WRC WATER RESEARCH C

22511

# DETERMINATION OF POLLUTANTS IN EFFLUENTS
(PLC 4332CD)

# PROPOSED ENVIRONMENTAL QUALITY STANDARDS FOR SULPHIDE IN WATER AND ASSOCIATED MATERIALS

Project Leader: G. Mance
Authors: A.R. O'Donnell
J.A. Campbell

With Annexes prepared by
J. Fawell
WRC

July 1984

778-M

RESTRICTION: This report has the following restriction distribution

EXTERNAL: DOE Nominated Officer - 20 copies
EQO Sub-Group - 14 copies
Steering group - 9 copies

INTERNAL: Directors, appropriate Assistant Directors and Managers plus 5 copies to Scientific Staff

DOE CONTRACT REFERENCE: PECD 7/7/074

WRC ENVIRONMENT
MEDMENHAM LABORATORY: Henley Road,
Medmenham, P.O. Box 16, Marlow, Bucks. SL7 2HD
Tel: Hambleden (Bucks) (049 166) 531

# DETERMINATION OF POLLUTANTS IN EFFLUENTS
(PLC 4332CD)

# PROPOSED ENVIRONMENTAL QUALITY STANDARDS FOR SULPHIDE IN WATER AND ASSOCIATED MATERIALS

Project Leader: G. Mance
Authors: A.R. O'Donnell
J.A. Campbell

With Annexes prepared by
J. Fawell
WRC

July 1984

778-M

RESTRICTION: This report has the following restriction distribution

EXTERNAL: DOE Nominated Officer - 20 copies
EQO Sub-Group - 14 copies
Steering group - 9 copies

INTERNAL: Directors, appropriate Assistant Directors and Managers plus 5 copies to Scientific Staff

DOE CONTRACT REFERENCE: PECD 7/7/074

**WRC ENVIRONMENT**
MEDMENHAM LABORATORY: Henley Road,
Medmenham, P.O. Box 16, Marlow, Bucks. SL7 2HD
Tel: Hambleden (Bucks) (049 166) 531

# SUMMARY

Under the EC Dangerous Substances Directive, Member States are required to reduce pollution of both fresh and salt waters, resulting from the discharge of List II substances, by the Environmental Quality Objectives (EQO) approach. The Department of the Environment have contracted the Water Research Centre to recommend Environmental Quality Standards (EQSs) for selected List II substances. This report is one of eleven prepared in fulfilment of this contract.

The chemistry of sulphides in water is reviewed. EQSs have been recommended for the protection of fish and other aquatic organisms in fresh and salt waters. There are no data for the toxicity of sulphides to marine fish and it is assumed that the EQS for other marine life will afford adequate protection. Unfortunately this EQS is itself based on very poor data. An EQS has also been recommended for recreational and amenity waters because of the potential aesthetic problems arising from the pungent smell of hydrogen sulphide.

There are very few data on environmental concentrations of sulphides and it has not been possible to compare the EQSs proposed on the basis of the literature information with field observations. The EQSs are therefore tentative.

The recommended EQS values are summarised in an annotated table.

Sulphides are seldom the sole cause of water pollution in the UK and it seems unlikely that these proposals will cause an increase in the cost of monitoring the quality of UK waters.

# CONTENTS

# 1. INTRODUCTION

This report is one of a series on the selection of environmental quality standards for List II substances in connection with the EC Directive on Dangerous Substances(1), and is produced in fulfilment of a contract placed by the Department of the Environment (DOE) with the Water Research Centre (WRC).

A general introduction to this series of reports has been prepared(2). This discusses the environmental quality objective (EQO) approach, the methods used to derive environmental quality standards (EQS) and the uncertainties in EQS values resulting from inadequacies in the available data. The principal uses of water for which EQS values may need to be set have also been listed.

All of the water-uses listed in reference 2 are considered below.

Information on the chemistry and behaviour of sulphide in aquatic environments, its effects on organisms, and concentrations of sulphide reported in waters and associated materials has been summarised. This information has been used to derive the EQS values proposed in Table 3.

# 2. SULPHIDE IN THE ENVIRONMENT

The available information on the natural occurrence and chemistry of sulphide and its distribution and behaviour in the environment has been reviewed and discussed.

## 2.1. NATURAL OCCURRENCE

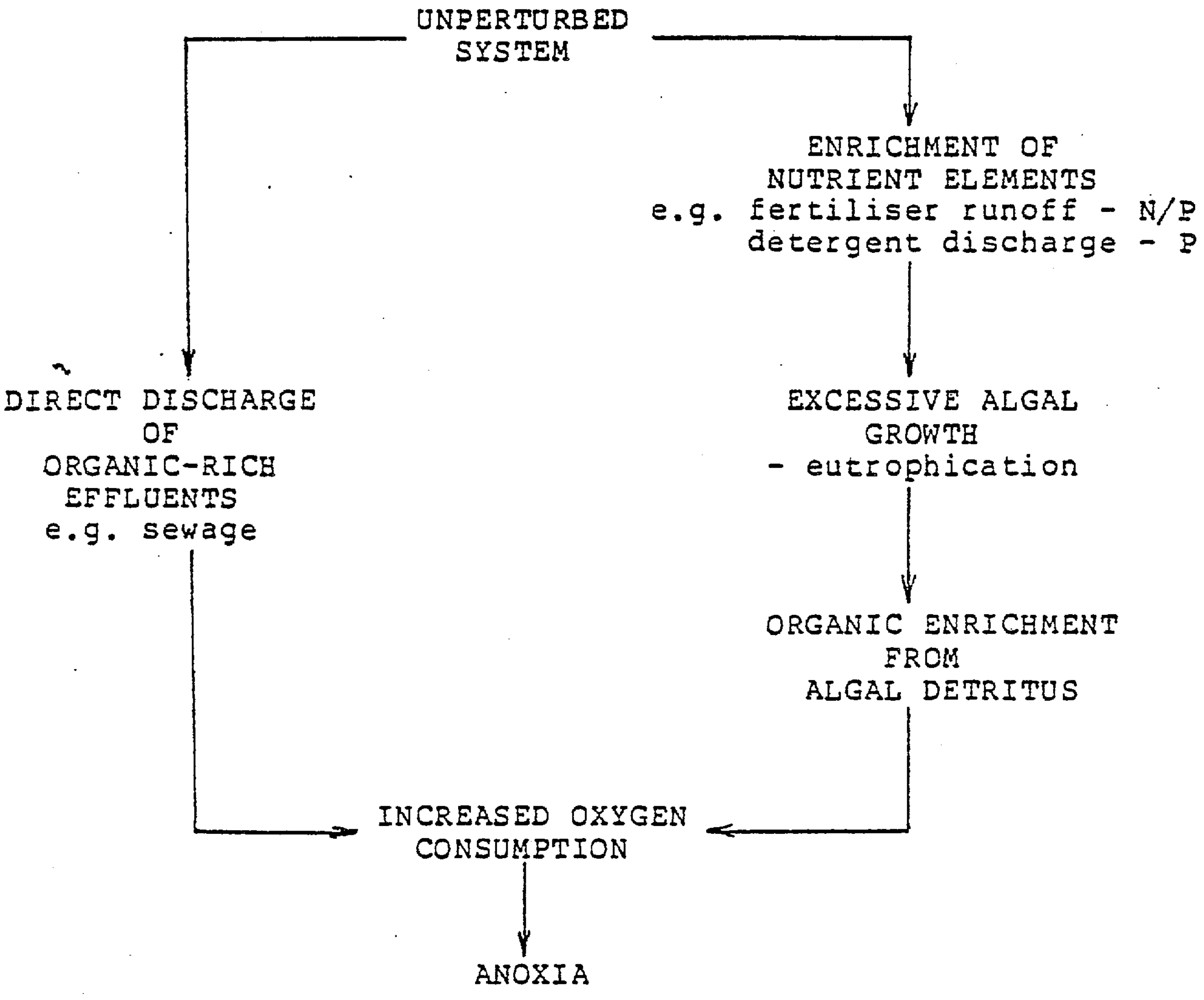
The occurrence of sulphide or reduced sulphur species in natural aquatic and sedimentary environments (both fresh and saline) is, in most cases, a consequence of an imbalance between the rate of supply of dissolved oxygen and the rate of its consumption by decomposition and mineralisation of organic detritus. Reduction of sulphate to sulphide in aqueous environments is one of a sequence of chemical conversions, many of which are microbially mediated, which can occur when dissolved oxygen is depleted. In order of thermodynamic possibility, the initial reduction involves conversion of nitrate to nitrogen, followed by manganese dioxide reduction, FeOOH to $Fe^{2+}$ reduction, fermentation reactions, sulphate to sulphide reduction and in extreme cases methane generation. Complete exhaustion of the dissolved oxygen content of natural water bodies (anoxia) has long been recognised where a combination of physical barriers and density stratification severely limits the advection of dissolved oxygen to deep water. Typical examples of such situations in marine waters are the Black Sea, the Baltic Sea and certain fjords along the coast of Norway and Western Canada. (The chemistry of marine reducing environments has been reviewed by Deuser(3)). Moreover, many workers have reported studies on eutrophic lakes in which seasonal warming of surface waters leads to intense density stratification and, subsequently, anoxia in bottom waters. Oxygen deficiency leading to sulphide generation has also been identified in open-ocean regions such as the north-east Pacific and North Indian oceans where high productivity is promoted by upwelling of nutrient-rich deep waters.

Under conditions of anoxia the concentration of reduced sulphur species in the aqueous environment will depend on the amount of sulphate available for the oxidation of organic matter. Thus total hydrogen sulphide concentrations of 20.4 mg/l have been measured in the saline deep waters of a stagnant fjord although in extreme conditions up to 68 mg/l has been recorded. In nearshore, estuarine and fresh-water sediments, near-surface oxygen depletion and sulphate reduction in the interstitial water are commonly found.

## 2.2. ANTHROPOGENIC INFLUENCES

The controlled discharge of sulphide-containing effluents to natural oxygenated aquatic systems does not constitute a major burden on these regimes since the reduced species are rapidly oxidised in oxic waters. Nevertheless, anthropogenic activities leading to excessive organic enrichment of natural waters can seriously reduce the availability of oxygen and lead to anoxia and sulphide production. The principal pathways to the establishment of reducing conditions in natural waters as a result of anthropogenic inputs are summarised in Fig. 1.

