8 ~~122~~

REVIEW OF LITERATURE

ON THE EFFECT OF COPPER IN SEDIMENTS ON AQUATIC ORGANISMS

by

John S. Alabaster
Consultant, Pollution and Fisheries
1 Granby Road,
Stevenage, SG1 4AR

June 1989

CONTENTS

1. INTRODUCTION

It is clear that there are relatively few data available on the effect of particulate copper on aquatic communities in either rivers or estuaries, most information being on the effect of 'soluble' copper in the water column, as reviewed, for example, by Alabaster & Lloyd (1982) for freshwater and by Lewis & Cave (1982) for marine conditions. Furthermore, up to the year 1984 at least, no study appears to have defined sediment quality criteria for individual toxicants in fresh-water (Cairns **et al.**, 1984). More recently, however, standards have been proposed based on the 'equilibrium partitioning approach' whereby the concentration of copper in the interstitial water is restricted to the concentration that would be acceptable in the overlying water (Pavlou, 1987); for example, a safe level of 68 mg Cu/kg is proposed, based upon an organic carbon content of 2% and is similar to historical limits of 250-50 mg Cu/kg developed for the Great Lakes.

The related, and relevant subject of the chemistry of copper in sediments and in the overlying water has already been discussed elsewhere in detail, e.g. by Hunt (1982) and Salomans (1987) and is, therefore, not dealt with here, although it is referred to in passing. Suffice it to say that the biological effects of copper in sediment hinge upon the bio-availablility of the metal and that this is not readily amenable to direct measurement other than by measuring the responses of the organisms involved; the problem has been recently reviewed (Campbell **et al.**, 1988).

The approach adopted here is to present a critical summary of each paper in turn and to draw the more general conclusions later. Unless otherwise stated, concentrations of copper are expressed as mg Cu/kg dry weight in both sediment and organisms.

2. INVERTEBRATES

2.1. Laboratory data

2.1.1. Uptake of copper

Prosi & Back (1985) reported very briefly on the uptake of copper by tubificid worms (**Limnophilus sp.**) and indicated an increase of 1.4- to 2.6-fold over control values (which were rather high at 72 mg Cu/kg) after 4 weeks exposure to sediments from Hamburg harbour and the Neckar river, Germany which contained 258 and 281 mg Cu/kg, respectively. The difference between the two rates of uptake may be related to differences in other metals present in the sediment; the lower rate occured where the concentrations of zinc and lead were particularly high at 1719 and 370 mg/kg, respectively, compared with 652 and 233 mg/kg, respectively in the case of the higher rate of uptake; this suggests the possibility of competition between copper and other metals.

Diks & Allen (1983) kept tubificid worms for up to 12 days in solutions containing 5% suspensions of river sediments from the Des Plains river, Calumit river, Flatford river and Wabash river, USA, both as collected and also when spiked with up to 10 mg Cu/l and equilibrated for 72 h before the addition of the worms. The sediments were analysed in a 5-step sequence using: 1) 1M magnesium chloride at pH 7 for 1 h (for the

absorbed and exchanged phase of copper),
2) 1M sodium acetate at pH 5 for 5 h (for the carbonate phase), 3) 0.1 M ammonium hydroxide/hydrochloric acid + 0.01 M nitric acid at pH 2 for 30 min. (for the easliy reducible - manganese oxides and amorphous iron oxides - phase),
4) 30% hydrogen peroxide + 1 M ammonium acetate at 85°C for 5 h (for the organic phase) and
5) 1 M ammonium hydroxide/hydrochloric acid in 25% acetic acid at 96°C for 6 h (for the moderately reducible - hydrous iron oxides - phase). The total concentration of copper in the sediments was increased from a range of 7-63 mg Cu/kg in the natural sediments to 204-269 mg Cu/kg in those spiked. Aqueous concentrations were not given, but they were apparently not significantly correlated with the concentrations found in the worms. The most significant correlation of concentration in the worms was found with the easily reducible fraction which ranged from 0.5 to 47 mg Cu/kg, not the 'exchangeable' fraction as found by Hall and Bindra (1979). However, the next most significant correlation was found with the total copper (0.5 N nitric acid extract).

