time intervals and, in the absence of precise information on the way in which fish populations are likely to be adversely affected by particular levels at certain times of the year, an arbitrary method has to be used to take such effects into account in water quality criteria for fish.

(97) It is proposed that water quality should be expressed as annual 50 and 95 percentile concentrations of "soluble" cadmium (i.e., that passing through a filter having a porosity of $0.45 \mu m$) and that the maximum levels not inimical to fisheries should be taken as 0.05 and 0.1 respectively of the median threshold concentration for survival, taking into account the effect of hardness of the water. Table 1 shows the values appropriate to rainbow trout and perch.

(98) Values for common carp should be taken to be the same as those for rainbow trout pending further data on long-term effects. The corresponding values for brown trout and pike appear to be about twice as high as those for rainbow trout, while those for the more insensitive non-salmonid fish such as perch and minnow could be tentatively taken to be about thirty-eight times higher (Table 1).

(99) The values in Table 1 should be decreased to allow for low concentration of dissolved oxygen and for the presence of other poisons. The values may also have to be increased to allow for a reduction in toxicity caused by the presence of sub-lethal concentrations of zinc.

Table 1

Approximate maximum annual 50 and 95 percentile concentrations of soluble cadmium (µg Cd/l) for freshwater fish. Adjustment should be made for the presence of other harmful substances, low concentration of dissolved oxygen and other species (paragraphs (98) and (99))

Water hardness (mg/l as $CaCO_3$)	(a) Rainbow trout		(b) Perch	
	50 percentile	95 percentile	50 percentile	95 percentile
10	0.3	0.6	10	20
50	0.4	0.9	15	30
100	0.5	1.0	19	38
300	0.75	1.5	25	50

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