Fig. 1. Direct and indirect pathways leading to anoxia in natural waters



## 2.3. CHEMISTRY

Methods for the determination of hydrogen sulphide in natural (particularly saline) waters have been reviewed by Riley(4). These include procedures involving titrimetry, a photometric method using methylene blue, a spectrofluorometric method and the determination of hydrogen sulphide using specific ion electrodes.

The reduction of sulphate by organic matter in oxygen-depleted waters to generate hydrogen sulphide follows the stoichiometry

$$SO_4^{2-} + 2CH_2O + 2H^+ \rightleftharpoons 2CO_2 + H_2S + 2H_2O$$

although there is strong evidence that the reaction is catalysed and mediated by specialist sulphate-reducing bacteria. Thermodynamic considerations do not support an elemental sulphur intermediate in the reduction. The distribution of sulphur species as a function of pE (indicating redox status) and pH is summarised in Fig. 2. (The diagram is constructed assuming a total sulphur concentration of 0.02M and temperature of 25°C.) In aqueous solution, hydrogen sulphide is a dibasic acid and rapidly dissociates to $H^+$ and $HS^-$ at natural pH (i.e. pH 7 to 8). Further dissociation of bisulphide occurs at pH greater than 10. The following equilibria illustrate the dissociation of $H_2S$

$$H_2S \rightleftharpoons H^+ + HS^- \quad K_1 = ([H^+][HS^-])/[H_2S] \qquad (1)$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \quad K_2 = ([H^+][S^{2-}])/[HS^-] \qquad (2)$$

The apparent equilibrium dissociation constants $K_1$ and $K_2$ are more conveniently expressed using the notation $pK_1$ and $pK_2$ (i.e. negative logarithms to base 10). Mosey and Jago have summarised reported values for $pK_1$ and $pK_2$(9). While there is good agreement for estimates of $pK_1$, relevant to the dominant process under environmental conditions (pH less than 10), a range of values of $pK_2$ has been reported. Only the first dissociation equilibrium is pertinent to this study.

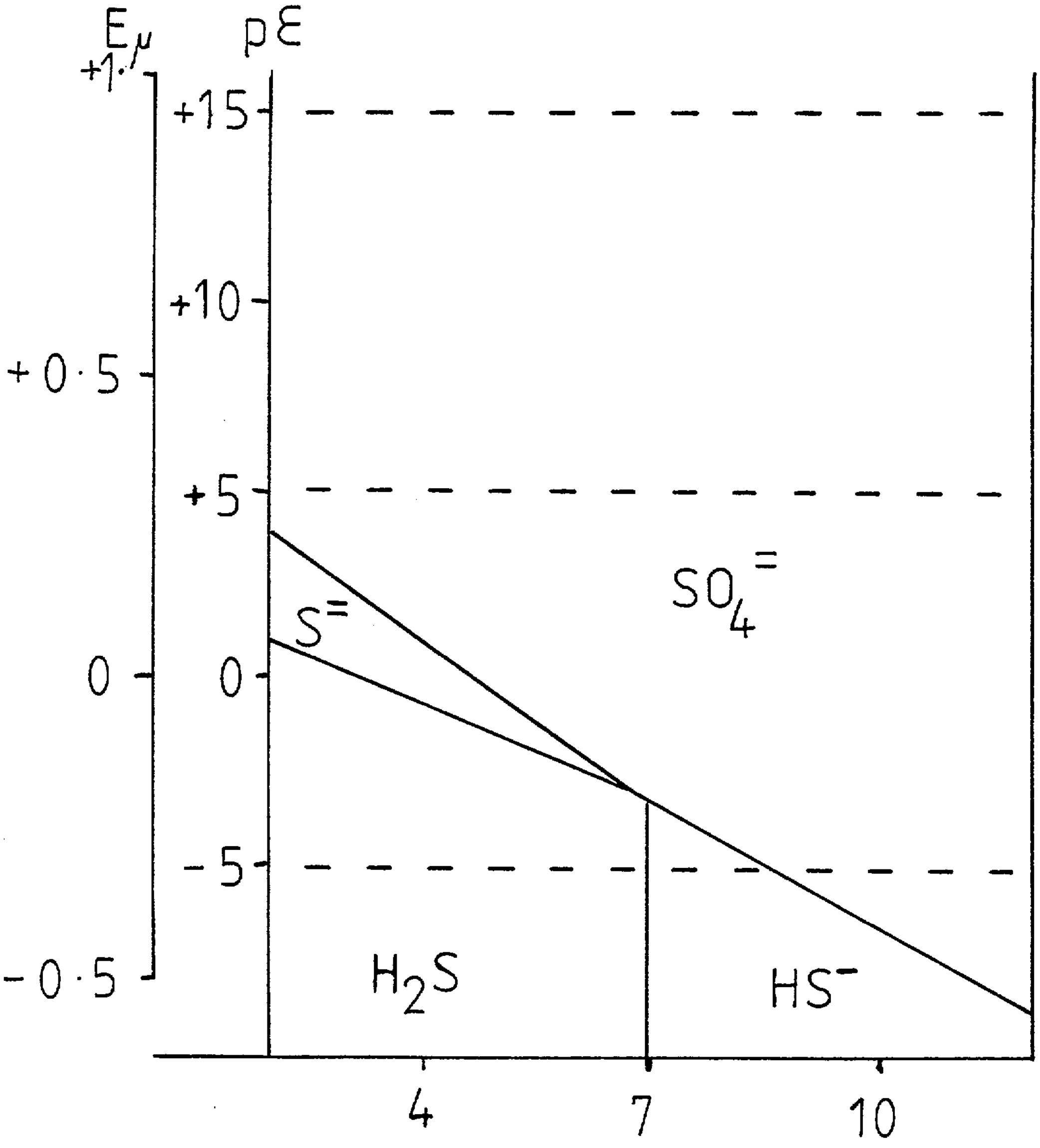


Figure 2. pE-pH phase diagram for the distribution of sulphur species in natural waters (total sulphur conc. 0.02 m T = 25°C) (after Stumm and Morgan, 1981 (5)).

Dissociation of hydrogen sulphide is dependant on temperature. Table 1 summarises ratios of the concentration of undissociated aqueous hydrogen sulphide to that of total hydrogen sulphide in relation to both pH and temperature ($pK_1 = 7$)(10). Furthermore, $pK_1$ is dependant on ionic strength which, though negligible in fresh waters, will be important in estuarine and coastal waters. Thus for a given temperature and pH, the proportion of undissociated hydrogen sulphide decreases with increasing salinity. Goldhaber and Kaplan(11) have proposed the following equation relating $pK_1$ to both ionic strength (expressed in terms of chloride concentration) and temperature:

$$pK_1 = 2.527 - 0.169\ Cl^{1/3} + 1359.96/T \qquad (3)$$

where Cl is given in ‰ and T in degrees Kelvin. It is therefore possible to calculate concentrations of undissociated hydrogen sulphide using $pK_1$ values derived from Equation 3 by the expression:

$$\frac{[H_2S]\ \text{undissociated}}{[H_2S]\ \text{total}} = \frac{1}{(1 + 10^{pH-pK_1})} . \qquad (4)$$

Ratios of undissociated hydrogen sulphide to 'total sulphide' as a function of temperature,pH and salinity are given in Table 2.

The oxidation of bisulphide and hydrogen sulphide is a complicated process and numerous studies have proposed a range of oxidation products, such as $S_8$, $S_2O_3^{2-}$, $SO_3^{2-}$, $S_4O_6^{2-}$, $S_4^{2-}$, $S_5^{2-}$ and $SO_4^{2-}$. The rate of oxidation is also markedly influenced by metals, anions and organic molecules. Reduced sulphur species and oxygen can, under certain conditions, coexist, the half life for sulphide autoxidation in water being estimated to be of the order of several hours. Where oxygenated water overlies an

Table 1. Calculated values of the ratio of the concentration of undissociated aqueous hydrogen sulfide to the total original concentration of hydrogen sulfide in solution versus pH and temperature$^{a}$(10).

|  | $C_{H_2S(aq)}/C_{\Sigma H_2S(sol)}$ |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| pH | 0°C | 5°C | 10°C | 15°C | 20°C | 25°C | 30°C |
| 6.0 | 0.9592 | 0.9495 | 0.9400 | 0.9307 | 0.9215 | 0.9125 | 0.9037 |
| 6.1 | 0.9492 | 0.9373 | 0.9256 | 0.9143 | 0.9032 | 0.8923 | 0.8817 |
| 6.2 | 0.9369 | 0.9223 | 0.9081 | 0.8944 | 0.8811 | 0.8681 | 0.8555 |
| 6.3 | 0.9218 | 0.9041 | 0.8871 | 0.8706 | 0.8547 | 0.8394 | 0.8246 |
| 6.4 | 0.9035 | 0.8822 | 0.8618 | 0.8424 | 0.8238 | 0.8059 | 0.7888 |
| 6.5 | 0.8815 | 0.8561 | 0.8321 | 0.8093 | 0.7878 | 0.7674 | 0.7479 |
| 6.6 | 0.8553 | 0.8254 | 0.7974 | 0.7713 | 0.7468 | 0.7238 | 0.7021 |
| 6.7 | 0.8244 | 0.7896 | 0.7577 | 0.7281 | 0.7008 | 0.6754 | 0.6518 |
| 6.8 | 0.7885 | 0.7489 | 0.7129 | 0.6803 | 0.6504 | 0.6231 | 0.5979 |
| 6.9 | 0.7476 | 0.7031 | 0.6636 | 0.6283 | 0.5964 | 0.5677 | 0.5415 |
| 7.0 | 0.7018 | 0.6529 | 0.6104 | 0.5731 | 0.5400 | 0.5105 | 0.4841 |
| 7.1 | 0.6514 | 0.5991 | 0.5545 | 0.5161 | 0.4826 | 0.4531 | 0.4270 |
| 7.2 | 0.5975 | 0.5428 | 0.4972 | 0.4586 | 0.4255 | 0.3969 | 0.3719 |
| 7.3 | 0.5411 | 0.4853 | 0.4399 | 0.4022 | 0.3704 | 0.3433 | 0.3198 |
| 7.4 | 0.4837 | 0.4282 | 0.3842 | 0.3483 | 0.3185 | 0.2934 | 0.2719 |
| 7.5 | 0.4266 | 0.3730 | 0.3313 | 0.2980 | 0.2707 | 0.2480 | 0.2288 |
| 7.6 | 0.3715 | 0.3209 | 0.2824 | 0.2522 | 0.2277 | 0.2076 | 0.1907 |
| 7.7 | 0.3195 | 0.2729 | 0.2382 | 0.2113 | 0.1898 | 0.1723 | 0.1577 |
| 7.8 | 0.2716 | 0.2297 | 0.1989 | 0.1754 | 0.1569 | 0.1419 | 0.1295 |
| 7.9 | 0.2285 | 0.1915 | 0.1648 | 0.1446 | 0.1288 | 0.1161 | 0.1056 |
| 8.0 | 0.1905 | 0.1583 | 0.1355 | 0.1184 | 0.1051 | 0.0945 | 0.0858 |
| 8.1 | 0.1575 | 0.1300 | 0.1107 | 0.0964 | 0.0853 | 0.0765 | 0.0694 |
| 8.2 | 0.1293 | 0.1061 | 0.0900 | 0.0781 | 0.0690 | 0.0617 | 0.0559 |
| 8.3 | 0.1055 | 0.0862 | 0.0728 | 0.0630 | 0.0556 | 0.0497 | 0.0449 |
| 8.4 | 0.0856 | 0.0697 | 0.0587 | 0.0507 | 0.0447 | 0.0399 | 0.0360 |
| 8.5 | 0.0693 | 0.0562 | 0.0472 | 0.0407 | 0.0358 | 0.0319 | 0.0288 |
| 8.6 | 0.0558 | 0.0451 | 0.0379 | 0.0326 | 0.0286 | 0.0255 | 0.0230 |
| 8.7 | 0.0448 | 0.0362 | 0.0303 | 0.0261 | 0.0229 | 0.0204 | 0.0184 |
| 8.8 | 0.0360 | 0.0290 | 0.0242 | 0.0208 | 0.0183 | 0.0163 | 0.0147 |
| 8.9 | 0.0288 | 0.0231 | 0.0193 | 0.0166 | 0.0146 | 0.0130 | 0.0117 |
| 9.0 | 0.0230 | 0.0185 | 0.0154 | 0.0132 | 0.0116 | 0.0103 | 0.0093 |