Gunn **et al.** (in preparation) in 14-day tests, also using tubificids, measured the uptake of copper from natural sediment and from sediments spiked with copper added in various different phases of availability. Using concentrations of up to about 80 mg Cu/kg, they demonstrated poor relationships between uptake and total copper in sediments spiked with copper associated with iron hydroxide, organic matter and carbonate, the concentrations in the worms being about 50 mg Cu/kg. Good relationships were found between uptake and total copper in sediments spiked either with copper associated with kaolin or directly with inorganic copper; the concentrations in the worms at 70 mg Cu/kg were about 80 and 95 mg Cu/kg, respectively. Inclusion of the 'carbonate fraction' (obtained by shaking for 5 h with 1M sodium acetate adjusted to pH 5 with acetic acid) produced poorer correlations of uptake with sediment concentrations because it recovered copper that was evidently not taken up by the worms. The results overall showed a good correlation with copper in the 'exchangeable' fraction (obtained by shaking with 1M manganese sulphate at pH 2 for 1 h). Inclusion of the fraction extracted with 1M ammonium acetate/0.25M calcuium chloride at pH 6 gave a much better correlation, although it was recognised that, while this extracted 90% of the copper from kaolin, it also extracted 30% from calcium carbonate.

2.1.2. Toxicity

Freshwater

Malueg **et al.** (1984a) found that a sample of sediment from the northern part of the Keweenaw waterway was toxic to the cladoceran, **Daphnia magna** when tested in the presence of the burrowing mayfly nymph, **Hexagenia limbata**; significant and increasing concentrations of total and dissolved copper were present in the overlying water. These authors also showed that the toxicity of the overlying water increased with time.

Krantzberg & Stokes (1981) had already shown that benthic macro-invertebrates stimulated the flux of copper from the sediment (spiked with copper) to the overlying (acidic) water, and also caused a change in the copper in the sediment from the more strongly complexed forms of the metal to the adsorbed and cation-exchangeable forms. Malueg **et al.** (1983) had also already concluded that tests with **Daphnia magna** in water overlying sediments containing copper were more sensitive when conducted in the presence of **Hexagenia limbata**, which increased the turbidity of the overlying water, than they were when conducted in their absence.

Malueg **et al.** (1984b) also carried out similar toxicity tests with these two organisms and sediments high in copper from other areas (the Phillips Chain of lakes and Torch lake, Michigan and the little Grizzly Creek system, California). Graphical examination of their data indicate that, in broad terms, the 2-d LC50 for **Daphnia** and the 10-d LC50 for **Hexagenia** were about 500 mg Cu/kg, but that this also corresponded to a concentration of total copper of 0.17 mg/l in the water; 'soluble' copper was not measured.

Cairns **et al.** (1984) spiked the sediments from two Oregon sites (Tualatin river and Soap Creek pond) with copper and, following repeated replacement of the overlying water until the concentration there was at equilibrium with that in the sediment, carried out static toxicity tests with invertebrates. The 2-d LC50 for **Daphnia magna** was 937 and 681 mg Cu/kg, respectively, and the 10-d LC50 values were: for the larvae of the midge, **Chironomus tentans**, 2296 and 857 mg Cu/kg, respectively, for the two sites and for the amphipods, **Hyalella azteca**, and **Gammarus lacustris** (Soap Creek pond only), they were 1078 and 964 mg Cu/kg, respectively in the sediment. Aqueous concentrations of 'soluble' copper, which increased with those in the sediment, probably accounted for the result in one of the tests (Soap Creek pond) in which they were measured; the corresponding LC50 values were 30 ug Cu/l for **Daphnia**, 38 ug Cu/l for **Chironomus**, 39 ug Cu/l for **Hyalella** and 61 ug Cu/l for **Gammarus**. The corresponding concentration of total copper for the LC50 for **Daphnia** was about 0.2 mg Cu/l compared with 0.17 mg Cu/l found by Malueg **et al.** (1984b), although the corresponding value found for Tualatin river was 0.08 mg Cu/l.