[b] Ionic strength = 0.0033.

TABLE 2. RATIO OF UNDISSOCIATED HYDROGEN SULPHIDE TO THE TOTAL PRESENT
IN RELATION TO SALINITY, pH AND TEMPERATURE.

| TEMPERATURE °C | pH | SALINITY (g/kg)<br>5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 6.50 | 0.840 | 0.815 | 0.796 | 0.780 | 0.766 | 0.753 | 0.741 | 0.729 |
| 0 | 7.00 | 0.647 | 0.628 | 0.599 | 0.575 | 0.555 | 0.538 | 0.522 | 0.507 |
| 0 | 7.50 | 0.388 | 0.348 | 0.321 | 0.300 | 0.283 | 0.269 | 0.257 | 0.246 |
| 0 | 8.00 | 0.167 | 0.144 | 0.130 | 0.119 | 0.111 | 0.104 | 0.098 | 0.093 |
| 0 | 8.50 | 0.060 | 0.051 | 0.045 | 0.041 | 0.038 | 0.035 | 0.033 | 0.032 |
| 5 | 6.50 | 0.810 | 0.782 | 0.761 | 0.743 | 0.727 | 0.712 | 0.699 | 0.687 |
| 5 | 7.00 | 0.574 | 0.532 | 0.501 | 0.477 | 0.457 | 0.439 | 0.424 | 0.409 |
| 5 | 7.50 | 0.299 | 0.264 | 0.241 | 0.224 | 0.210 | 0.198 | 0.189 | 0.180 |
| 5 | 8.00 | 0.119 | 0.102 | 0.091 | 0.084 | 0.078 | 0.073 | 0.068 | 0.065 |
| 5 | 8.50 | 0.041 | 0.035 | 0.031 | 0.028 | 0.026 | 0.024 | 0.023 | 0.021 |
| 10 | 6.50 | 0.778 | 0.746 | 0.723 | 0.703 | 0.685 | 0.670 | 0.656 | 0.642 |
| 10 | 7.00 | 0.525 | 0.482 | 0.452 | 0.428 | 0.408 | 0.391 | 0.376 | 0.362 |
| 10 | 7.50 | 0.259 | 0.227 | 0.207 | 0.191 | 0.179 | 0.169 | 0.160 | 0.152 |
| 10 | 8.00 | 0.100 | 0.085 | 0.076 | 0.070 | 0.064 | 0.060 | 0.057 | 0.054 |
| 10 | 8.50 | 0.034 | 0.029 | 0.025 | 0.023 | 0.021 | 0.020 | 0.019 | 0.018 |
| 15 | 6.50 | 0.743 | 0.708 | 0.682 | 0.661 | 0.643 | 0.626 | 0.611 | 0.597 |
| 15 | 7.00 | 0.477 | 0.434 | 0.405 | 0.382 | 0.363 | 0.346 | 0.332 | 0.319 |
| 15 | 7.50 | 0.224 | 0.195 | 0.177 | 0.163 | 0.152 | 0.143 | 0.136 | 0.129 |
| 15 | 8.00 | 0.084 | 0.071 | 0.064 | 0.059 | 0.054 | 0.050 | 0.047 | 0.045 |
| 15 | 8.50 | 0.028 | 0.024 | 0.021 | 0.019 | 0.018 | 0.016 | 0.015 | 0.015 |
| 20 | 6.50 | 0.706 | 0.668 | 0.641 | 0.618 | 0.599 | 0.582 | 0.566 | 0.552 |
| 20 | 7.00 | 0.431 | 0.389 | 0.361 | 0.339 | 0.321 | 0.306 | 0.292 | 0.280 |
| 20 | 7.50 | 0.193 | 0.168 | 0.151 | 0.139 | 0.130 | 0.122 | 0.115 | 0.110 |
| 20 | 8.00 | 0.070 | 0.060 | 0.053 | 0.049 | 0.045 | 0.042 | 0.040 | 0.037 |
| 20 | 8.50 | 0.023 | 0.020 | 0.018 | 0.016 | 0.015 | 0.014 | 0.013 | 0.012 |
| 25 | 6.50 | 0.667 | 0.628 | 0.599 | 0.575 | 0.555 | 0.538 | 0.522 | 0.507 |
| 25 | 7.00 | 0.388 | 0.348 | 0.321 | 0.300 | 0.283 | 0.269 | 0.257 | 0.246 |
| 25 | 7.50 | 0.167 | 0.144 | 0.130 | 0.119 | 0.111 | 0.104 | 0.098 | 0.093 |
| 25 | 8.00 | 0.060 | 0.051 | 0.045 | 0.041 | 0.038 | 0.035 | 0.033 | 0.032 |
| 25 | 8.50 | 0.020 | 0.017 | 0.015 | 0.013 | 0.012 | 0.011 | 0.011 | 0.010 |

anoxic layer, significant sulphide concentrations penetrate the oxic stratum for some distance above the interface owing to rapid diffusion of $HS^-$ relative to its oxidative conversion to sulphate.

The ability of reduced sulphur species to complex with and mobilise trace metals from sedimentary material and suspended matter may represent a potential pathway for the transport of pollutant trace elements in both marine and freshwater environments(5). Concentrations of trace metals in the interstitial waters of estuarine sediments are often reported to be several orders of magnitude higher than in overlying waters. The most striking enrichments have been observed for iron and manganese which undergo reduction more readily than sulphate. Significant fluxes of these metals across the sediment-water interface have been observed.

However, contradictory evidence has been presented for other trace metals. For example, Elderfield and Hepworth(6) suggested significant fluxes of Fe, Ni, Co, Cu and Zn from estuarine pore water to overlying water, whereas Lu and Chen(7) found in laboratory experiments that Mn and Fe were mobilised from reducing sediments, but that Ni, Cu, Zn, Cd and Pb were released from oxidising sediments. The specific chemical reactions which control interstitial metal concentrations and subsequent metal mobility are still obscure and the role of sulphate-sulphide reduction in these processes has yet to be conclusively proved. In deep waters of the Baltic Sea, Kremling(8) has shown that the concentrations of Ni, Cu, Zn and Cd decrease sharply across the redox interface, presumably due to precipitation as sulphides. A model calculation demonstrated that the solubility of these elements was controlled by formation of bisulphide and polysulphide complexes.

From the preceding discussion it is clear that the role of sulphide in the marine environment, with respect to mobilisation of trace elements, is not yet fully understood. The apparent inter-relationship between sulphate and metal concentrations in interstitial waters may be coincidental and additional factors in sedimentary environments such as complexation with organic species and the nature and availability of the complexing species may explain the apparent remobilisation of trace metals from sedimentary material in reducing environments.

In summary, the redox cycling of sulphur in natural waters is of considerable importance both through the direct impact of free sulphide on living systems and through indirect pathways involving the mobilisation of potential pollutants, such as trace metals, in reducing environments. While the end members of the sulphur redox process have been well characterised with respect to their environmental impact, the importance of intermediate species and the role of bacteria in effecting the redox transformation are poorly understood. Also the mechanisms through which trace elements may be mobilised from solid phases are not known and much work is required to rationalise the anomalous behaviour of trace metal-sulphide associations in interstitial waters and overlying anoxic waters.

## 2.4. ENVIRONMENTAL CONCENTRATIONS OF SULPHIDES

Sulphides, whether as hydrogen sulphide or as a metal sulphide, are not routinely measured in water in the United Kingdom or in the other EC Member States. Two studies of freshwater systems in the United States(12,13) reported maximum concentrations of undissociated hydrogen sulphide of 500 g/l. In contrast concentrations as high as 7 mg/l have been reported from an anoxic region of the Black Sea(14). Much lower concentrations have been reported elsewhere: for example a maximum of 14 µg/l in the Arabian Sea(14) and undetected in Florida Bay (USA)(15).

In the Thames estuary during the 1950's, sulphide concentrations were extensively monitored(16) and it was concluded that hydrogen sulphide appeared in solution after the onset of anoxic conditions in the mid-reach of the estuary during the summer months. It was rarely found when aerobic conditions prevailed. Observed concentrations of undissociated hydrogen sulphide in the water were as high as 4 mg/l. The kinetics of sulphide evolution in bottom muds and water are extensively discussed in this report(16).

Concentrations of sulphide in marine sediments can be high, for instance concentrations of 5.8 mg/l undissociated hydrogen sulphide have been recorded in the interstitial water of North Sea mud flats(14). In other marine sediments higher concentrations have been recorded(17,18). In one sediment(18) the total sulphide present ranged from 960 to 12800 mg/l of which 89 mg/l were present as undissociated hydrogen sulphide.

A study of sediments in the River Carron in Scotland(19) reported sulphide concentrations ranging from <10 to 5560 mg $S.kg^{-1}$ (dry weight) with a mean of 1300 mg $S.kg^{-1}$ (dry weight). Data from Clyde River Purification Board indicates a wider range of sulphide concentrations in sediments from the Clyde estuary. Concentrations of 40 mg $S.kg^{-1}$ were recorded 19 km seawards of the tidal limit compared with 8790 mg $S.kg^{-1}$ at 7 km from the tidal limit. At the latter site water concentrations ranged from <0.01 to 1.3 $\mu g$ $S.l^{-1}$ with a mean of 0.36 $\mu g$ $S.l^{-1}$. Unfortunately the data do not permit estimation of the concentrations of the undissociated hydrogen sulphide.

## 3. LIMITATION OF THE PRESENCE OF SULPHIDES ON USES OF WATER

This section gives information to justify the EQS values listed in Table 3.

### 3.1. POTABLE WATER

Sulphides are not among the parameters covered by the EC Surface Water Abstraction Directive (75/440/EEC)(20). J. Fawell of the WRC has reviewed the available information (Annex A) and concludes that the taste and odour threshold concentrations for hydrogen sulphide and for sulphides are substantially below the concentrations likely to produce human health effects. For hydrogen sulphide, taste and odour problems may result from concentrations greater than 50 μg/l. However, this effect is only of consequence at the point of supply and it is not therefore considered necessary or relevant to recommend an EQS for water at the point of abstraction to potable supply. The Drinking Water Directive (80/778/EEC) requires that hydrogen sulphide be undetectable organoleptically.

## 3.2. FOOD FOR HUMAN CONSUMPTION

Hydrogen sulphide is rapidly eliminated by aquatic organisms and is non-accumulative. It is therefore extremely unlikely that tissue concentrations in aquatic organisms would reach levels likely to cause health effects if consumed by humans. Furthermore taste problems are likely to arise at considerably lower concentrations. In the UK, environmental sulphide concentrations are not considered to pose a problem to food derived from aquatic systems and a standard is not considered relevant.

## 3.3. PROTECTION OF FRESHWATER FISH

Information on the toxicity of sulphides to freshwater fish is largely restricted to studies of hydrogen sulphide and is summarised in Table 4, although in many of the toxicity tests the sulphide has been added as sodium sulphide. It is generally accepted that the toxic effects are primarily attributable to the undissociated hydrogen sulphide(24) and most of the studies report the observed effect concentrations as this chemical form. However, without exception it is the total concentration of hydrogen sulphide that is actually measured and the concentration of undissociated hydrogen sulphide is then calculated on the basis of pH and temperature (see Section 2.3). Only three of the studies reported in Table 4 state the dissociation constants used in this calculation(24,25,26). Fortunately at pH values normally measured in freshwater the predominant reaction is dissociation to the bisulphide ion(4,5) and there is close agreement in the various predictions over the temperature range 10°C to 30°C. The values in Table 4 are therefore comparable.

The information in Table 4 indicates that there is little variation in the sensitivity of the fish species tested, thus reducing the significance of the lack of information for species indigenous to the United Kingdom. Two studies span several months(24,33) and in one case 2 years(24) with resultant chronic effects at estimated concentrations as low as 1 μg/l of undissociated hydrogen sulphide. Comparison of these chronic values with acute toxicity data for the same species of fish indicates that the toxicity of hydrogen sulphide does not increase dramatically with an increase in the duration of exposure. This is not inconsistent with the hypothesis that hydrogen sulphide is a non-cumulative poison which is rapidly detoxified or eliminated from the body(13). Thus acutely toxic concentrations (10-30 μg/l) are often only an order of magnitude higher than the chronically toxic concentrations.

Examination of the information in Table 4 suggests that, at acutely toxic concentrations, fry are the most sensitive life stage, although the difference in sensitivity between life stages is often small. As already indicated both pH and temperature are important in determining the concentration of undissociated hydrogen sulphide present. Limited information for acute toxicity indicates that temperature may also increase the susceptibility of fish to hydrogen sulphide by a factor of 2 or 3 for an increase in temperature of 10°C (studies generally report tests at temperatures around 10°C and 20°C).

The adverse sub-lethal effects of undissociated hydrogen sulphide reported in the range 1 to 5 μg/l relate to test conditions of high temperature (approximately 20°C) and high dissolved oxygen (in excess of 5 mg $O_2$/l).

In recommending values for the EQS to protect fish, due account must be taken of the small margin between concentrations causing acute and chronic toxicity, and the effects of temperature and of dissolved oxygen concentrations. EQS values are therefore proposed for two temperatures and two ranges of oxygen concentration. For each condition the EQS is expressed in two ways: as an annual average concentration, and as an extreme percentile which, if exceeded, will almost certainly result in fish mortalities. The lowest adverse effect concentration reported(24) (1 μg/l undissociated hydrogen sulphide) relates to conditions of high temperature (i.e. above 15°C) and high dissolved oxygen (i.e. above 5 mg $O_2$/l). For these conditions it is recommended the EQS should be 0.5 μg/l of undissociated hydrogen sulphide as an annual average concentration. Examination of the acute toxicity data for these same conditions suggests a concentration of undissociated hydrogen sulphide 10 times greater than 0.5 μg/l cannot be tolerated for more than 48 hours and it is therefore recommended that an EQS of 5 μg/l as a maximum 24-hour average concentration of undissociated hydrogen sulphide should also apply.

On the basis of the limited information relating to the effects of temperature and of dissolved oxygen it is recommended (on the assumption of a twofold effect by each) that the following EQSs should apply as relevant (all expressed as μg/l of undissociated hydrogen sulphide):-

| Temperature °C | Dissolved oxygen mg $O_2$/l | EQS concentration (μg/l) Annual average | 24 h maximum average |
|---|---|---|---|
| Low (<15) | Low (<5) | 0.5 | 5.0 |
| Low (<15) | High (>5) | 1.0 | 10.0 |
| High (>15) | Low (<5) | 0.25 | 2.5 |
| High (>15) | High (>5) | 0.5 | 5.0 |

Temperature and dissolved oxygen here relate to annual averages. However, in consenting discharges the regulatory agencies may wish to make use of any seasonality in the temperature and dissolved oxygen of receiving waters in applying the maximum 24-h average concentrations.

## 3.4. PROTECTION OF OTHER FRESHWATER LIFE

The literature information for the toxicity of hydrogen sulphide to aquatic invertebrates (primarily crustaceans) is summarised in Table 5. Examination of this information indicates close similarities with the data for freshwater fish with less than an order of magnitude between concentrations showing chronic and acute toxicity. At acutely toxic concentrations temperature appears to affect the susceptibility of <u>Gammarus</u> and <u>Procambarus</u>(24), although this effect was not evident during prolonged exposure. The effect of dissolved oxygen concentrations cannot be ascertained from the available data. On the basis of the available information it is recommended that two values be adopted for the EQS:- an annual average concentration and a 24 h maximum concentration. The lowest adverse effect concentration is 4 $\mu$g/l undissociated hydrogen sulphide which reduced survival and reproduction of <u>Gammarus</u> after 105 d at 15°C(24). It is recommended that the EQS should be half this concentration (i.e. 2 $\mu$g/l) of undissociated hydrogen sulphide as an annual average concentration, and that the 24 h maximum average concentration should be 10 times this value. Furthermore EQSs should relate to two temperature ranges (with a change at 15°C) as follows:-

| | EQS concentration ( $\mu$g/l) | |
|---|---|---|
| Temperature °C | Annual average | 24 h maximum average |
| Low (<15) | 2 | 20 |
| High (>15) | 1 | 10 |

## 3.5. PROTECTION OF MARINE LIFE

The toxicity information for marine life is summarised in Table 6. There are no data relating to marine fish. The test conditions are poorly reported and for only one study could the concentration of undissociated hydrogen sulphide be estimated with any confidence. These few data relate to acute toxicity tests. On the basis of these data objective derivation of the EQS is not possible. There is evidence of faunal assemblages living in anaerobic sediments with interstitial water concentrations of undissociated hydrogen sulphide of 10s or even 100s of mg/l(14,17,18).

It is recommended that effluents should not cause the concentration of undissociated hydrogen sulphide in the water column to exceed 10 µg/l as a 24 h maximum average concentration. This value is 0.1 (approximately) of the only available LC50 values and these relate to time periods as short as 24 h. Furthermore in the absence of relevant information for marine fish it must be assumed that this value will afford sufficient protection. This EQS is arbitrary and tentative and therefore should be revised as and when additional information becomes available.

## 3.6. AGRICULTURAL USES

Sulphides are not mentioned in the relevant ADAS leaflet (No. 776) concerning the quality of irrigation water, and information on the toxicity of sulphides to plants other than via the atmosphere is very limited. Therefore it has not been possible to recommend an EQS value for irrigation water. In the case of livestock watering there is also a lack of information, although ill effects are unlikely to result from consumption of water that is below the taste and odour threshold. As a consequence no EQS has been recommended.

## 3.7. INDUSTRIAL USES

In the absence of an EQS for water abstracted for potable supply it has not been possible to recommend an EQS for water abstracted for use in the food processing industry. It may be necessary to impose local EQS values to protect certain industrial applications of water, although it is expected that such special needs would usually be met by treatment within the industrial plant.

Saline water is only likely to be required for cooling purposes, which are unlikely to be affected by the presence of sulphides. Consequently no EQS value has been proposed for this use.

## 3.8. RECREATIONAL AND AESTHETIC CONSIDERATIONS

The recreational use and aesthetic acceptability of waters is likely to be limited by concentrations of hydrogen sulphide that exceed the taste and odour threshold. It is therefore recommended that the concentration of hydrogen sulphide present in recreational and amenity waters should not exceed 40 μg/l as a maximum 24 hour average concentration.

## 4. RECOMMENDED ENVIRONMENTAL QUALITY STANDARDS

Environmental quality standards recommended by WRC are given in Table 3. These values are based on existing knowledge of the chemistry and behaviour of sulphide in the environment and the effects of sulphide on human consumers, fish, other biota, agricultural crops etc., as summarised in Sections 2 and 3 and in the Annex. Standards for similar water uses have not been proposed by other national bodies or international organisations.