The fine-grained sediments used by Krantzberg & Stokes (1981, **loc cit.**), and spiked with copper sulphate, contained about 40 mg Cu/kg, most (77%) of which was readily extractable with 0.5 N hydrochloric acid, and therefore consisted of organics and humic and fulvic acids; the percentages extractable with magnesium chloride (absorbed and cation-exchangeable), sodium acetate (carbonate- and sulphate-bonded) and a mixture of ammonium hydroxide and acetic acid (reducible Fe and Mn oxides and organics) were only 3.0, 9.5 and 7.7, respectively.

Wiederholm **et al.** (1987) kept 5 species of worms (**Tubifex tubifex**, three species of **Limnodrilus** and **Potomothrix hammoniensis**) for up to 500 days in four natural lake sediments (lakes Hjalmaren, Malaren, Rogsjon and Runn, Sweden) with concentrations of copper of 26, 100-200, 40 and 1870 mg/Cu/kg, respectively and also in a sample of the first of these spiked with copper suplphate to give concentrations of 1591 and 4520 mg Cu/kg. With all species, increase in concentration of copper showed adverse affects on survival, growth and reproduction, but the effect of 1591 mg Cu/kg in the spiked sample appeared to be less than that produced at similar concentrations in Runn lake, which suggests that other factors were important, including food supply and the presence of other metals. An important observation was that the effects were most severe when food was also a limiting factor. No measurements were made of copper in the supernatant or interstitial water.

Millbrink (1987) also found that the growth and reproduction of **Tubifex** were inhibited in sediment from Lake Runn, Sweden containing 1250 mg Cu/kg (range, 800-1800 mg Cu/kg) and also containing high concentrations of other metals, including mercury (3325 mg Hg/kg) and zinc (5900 mg Zn/kg). Even when the sediment was diluted with 3 volumes of sediment from Lake Hjalmaren containing much lower concentrations of metals (56 mg Cu/kg, 114 mg Hg/kg and 265 mg Zn/kg), the rate of growth and reproduction over a period of 300 days were about half those found in the sediment from Lake Hjalmaren; this mixture would have contained about 917 mg Hg/kg and 1689 mg Zn/kg as well as 355 mg Cu/kg.

Marine

Bryan and Hammerstone (1971) transferred the polychaete worm, **Nereis diversicolor** from the Plym estuary, UK, which was low in sedimentary copper (41 mg Cu/kg) to sediment from Rostronguet creek which contained on average 3020 mg Cu/kg; they reported that some individuals showed signs of toxicity by coming to the surface of the mud within 35 days and that at the end of this period their body burden of copper had increased from an initial value of 28 mg Cu/kg to 208 mg/Cu/kg, which is close to the value (220 ug Cu/l) shown to be lethal in tests with aqueous concentrations. In these tests the 37-d LC50 was about 0.2 ug Cu/l compared with 0.5 ug Cu/l for worms collected from the Restronguet sediment, showing that the latter were significantly more resistant to copper (see also Section 2.2.2).

Bryan & Gibbs (1983) also transferred the scrobicularid worms, **Abra tenuis** from the Plym estuary, and **Scrobicularia plana** from the relatively unpolluted estuaries of the Mylar and Tamar to sediment from Rostronguet creek; they found reduced survival (0-50%) compared with 100% in controls in sediment from the Mylar estuary over a period of 18 days and also found elevated concentrations of 298-440 mg Cu/kg in the survivors of **S. plana** compared with 260 mg Cu/kg in controls. The concentration of metals in the sediments were not given, but those in the overlying water were about 40 ug Cu/l and 300 ug Zn/l which are below the respective threshold LC50 values for **S. plana** (100 ug Cu/l and 1000 ug Cu/l, respectively). Similar experiments are said to have demonstrated the toxicity of the sediments to juvenile bivalves, including the cockle (**Cerastoderma edule**) and the clam (**Macoma baltica**), but no details were given.