It is recognised that existing knowledge of the behaviour and effects of sulphide is not adequate in many respects. It is noted that persistence of hydrogen sulphide may result from depletion of the dissolved oxygen concentrations in such waters and that direct control of the hydrogen sulphide concentrations may not be possible. As knowledge improves, the standards proposed in Table 3 will need to be reviewed and possibly updated.

Table 3. EQS values recommended by WRC (See Note 1)

| | Use | EQS value ( g/l undissociated hydrogen sulphide)<br>Annual average concentration | 24 h maximum average concentration | Note |
|---|---|---|---|---|
| FRESHWATER | | | | |
| (ai) | Direct abstraction to potable supply | - | - | 2 |
| (aiv) | Protection of freshwater fish | | | |
| | <15°C <5 mg $O_2$/l | 0.5 | 5.0 | 3 |
| | <15°C >5 mg $O_2$/l | 1.0 | 10.0 | 3 |
| | >15°C <5 mg $O_2$/l | 0.25 | 2.5 | 3 |
| | >15°C >5 mg $O_2$/l | 0.5 | 5.0 | 3 |
| (av) | Protection of other freshwater life and associated non-aquatic organisms | | | |
| | <15°C | 2.0 | 20.0 | 4 |
| | >15°C | 1.0 | 10.0 | 4 |
| (avi) | Irrigation of crops and livestock watering | - | - | 5 |
| (aviii) | Abstraction for food processing industry | - | - | 5 |
| (aix) | Bathing and contact water sports | - | 40.0 | 6 |
| (ax) | Aesthetically acceptable | - | 40.0 | 6 |
| SALT WATER | | | | |
| (bii) | Protection of saltwater fish and shellfish | - | 10.0 | 7 |
| (biii) | Protection of other saltwater life and associated non-aquatic organisms | - | 10.0 | 8 |
| (bv) | Bathing and contact water sports | - | 40.0 | 6 |
| (bvi) | Aesthetically acceptable | - | 40.0 | 6 |
| (aiii) + (bi) | Food for human consumption derived from fresh water | - | - | 9 |

## NOTES ON TABLE 3

1. The numbering of each water use follows the numbering system in reference 2.
2. Sulphides are not among the parameters covered by EC Council Directive concerning the quality of surface water intended for the abstraction of drinking water in the Member States. Official Journal L 194/26, 25 July 1975.
3. Sulphides are not among the parameters covered by the EC Council Directive of 18 July 1978 on the quality of fresh waters needing protection or improvement in order to support fish life. Official Journal L 222/21, 4 August 1978.
4. These EQSs are based on data for freshwater crustaceans and their relevance to other taxa is uncertain.
5. No EQS has been recommended because of the lack of relevant information.
6. This is based on the assumption that taste and odour problems will arise when the concentration exceeds 50-100 $\mu$g/l. It is also accepted that direct control of hydrogen sulphide concentrations may not be possible in anaerobic systems.
7. In the absence of toxicity data for marine fish it is assumed that the EQS for other saltwater life will afford adequate protection.
8. This value is extremely tentative and is based on acute toxicity data for a single species.
9. Sulphides are non-cumulative and problems are unlikely to arise as a result of environmental exposures.

## 5. CONCLUSIONS

The environmental quality objective approach is intended to provide a rational system for the control of discharges of contaminants to waters. Having identified the uses to which water is to be put, standards can be defined restricting levels of contaminants in the water so that the intended uses are protected. In the case of sulphides problems may arise not only from the direct discharge of sulphide-rich effluents, but also indirectly in waters depleted of oxygen as a result of effluents with a high oxygen demand. Standards for sulphide are proposed in this report for various uses of water, and justification for the values chosen has also been given. In the absence of information on the environmental concentrations of sulphides, it is not possible to comment on the relationship between these standards and the levels in fresh and saline waters in the UK and the uses to which those waters are being put.

The responsible authorities can make use of the standards by setting consents to discharges so that levels of sulphide in water do not exceed the standards, except within the immediate mixing zone. Monitoring is required to ensure that the standards are being met, and the ideal detection limit of the analytical method used should not exceed one tenth of the standards. In practice sulphide is seldom the sole cause of water pollution in the UK, although it may exacerbate the problems associated with severe oxygen depletion. It seems unlikely that these proposals will cause an increase in the cost of monitoring the quality of UK waters.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge assistance from a number of sources in preparing this report. Helpful comments and advice have been received from members of the Contract Steering Group (Dr R Otter, DOE; Mr R Lloyd, MAFF; Mr D Hammerton, Clyde RPB; Mr G M Woodward, Severn-Trent WA). Thanks are also due to the staff of Clyde RPB both for their advice and for making field data available.

# REFERENCES

1. COUNCIL OF EUROPEAN COMMUNITIES. Directive on the Discharge of Dangerous Substances, 4 May 1976. 76/464/EC - Official Journal L129, 18 May 1976.
2. GARDINER, J. and MANCE, G. Environmental Quality Standards for List II Substances. Water Research Centre Technical Report, TR206, 1984.
3. DEUSER, W.G. Reducing Environments. In Chemical Oceanography, Volume 3, (eds. J.P. Riley and G. Skirrow), Academic Press, 1975.
4. RILEY, J.P. Analytical chemistry of seawater. In Chemical Oceanography, Volume 3. (eds. J.P. Riley and G. Skirrow), Academic Press, 1975.
5. STUMM, W. and MORGAN, J.J. Aquatic Chemistry (2nd Edition), John Wiley and Sons, 1981, 780 pp.
6. ELDERFIELD, H. and HEPWORTH, A. Diagnosis of metals and pollution in estuaries. Marine Pollution Bulletin, 1975, 6, 85-87.
7. LU, J.C.S. and CHEN, K.Y. Migration of trace metals in interfaces of seawater and polluted surficial sediments. Environmental Science and Technology, 1977, 11, 174-182.
8. KREMLING, K. The behaviour of Zn, Cd, Cu, Ni, Co, Fe, and Mn in anoxic Baltic waters. Marine Chemistry, 1983, 87-108.
9. MOSEY, F. and JAGO, D.A. The determination of dissolved sulphide using a sulphide-selective electrode. WRC TR53, 1977.
10. FUNG, D.K., and BERWICK, P.H. Short term toxicity of Aqueous Hydrogen Sulphide to representative fish species of Lake Huron. Aquatic Toxicology, 1980, 377-396.
11. GOLDHABER, M.B. and KAPLAN, I.R. Apparent dissociation constants of hydrogen sulfide in chloride solutions. Marine Chemistry, 1975, 83-104.
12. SMITH, Jr. L.L., and OSEID, D.M. Effect of hydrogen sulfide on development and survival of eight freshwater fish species. Paper No. 8340, Scientific Journal Series, Minnesota Agricultural Station, Minnesota, USA.

13. TORRANS, E.L., and CLEMMENS, H.P. Physiological and biochemical effects of acute toxicity of fish to hydrogen sulfide. Comparative biochemistry and physiology, 1982, 71, 183-190.

14. THEEDE, H., PONAT, A., HIROKI, K. and SCHIOPER, G. Studies on the resistance of marine bottom invertebrates to oxygen deficiency and hydrogen sulphide. Marine Biology, 1969, 2, 325-337.

15. OSTLUND, H.G., and ALEXANDER, J. Oxidation rate of sulphide in sea water, a preliminary study. Journal of Geophysical Research, 1968, 68 (13) 3995-3997.

16. DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH. Effects of polluting discharges on the Thames Estuary. Water Pollution Research Technical Paper No. 11. 1964. HMSO, London.

17. FENCHEL, T.M. and RIEDL, R.J. The sulfide system, a new biotic community underneath the oxidised layer of marine sand bottoms. Marine Biology 1970, 7, 255-268.

18. JORGENSEN, B.B. The sulfur cycle of a coastal marine sediment (Limfjorden, Denmark). Limnology and Oceanography 1977, 22(5), 814-832.

19. CRAIG, P.J. and MORETON, P.A. Total mercury, methyl mercury and sulphide in River Carron sediments. Marine Pollution Bulletin, 1983, 14 (11), 408-411.

20. COUNCIL OF EUROPEAN COMMUNITIES. Directive on drinking water. Concerning the quality required of surface water intended for abstraction of drinking water in Member States. 16 June 1975. 75/440/EC - Official Journal 194, 25 July 1975.

21. BROWN, K.A. Sulphur in the Environment: a review. Environmental Pollution (Series B) 1982, 3, 47-80.

22. REYNOLDS, F.A., and HAINES, T.A. Effects of chronic exposure to hydrogen sulphide on newly hatched brown trout, Salmo Trutta L. Environmental Pollution A, 1980, 22 (1), 11-17.

23. SMITH, L.L. and OSEID, D.M. Effects of hydrogen sulfide on fish eggs and fry. *Water Research*, 1972, *6*, 711-720.

24. SMITH, L.L., OSEID, D.M., ADELMAN, I.R. and BRODERIUS, S.J. *Effect of hydrogen sulphide on fish and invertebrates, Part I. Acute and chronic toxicity studies*. US EPA Off. Res. Nev. (Rep.) EPA 1976, EPA-600/3-76-062A.

25. ADELMAN, I.R. and SMITH, L.L. Effect of hydrogen sulfide on northern pike eggs and sac fry. *Transactions American Fisheries Society*, 1970, *3*, 501-509.

26. SMITH, L.L., OSEID, D.M., KIMBALL, G.L. and EL-KANDELGY, S.M. Toxicity of hydrogen sulfide to various life history stages of bluegill, (*Lepomis macrochirus*). *Transactions American Fisheries Society*, 1976, *105*(3), 442-449.

27. OSEID, D., and SMITH, L.L. Swimming endurance and resistance to copper and malathion of bluegills treated by long-term exposure to sublethal levels of hydrogen sulfide. *Transactions American Fisheries Society*, 1972, *4*, 620-625.

28. ADELMAN, I.R. and SMITH, L.L. Toxicity of hydrogen sulfide to Goldfish (*Carassius auratus*) as influenced by temperature, oxygen, and bioassay techniques. *Journal Fisheries Research Board of Canada*, 1972, *29(9)*, 1309-1317.

29. BONN, E.W., and FOLLIS, B.J. Effects of hydrogen sulfide on Channel Catfish, *Ictalurus punctatus.* *Trans. Am. Fish. Soc*. 1967, *96*, 31-36.

30. BRODERIUS, S.J. and SMITH, L. *Effect of hydrogen sulphide on fish and invertebrates. Part II. Hydrogen sulphide determination and relation between pH and sulphide toxicity*. US EPA Off. Res. Dev. (Rep) EPA 1976. EPA-600/3-76-06213.

31. SMITH, L.L., OSEID, D.M. and OLSON, L.E. Acute and chronic toxicity of hydrogen sulphide to the fathead minnow, *Pimephales promelas*. *Environmental Science Technology*, 1976, *10(6)*, 565-568.

32. BRODERIUS, S.J., SMITH, L.L. and LIND, D.I. Relative toxicity of free cyanide and dissolved sulfide forms to the Fathead Minnow, (Pimephales promelas). Journal of the Fisheries Research Board of Canada, 1977, 34, 2323-2332.

33. IVANDV, V.N., USENKO, T.G., and PARKHOMENKO, A.V. Effect of hydrogen sulphide on the survival of spawn and embryonal mitoses of Black Sea Turbot. Gidrobiol. Zh., 1976, 12(2), 75-77.

34. OSEID, D.M. and SMITH, Jnr. L.L. Factors influencing acute toxicity estimates of hydrogen sulfide to freshwater invertebrates. Water Research 1974, 8, 739-746.

35. OSEID, D.M. and SMITH, JR. L.L. Chronic toxicity of Hydrogen Sulfide to Gammarus pseudolimnaeus. Transactions of the American Fisheries Society, 1974, 4, 819-822.

36. PRASADD, Y. The effect of kraft pulpmill waste components on some aquatic organisms. Indian Journal of Environmental Health, 1980, 22(4), 340-341.

37. GHOSH, T.K. and KONAR, S.K. Toxicity of chemicals and wastewaters of paper and pulp mills to worms, plankton and molluscs. Indian Journal of Environmental Health, 1980, 22(4), 278-285.

38. ADMIRAAL, W. and PELETIER, H. Sulphide tolerance of benthic diatoms in relation to their distribution in an estuary. British Phycology Journal, 1979, 14, 185-196.

39. GROENENDAAL, M. Tolerance of the lugworm (Arenicola marina) to sulphide. Netherlands Journal of Sea Research, 1980, 4(2), 200-297.

40. HALL, L.W., BUIKEMA, A.L. and CAIRNS, J. The effects of a simulated refinery effluent on the Grass Shrimp, (Palaemonetes). Archives of Environmental Contamination and Toxicology, 1978, 7, 23-25.

41. MEADOWS, P.S., DEANS, E.A. and ANDERSON, J.G. Responses of Corophium volutator to sediment sulphide. Journal of the Marine Biol Ass. UK, 1981, 61, 739-748.

Table 4. Toxicity of hydrogen sulphide to freshwater fish.

| ORGANISM | STAGE | EFFECT | TOTAL SULPHIDE (mg/l S) | UNDISSOCIATED H2S (mg/l S) | COMMENTS | REFERENCE |
|---|---|---|---|---|---|---|
| Salmonid species | - | 120h-LC100 | 1.0 | - |  | (in 21) |
| Trout | - | 2h survival | 3.2 | - | Na2S, pH 9.0 | (in 21) |
| Trout | - | 4min survival | 3.2 | - | Na2S, pH 6.0 | (in 21) |
| Salmo trutta | fry | 96h-LC50 | - | 0.007 | pH 7.1 | (22) |
| Salmo gairdneri | eggs | 96h TL50 | - | 0.049 | pH 7.6 - 8.0 | (23) |
|  | eggs | 7d LC50 | - | 0.022 | pH 7.6 - 8.0 | (12) |
|  | eggs | 29d LC50 | - | 0.014 |  | (24) |
|  | eggs | 29d LC50 | - | 0.015 | pH 7.6 - 8.0 | (12) |
|  | sac fry | 24h LC50 | - | 0.033 | pH 8.0 10°C | (10) |
|  | sac fry | 48h LC50 | - | 0.025 | pH 8.0 10°C | (10) |
|  | sac fry | 72h LC50 | - | 0.025 | pH 8.0 10°C | (10) |
|  | sac fry | 96h LC50 | - | 0.025 | pH 8.0 10°C | (10) |
|  | swim up fry | 5d LC50 | - | 0.013 | pH 7.6 - 8.0 | (12) |
|  | swim up fry | 20d LC50 | - | 0.006 | pH 7.6 - 8.0 | (12) |
|  | fry | 96h 100% mortality | - | 0.020 | pH 7.6 - 8.0 | (23) |
|  | juvenile | 96h LC50 | - | 0.017 | pH 7.6 - 8.0 | (12) |
|  | juveniles | 96h LC50 | - | 0.023 | pH 7.5 7°C | (10) |
|  | juvenile | 96h LC50 | - | 0.012 |  | (24) |
|  | juvenile | 17d LC50 | - | 0.009 | pH 7.6 - 8.0 | (12) |
|  | adults | 96h LC50 | - | 0.043 | pH 7.5 7°C | (10) |
|  | adult | Reduced survival | - | 0.003 |  | (24) |
|  | adult | Retarded growth | - | 0.007 |  | (24) |
|  | adults | Reduced breeding 29d | - | 0.006 | pH 7.6 - 8.0 | (12) |
|  | adults | Reduced breeding 29d | - | 0.012 | pH 7.6 - 8.0 | (12) |
| Salvelinus fontinalis | eggs | 96h LC50 | - | >0.097 |  | (24) |
|  | eggs | 96h LC50 | - | 0.054 | pH 7.6 - 8.0 | (12) |
|  | sac fry | 96h LC50 | - | 0.031 | pH 7.6 - 8.0 | (12) |
|  | sac fry | 96h LC50 | - | 0.014 |  | (24) |
|  | swim up fry | 96h LC50 | - | 0.022 | pH 7.6 - 8.0 | (12) |
|  | feeding fry | Lethal threshold | - | 0.020 |  | (24) |
|  | juvenile | 96h LC50 | - | 0.017 | pH 7.6 - 8.0 | (12) |
|  | juveniles | 96h LC50 | - | 0.025 | 8.5 deg.C | (24) |
|  | juveniles | 96h LC50 | - | 0.017 | 21 deg.C | (24) |
|  | adults | Reduced growth | - | 0.006 |  | (24) |
|  | adults | Reduced breeding 76d | - | 0.005 | pH 7.6 - 8.0 | (12) |
|  | adults | " " 76d | - | 0.008 | pH 7.6- 8.0 | (12) |
| Esox lucius | eggs | 96h LC50 | - | 0.037 | pH 7.6 - 8.0 | (12) |
|  | eggs | 96h TL50 | - | 0.034 | pH 7.6 - 8.0 | (23) |
|  | eggs | 96h LC50 | - | 0.037 | 6mg/l O2 | (25) |
|  | eggs | 48h LC50 | - | 0.076 | 2 mg O2/l<br>pH 7.3 - 8.0 | (25) |
|  | eggs | 48h LC50 | - | 0.046 | 6 mg O2/l<br>pH 7.3 - 8.0 | (25) |
|  | sac fry | 48h LC50 | - | 0.016 | 2 mg O2/l<br>pH 7.3 - 8.0 | (25) |
|  | sac fry | 48h LC50 | - | 0.047 | 6 mg O2/l<br>pH 7.3 - 8.0 | (25) |
|  | sac fry | 96h LC50 | - | 0.026 | pH 7.6 - 8.0 | (12) |
|  | sac fry | 96h LC50 | - | 0.026 | 6mg/l O2 | (25) |
|  | adults | Reduced breeding 29d | - | 0.018 | pH 7.6 - 8.0 | (12) |

Table 4 Continued. Toxicity of hydrogen sulphide to freshwater fish.

| ORGANISM | STAGE | EFFECT | TOTAL SULPHIDE (mg/l S) | UNDISSOCIATED H2S (mg/l S) | COMMENTS | REFERENCE |
|---|---|---|---|---|---|---|
| Lepomis macrochirus | eggs | 72h LC50 | - | 0.016 | pH 7.6 - 8.0 | (12) |
| | eggs | 66 - 72h LC50 | - | 0.014 | | (24) |
| | eggs | 72h LC50 | - | 0.0190 | pH 7.6 - 8.0 | (26) |
| | sac fry | 72h LC50 | - | 0.030 | pH 7.6 - 8.0 | (12) |
| | sac fry | 96h LC50 | - | 0.008 | | (24) |
| | sac fry | 7d LC50 | - | 0.029 | pH 7.6 - 8.0 | (12) |
| | swim up fry | 72h LC50 | - | 0.009 | pH 7.6 - 8.0 | (12) |
| | swim up fry | 7d LC50 | - | 0.008 | pH 7.6 - 8.0 | (12) |
| | fry | 96h LC50 | - | 0.0131 | pH 7.6 - 8.0 | (26) |
| | juvenile | 72h LC50 | - | 0.032 | pH 7.6 - 8.0 | (12) |
| | juveniles | 96h LC50 | - | 0.0478 | pH 7.6 - 8.0 | (26) |
| | juvenile | 96h LC50 | - | 0.032 | pH 7.9 20°C | (27) |
| | juvenile | 7d LC50 | - | 0.032 | pH 7.6 - 8.0 | (12) |
| | juvenile | 96h LC50 | - | 0.030 | Acclimation observed | (24) |
| | juvenile | Reduced swimming ability 126d exposure | | 0.0015 | pH 7.9 20°C | (27) |
| | adult | 96h LC50 | - | 0.028 | | (24) |
| | adults | 96h LC50 | - | 0.0448 | pH 7.6 - 8.0 | (26) |
| | adult | Reduced survival | - | 0.001 | | (24) |
| | adult | Reduced growth | - | 0.006 | Tolerance to Cu increased. Malathion decreased. | (24) |
| | adults | Reduced spawning 97d | - | 0.001 | pH 7.6 - 8.0 | (26) |
| | adults | Reduced feeding | - | 0.0085 | pH 7.6 - 8.0 | (26) |
| | adult | Reduced breeding 28m | - | 0.002 | pH 7.6 - 8.0 | (12) |
| | adults | Egg laying prevented 826d | | 0.0022 | pH 7.6 - 8.0 | (26) |
| Carassius auratus | eggs | 72h-LC50 | - | 0.020 | pH 7.6 - 8.0 | (12) |
| | egg | 96h LC50 | - | 0.021 | | (24) |
| | eggs | 96h LC50 (normal fry) | - | 0.019 | | (24) |
| | fry | 96h LC50 | - | 0.024 | | (24) |
| | sac fry | 72h LC50 | - | 0.025 | pH 7.6 - 8.0 | (12) |
| | juvenile | 96h LC50 | - | 0.090 | pH 7.6 - 8.0 | (12) |
| | juvenile | 96h LC50 | - | 0.130 | 14 deg.C | (24) |
| | juvenile | 96h LC50 | - | 0.059 | 26 deg.C | (24) |
| | adult | Reduced breeding 3d | - | 0.010 | pH 7.6 - 8.0 | (12) |
| | adult | 96h LC50 | - | 0.530 | 6 deg.C | (28) |
| | adult | 96h LC50 | - | 0.004 | 25 deg.C | (28) |
| | adult | 96h LC50 | - | 0.062 | 6 mg O2/l | (28) |
| | adult | 96h LC50 | - | 0.048 | 1.5 mg O2/l | (28) |
| | adults | Reduced growth | - | 0.007 | | (24) |
| | adults | Reduced spawning | - | 0.005 | | (24) |
| Coregonus clupeaformis | sac fry | 48h LC50 | - | 0.002 - 0.008 | pH 8.0 | (10) |
| | sac fry | 96h LC50 | - | 0.002 - 0.005 | pH 8.0 | (10) |
| | juveniles | 48h LC50 | - | >0.014 | pH 8.0 | (10) |
| | juveniles | 96h LC50 | - | 0.012 | pH 8.0 | (10) |