Long & Chapman (1985) reported on various studies on the toxicity of sediments from Puget Sound, United States, which contained heavy metals and organic toxicants. Significant effects were not observed on the (presumably short-term) mortality of the amphipod, **Rhepoxynius abronius** with some 7 samples, at concentrations of between 15 and 581 mg Cu/kg, but were found with 7 other samples ranging from 91 to 276 mg Cu/kg. The development of the larvae of the surf smelt (**Hypomesus pretiosus**) was affected in all four samples containing between 54 and 178 mg Cu/kg. Significant effects on the development and survival of larvae of the **ata** were not found with 3 samples containing 52 was also a limiting factor. No measurements were made of copper in the supernatant or interstitial water.

Millbrink (1987) also found that the growth and reproduction of **Tubifex** were inhibited in sediment from Lake Runn, Sweden containing 1250 mg Cu/kg (range, 800-1800 mg Cu/kg) and also containing high concentrations of other metals, including mercury (3325 mg Hg/kg) and zinc (5900 mg Zn/kg). Even when the sediment was diluted with 3 volumes of sediment from Lake Hjalmaren containing much lower concentrations of metals (56 mg Cu/kg, 114 mg Hg/kg and 265 mg Zn/kg), the rate of growth and reproduction over a period of 300 days were about half those found in the sediment from Lake Hjalmaren; this mixture would have contained about 917 mg Hg/kg and 1689 mg Zn/kg as well as 355 mg Cu/kg.

Marine

Bryan and Hammerstone (1971) transferred the polychaete worm, **Nereis diversicolor** from the Plym estuary, UK, which was low in sedimentary copper (41 mg Cu/kg) to sediment from Rostronguet creek which contained on average 3020 mg Cu/kg; they reported that some individuals showed signs of toxicity by coming to the surface of the mud within 35 days and that at the end of this period their body burden of copper had increased from an initial value of 28 mg Cu/kg to 208 mg/Cu/kg, which is close to the value (220 ug Cu/l) shown to be lethal in tests with aqueous concentrations. In these tests the 37-d LC50 was about 0.2 ug Cu/l compared with 0.5 ug Cu/l for worms collected from the Restronguet sediment, showing that the latter were significantly more resistant to copper (see also Section 2.2.2).

Bryan & Gibbs (1983) also transferred the scrobicularid worms, **Abra tenuis** from the Plym estuary, and **Scrobicularia plana** from the relatively unpolluted estuaries of the Mylar and Tamar to sediment from Rostronguet creek; they found reduced survival (0-50%) compared with 100% in controls in sediment from the Mylar estuary over a period of 18 days and also found elevated concentrations of 298-440 mg Cu/kg in the survivors of **S. plana** compared with 260 mg Cu/kg in controls. The concentration of metals in the sediments were not given, but those in the overlying water were about 40 ug Cu/l and 300 ug Zn/l which are below the respective threshold LC50 values for **S. plana** (100 ug Cu/l and 1000 ug Cu/l, respectively). Similar experiments are said to have demonstrated the toxicity of the sediments to juvenile bivalves, including the cockle (**Cerastoderma edule**) and the clam (**Macoma baltica**), but no details were given.