Table 4 Continued. Toxicity of hydrogen sulphide to freshwater fish.

| ORGANISM | STAGE | EFFECT | TOTAL SULPHIDE (mg/l S) | UNDISSOCIATED H2S (mg/l S) | COMMENTS | REFERENCE |
|---|---|---|---|---|---|---|
| Perca flavescens | sac fry | 48h LC50 | - | 0.031 | pH 7.5 10°C | (10) |
| | sac fry | 48h LC50 | - | <0.002 | pH 8.0 20°C | (10) |
| | Juveniles | 48h LC50 | - | 0.010 | pH 8.0 20°C | (10) |
| | Juveniles | 96h LC50 | - | 0.036 | pH 7.5 10°C | (10) |
| | Juveniles | 96h LC50 | - | 0.008 | pH 8.0 20°C | (10) |
| Micropterus salmoides | sac fry | 96h LC50 | - | 0.011 | pH 7.5 20°C | (10) |
| | juveniles | 96h LC50 | - | 0.063 | pH 7.5 15°C | (10) |
| Rhomous maeoticus | eggs | LC100 | 2.4 | - | | (33) |
| Catostomus commersoni | eggs | 96h LC50 | - | 0.028 | pH 7.6 - 8.0 | (23) |
| | eggs | 96h LC50 | - | 0.033 | | (24) |
| | eggs | deformed fry | - | 0.023 | pH 7.6 - 8.0 | (23) |
| | Juvenile | 96h LC50 | - | 0.018 | pH 7.6 - 8.0 | (12) |
| | Juveniles | 96h LC50 | - | 0.021 | | (24) |
| | fry | 96h LC50 | - | 0.013 | pH 7.6 - 8.0 | (23) |
| Pimephales promelas | egg | 96h LC50 | - | 0.0536 | pH 7.9 | (32) |
| | fry | 96h LC50 | - | 0.0107 | pH 7.9 | (32) |
| | fry | 96h LC50 | - | 0.007 | | (24) |
| | Juvenile | 96h LC50 | - | 0.049 | pH 6.4 | (33) |
| | Juvenile | 96h LC50 | - | 0.014 | pH 8.7 | (33) |
| | Juvenile | 96h LC50 | - | 0.024 - 0.776 | pH 7.9 | (32) |
| | Juveniles | 96h LC50 | - | 0.026 | 25 deg.C | (24) |
| | Juveniles | 96h LC50 | - | 0.546 | 6.5 deg.C | (24) |
| | adults | Growth, survival, fecundity reduced 191d | | 0.008 | pH 7.9 | (32) |
| | - | 96h LC50 | 57.3 | - | pH 7.1 | (31) |
| | - | 96h LC50 | 14.9 | - | pH 8.7 | (31) |
| | adults | Growth reduced | - | 0.005 | | (24) |
| | adults | Lower survival | - | 0.007 | | (24) |
| | adults | Growth reduced | - | 0.003 | | (24) |
| Ictalurus punctatus | fry | 3h LC50 | - | 0.8 | pH 6.8 | (30) |
| | fry | 3h LC50 | - | 0.53 | pH 7.8 | (30) |
| | fingerling | 3h LC50 | - | 1.0 | pH 7.0 | (30) |
| | adult | 3h LC50 | - | 1.4 | pH 7.0 | (30) |
| | - | Enzyme inhibition after 5 min reversible | | 0.1 | | (13) |
| Stizostedion vitreum | eggs | 96h LC50 | - | 0.052 | pH 7.6 - 8.0 | (23) |
| | eggs | 96h LC50 | | 0.052 | pH 7.6 - 8.0 | (12) |
| | eggs | deformed fry | - | 0.039 | pH 7.6 - 8.0 | (23) |
| | fry | 96h LC50 | - | 0.007 | pH 7.6 - 8.0 | (23) |
| | juvenile | 96h LC50 | - | 0.018 | | (24) |
| | juvenile | 96h LC50 | - | 0.020 | pH 7.6 - 8.0 | (12) |
| | adult | Reduced swimming | - | 0.005 | | (24) |
| | adult | Reduced survival | - | 0.003 | | (24) |
| | adult | Reduced breeding 26d | - | 0.012 | pH 7.6 - 8.0 | (12) |

Table 5. The toxicity of sulphide to fresh water organisms other than fish

| ORGANISM | EFFECT | TOTAL SULPHIDE (mg/l S) | UNDISSOCIATED $H_2S$ (mg/l S) | COMMENTS | REFERENCE |
|---|---|---|---|---|---|
| Asellus militaris | 96h LC50 | - | 1.07 | 2 mg$O_2$/l 15.2°C pH 7.5 | (24) |
| Gammarus pseudolimnaeus | 96h LC50 | - | 0.059 | 5.9 mg$O_2$/l 15°C pH 7.5 | (34) |
| | 96h LC50 | - | 0.021 | 8 mg $O_2$/l 18°C pH 7.7 | (35) |
| | 96h LC50 | - | 0.032 | 18°C pH 7.8 | (24) |
| | 10d LC50 | | 0.011 | " " " | (35) |
| | 10d LC50 | | 0.049 | 6 mg$O_2$/l 10°C pH7.5 | (34) |
| | 10d LC50 | | 0.049 | 4 mg$O_2$/l 10°C pH 7.5 | (34) |
| | reduced reproduction and survival 105d | | 0.004 | 18°C pH 7.7 | (24) |
| Procambarus clarkii | | | | | |
| eggs | 96h LC50 | - | 0.370 | 22°C pH 7.7 6 mg$O_2$/l | (24) |
| eggs | reduced survival 447d | | 0.009 | 18°C pH 7.6 6 mg$O_2$/l | (24) |
| larvae | 96h LC50 | - | 0.058 | 18°C pH 7.6 7.2 mg$O_2$/l | (24) |
| juvenile | 96h LC50 | - | 0.034 | 22°C pH 7.7 6.4 mg$O_2$/l | (24) |
| juvenile | 96h LC50 | - | 0.147 | 14°C pH 7.7 6.4 mg$O_2$/l | (24) |
| juvenile | reduced growth 196d | | 0.006 | 14°C pH 7.7 6 mg$O_2$/l | (24) |
| juvenile | reduced growth 196d | | 0.006 | 21°C pH 7.7 6 mg$O_2$/l | (24) |
| sub-adult | 96h LC50 | - | 0.075 | 18°C pH 7.8 5.6 mg$O_2$/l | (24) |
| adult | 96h LC50 | - | 0.121 | 22°C pH 7.6 6.1 mg$O_2$/l | (24) |
| adult | 96h LC50 | - | 0.271 | 14°C pH 7.6 7.1 mg$O_2$/l | (24) |
| Cambarus diogenes | | | | | |
| sub-adult | 96h LC50 | - | 0.105 | 22°C pH 7.7 | (24) |
| sub-adult | 96h LC50 | - | 0.205 | 14°C pH 7.7 | (24) |
| Crangonyx richmondensis | 96h LC50 | - | 0.840 | 15°C pH7.4 2 mg$O_2$/l | (24) |
| Daphnia spp. | 96h LC50 | 6.0 | - | 30°C pH7-7.5 7.8mg$O_2$/l $Na_2S$ | (36) |
| | 96h LC50 | 3.0 | - | " " " $H_2S$ | (36) |
| Bosmina spp. | 96h LC50 | 5.0 | - | 30°C pH7-7.5 7.8mg$O_2$/l $Na_2S$ | (36) |
| | 96h LC50 | 2.0 | - | " " " $H_2S$ | (36) |
| Cyclops spp. | 96h LC50 | 5.0 | - | 30°C pH7-7.5 7.8mg$O_2$/l $Na_2S$ | (36) |
| | 96h LC50 | 2.0 | - | " " " $H_2S$ | (36) |
| Cyclops viridis | 96h LC50 | 37. | | 28.5°C pH 7.0 7.5 mg$O_2$/l NaS | (37) |
| Baetis vagans | 96h LC50 | - | 0.020 | 15°C pH 7.6 6.2 mg$O_2$/l | (24) |
| Ephemera simulans | 96h LC50 | - | 0.316 | 15°C pH 7.4 1.9 mg$O_2$/l | (24) |
| Hexagenia limbata | 96h LC50 | - | 0.111 | 15°C pH 7.7 2 mg$O_2$/l | (24) |
| | reduced nymph survival 138d | | 0.043 | 18°C pH 7.7 6 mg$O_2$/l | (24) |
| Chironomous spp. | 96h LC50 | 800. | - | 30°C pH7-7.5 7.8mg$O_2$/l $Na_2S$ | (36) |
| larvae | 96h LC50 | 550. | - | " " " $H_2S$ | (36) |
| Branchiura sowerbyi | 96h LC50 | 325. | | 28.5°C pH 7.0 7.5 mg$O_2$/l NaS | (37) |
| Lymnaea luteola | 96h LC50 | 100. | | 28.5°C pH 7.0 7.5 mg$O_2$/l NaS | (37) |

Table 6. Toxicity of sulphide to marine organisms other than fish

| ORGANISM | EFFECT | TOTAL SULPHIDE (mg/l S) | UNDISSOCIATED H2S (mg/l S) | COMMENTS | REFERENCE |
|---|---|---|---|---|---|
| Nitzschia closterium | 48h LC100 | 29.0 | - | 34g/kg pH 8.0 12°C | (38) |
| Stauroneis constricta | 48h LC100 | 29.0 | - | 34g/kg pH 8.0 12°C | (38) |
| Chaetocerus simplex | 48h LC100 | 29.0 | - | 34g/kg pH 8.0 12°C | (38) |
| Navicula arenaria | 48h LC36 | 218 | - | 34g/kg pH 8.0 12°C | (38) |
| Cyclotella spp. | 48h LC66 | 218 | - | 15g/kg pH 8.0 12°C | (38) |
| Littorina saxatilis | 72h LD50 | 6.67 | - | 30 g/kg<br>pH 8.2 - 8.45<br>low 02<br>added as NaS | (14) |
| Littorina littorea | 180h LD50 | 6.67 | - | | |
| Mytilus edulis | 600h LD50 | 6.67 | - | | |
| Gammarus oceanicus | 8h LC50 | 6.67 | - | pH 8.2 - 8.45<br>15g/kg<br>low 02<br>added as NaS | (14) |
| Nereis diversicolor | 96h LC50 | 6.67 | - | | |
| Carcinus maenas | 32h LD50 | 6.67 | - | | |
| Asterias rubens | 67h LD50 | 6.67 | - | | |
| Arenicola marina | 58h LT50 | 320 | - | 28g/kg pH 7.7 - 8.4 10°C low 02 | (39) |
| Nephtys cirrosa | 48h LT50 | 320 | - | 28g/kg pH 7.7 - 8.4 10°C low 02 | (39) |
| Owenica fusiformis | 128h LT50 | 320 | - | 28g/kg pH 7.7 - 8.4 10°C low 02 | (39) |
| Nephtys hombergi | 72h LT50 | 320 | - | 28g/kg pH 7.7 - 8.4 10°C low 02 | (39) |
| Palaemontes pugio | 96h LC50 | 2.3 | 114.0 | 9g/kg pH 8.0 - 8.2 20°C | (40) |
| | 48h LC50 | 2.9 | 92.0 | " " " | (40) |
| | 24h LC50 | 4.2 | 133.0 | 35 g/kg " " | (40) |
| Corophium volutator | Avoidance | 1.86 | - | Interstital conc. in sediment<br>35g/kg 10°C pH? | (41) |
| | Burrowing inhibited | 18.6 | - | | (41) |

# ANNEX A
# SULPHIDE IN RELATION TO POTABLE SUPPLY

Contributed by J Fawell
of the Water Research Centre

## INTAKE

Data on the intake of sulphides from food and water are very limited. Intake from air has been comparatively well studied since this was a major source of sulphide during periods of high air pollution(1-6).

Dimethyl sulphide is used in the manufacture of jellies, candy, soft drinks and cream in the UK, and the maximum likely intake has been estimated at 1.7 mg/day(7). A number of other foodstuffs and drinks may contain sulphides; these include beer, seafoods, warm milk, cooked meat and some vegetables(8). There appear to be no available data on sulphides in drinking water, although their presence may be detected by consumers if supplies are sufficiently anaerobic and sulphate-reducing bacteria are active. Such conditions are normally rare in the UK.

## ABSORPTION, DISTRIBUTION, EXCRETION & METABOLISM

Soluble alkali sulphides are rapidly absorbed from the gastrointestinal tract, as is hydrogen sulphide.

Excretion of the sulphide radical is primarily via the kidneys though some metallic sulphides are excreted through the gut(6,8,9). There is some evidence for excretion of sulphides through the lungs though this may be very limited in extent(6,8,9,10).

An unknown proportion of sulphide may be oxidised to sulphates and thiosulphates, and excreted through the kidney(6,9).

## TOXICITY

The toxicity of sulphide is thought to be due to the reversible inhibition of oxidative enzymes in the cell, primarily cytochrome C oxidase(1,4,6). This results in interruption of the respiratory electron transport chain and inhibition of aerobic metabolism. Consequently the most vulnerable organs are those particularly susceptible to oxygen deprivation such as the central nervous system and the heart.

Other enzymes reported to be inhibited by sulphides are succinate dehydrogenase, ATPase, DOPA oxidase, carbonic anhydrase, dipeptidase, benzamidase and some enzymes which contain iron(6).

Alkaline sulphides are irritants to mucous membranes and cause nausea, vomiting and epigastric pain on oral ingestion(9). Quantitative data on the toxicity of sulphides is limited, the greatest proportion referring to inhalation toxicity of hydrogen sulphide(1-4,6,11,12). An oral dose of 10,000 to 15,000 mg sodium sulphide is fatal to man, while the LD50 by intraperitoneal injection is 30 mg/kg in rat and 18 mg/kg in mouse(13). Dimethyl sulphide was found to produce no ill effects in rats at a dose of 250 mg/kg, when administered orally to rats daily for 14 weeks, indicating much higher toxicity of inorganic sulphides compared to organic sulphides(7).

There is some evidence that hydrogen sulphide is mutagenic in some *in vivo* test systems and sodium sulphide gave a positive result in a Drosophila test system(14). The significance of these results is unclear, particularly as sodium sulphide was found to be non-mutagenic in an *in vivo* test system.

No data appear to be available on the carcinogenicity or reproductive toxicity of these compounds.

Few experimental data are available on the chronic toxicity of sulphides and there appear to be no data on exposure by the oral route. This concurs with the findings of a WHO expert group on hydrogen sulphide(6), who stated that:

"little information is available in the published literature concerning the effects in experimental animals of long term, low-level exposure to hydrogen sulphide...........Furthermore, epidemiological data are lacking concerning the health consequences of long-term, low level exposures to hydrogen sulphide, in both the general, and industrial populations".

## DISCUSSION

The taste and odour thresholds for hydrogen sulphide are estimated to be between 0.05 and 0.1 mg/l, and for sulphides 0.2 mg/l(15,16). These concentrations are substantially below the concentrations likely to produce human health effects. The concentration of sulphide required to prevent organoleptic problems in drinking water would also be sufficiently low to protect health.

## REFERENCES

1. BURNETT, W.W., KING, E.G., GRACE, M., HALL, W.F. Hydrogen sulphide poisoning - A Review of 5 Years Experience. CMA Journal, Dec. 3rd 1977, 3, 1277-1280.
2. ADELSON, L. and SUNSHINE, I. Fatal Hydrogen sulphide intoxication. Arch. Path., 1966, 81, 375.
3. McCABE, L.C. and CLAYTON, C.D. Air Pollution by hydrogen sulphide in Poza Rica, Mexico. Arch Indust. Hyg. & Occup. Med., 1952, 6, 199-213.
4. STINE, R.J., SOLSBERG, B. and BEACHAN, B.E. Hydrogen Sulphide Intoxication. Annals of Internal Medicine 1976, 85, 756-758.
5. CALIFORNIA AIR RESOURCES BOARD. Ambient Air Quality Standards, 1970, Sacramento, California, California Air Resources Board, p69-75.
6. WORLD HEALTH ORGANIZATION, Environmental Health Criteria 19 - Hydrogen Sulphide, 1981, Geneva.
7. BUTTERWORTH, K.R., CARPANINI, F.M.B., CAUNT, I.F., HARDY, J., KISS, I.S. and GANGOLLI, S.P. Short Term Toxicity of Dimethyl Sulphide In the Rat. Food Cosmet. Toxicol, 1975, 13, 15.

8. MINISTRY OF NATIONAL HEALTH AND WELFARE. Guidelines for Canadian Drinking Water Quality, 1978, (supporting document). Minister of National Health and Welfare, Ottawa, Ontario.

9. THIENES, C.H. and HALEY, T.J. Clinical Toxicology (5th Edn), 1972, Philadelphia, Lea and Febiqer, p59-60.

10. SUSMAN, J.L., HORNIG, J.F., THOMAE, S.C. and SMITH, R.P. Pulmonary Excretion of Hydrogen Sulphide, Methane-thiol, Dimethyl Sulphide and Dimethyl disulphide in mice. Drug and Chemical Toxicology, 1978, 1 (4), 327-338.

11. HAGGARD, H.W. The Toxicology of Hydrogen Sulphide J. Indust. Hyg. 1925, 7 (3), 113-121.

12. EVANS, C.L. The Toxicity of Hydrogen Sulphide and other sulphides. Quart. J. Exp. Physiol, 1967, 52 (3), 231-248.

13. NIOSH. Registry of Toxic Effects of Chemical Substances 1983. US Department of Health, Education and Welfare, Cincinnati, Ohio.

14. GOCKE, E., KING, M-T., ECKHARDT, K. and WILD, D. Mutagenicity of Cosmetic Ingredients Licensed by The European Communities. Mutation Res. 1981, 90, 91-109.

15. McKEE, J.E. and WOLF, H.W. Water Quality Criteria (2nd Edn). Resources Agency of California State Water Resources Control Board, 1963.

16. ACREE, T.E. and SPLITTSTOESSER, D.F. Prevention of $H_2S$ in Wine Fermentation. NY Life Sci. Q. 1972, 5, 19.

WRC WATER RESEARCH CENTRE

WRC CONTRACTS LTD
Henley Road, Medmenham,
P.O. Box 16, Marlow,
Bucks. SL7 2HD
Tel: Hambleden (Bucks) (049 166) 531
Telex: 848632

WRC ENGINEERING
P.O. Box 85,
Frankland Road,
Blagrove, Swindon,
Wilts. SN5 8YR
Tel: Swindon (0793) 488301
Telex: 848632

WRC ENVIRONMENT
Medmenham Laboratory,
Henley Road, Medmenham,
P.O. Box 16, Marlow,
Bucks. SL7 2HD
Tel: Hambleden (Bucks) (049 166) 531
Telex: 848632

WRC INTERNATIONAL OFFICE
1 Queen Anne's Gate,
London. SW1H 9BL
Tel: 01 222 8111
Telex: 848632

WRC PROCESSES
Stevenage Laboratory,
Elder Way,
Stevenage, Herts.
SG1 1TH
Tel: Stevenage (0438) 312444
Telex: 826168

WRC REGISTERED OFFICE
Henley Road, Medmenham,
P.O. Box 16, Marlow,
Bucks. SL7 2HD
Tel: Hambleden (Bucks) (049 166) 531
Telex: 848632

WRC SCOTTISH OFFICE
1 Snowdon Place,
Stirling. FK8 2NH
Tel: Stirling (0786) 71580