Long & Chapman (1985) reported on various studies on the toxicity of sediments from Puget Sound, United States, which contained heavy metals and organic toxicants. Significant effects were not observed on the (presumably short-term) mortality of the amphipod, **Rhepoxynius abronius** with some 7 samples, at concentrations of between 15 and 581 mg Cu/kg, but were found with 7 other samples ranging from 91 to 276 mg Cu/kg. The development of the larvae of the surf smelt (**Hypomesus pretiosus**) was affected in all four samples containing between 54 and 178 mg Cu/kg. Significant effects on the development and survival of larvae of the polychaete, **Capitella capitata** were not found with 3 samples containing 52 to 131 mg Cu/kg, but were found with one sample containing 178 mg Cu/kg. More detailed information on the mortality of this species in 22 samples (Chapman & Fink, 1984), though without giving details of the chemical composition of the sediment or water, showed that this was, on aaverage, greater (53%) in the presence of sediment and elutriate over a period of 35 days than it was (31%) in the presence of elutriate alone after a 50-d exposure. Some of these adverse effects may have been caused by factors other than copper (see Section 2.2.1).

2.2. **Field studies**

2.2.1. Uptake of copper

Freshwater

Eyres & Pugh-Thomas (1978) found generally higher concentrations of copper in the detritivore, water hog-louse (**Asellus aquaticus**) than in the carnivorous leech, **Erpobdella octoculata**, in the River Irwell, UK, where concentrations in the substrate (scraped from the film coatings of stones) were 30-300 mg Cu/kg, whilst those in the water were less than 5 ug Cu/l; concentrations in **Asellus** appeared to decrease with increase in substrate concentration. A later study in the river by Dixit & Witcomb (1983) when contamination by copper had increased considerably to 100-5000 mg Cu/Kg in the substrate and to 30-75 ug Cu/l in the water, indicated that concentrations of copper in the organisms (oligochaetes, chironomids and **Erpobdella**) were directly related to those in the substrate, but no relation was evident for **Asellus.** However, multiple regression analysis of the data from both sources showed that the body burden of copper in **Epobdella** and oligochaetes were each related to substrate concentration of coppr, rather than to aqueous cooncentrations, while that of **Asellus** was related primarily (87%) to aqueous concentrations. The relationship found for chironomids was not significant.

Mathis & Cummings (1973), in a study of several metals in the Illinois river, USA found that mean concentrations of copper were about 1 ug Cu/l in the water (maximum 5.2 ug Cu/l), 1.2 mg Cu/kg (wet wt.) for the clam, **Amblema plicata,** 1.7 mg Cu/kg in each of the clams, **Fusconaia flava** and **Quadrula quadrula,** 23 mg Cu/kg in a mixed population of the tubificid worms, **Limnodrilus hoffmeister** and **Tubifix tubifix** and 19 mg Cu/kg (dry wt.) in the sediment (compared with 7.7 mg Cu/kg in the sediment from 3 non-industrialised streams). These organisms were not cleansed of sediment before analysis, but other studies (Hall & Merlini, 1979c) suggest that the effect on the results for the worms would be small.

Namminga & Wilson found only 1.9 mg Cu/kg in chironomids from Skeleton Creek, Oklahoma, USA where the concentrations in the sediment and water were 1.8 mg Cu/kg and 3.5 ug Cu/l. respectively.

Copper in sediment in Lake Superior at twice the background concentration appear not to have been associated with uptake in food chains (Keiller & Ragotzkie, 1976, in Lewis & Cave, 1982).

Hall & Merlini (1979a, 1979b) measured the concentration of copper in deposit-feeding oligochaetes and in the sediments, pore water and overlying water from 9 sites in the Toce river and Isole Barromee basin of Lake Maggiore, Italy. Although they did not find a relation between concentrations in the worms and those in the environment, examination of their data, excluding 4 sites where sampling for invertebrates, sediments and water was not simultaneous, shows a significant (P = 0.05) positive correlation of copper in the worms with that in the organic fraction of the sediment (accounting for 0.78 of the variance) according to the equation:

$$y = 6.6 + 38.9\ x$$

where y = concentration of copper on oligochaetes in mg Cu/kg dry weight and x = concentration of copper in the organic fraction of the sediment (extracted with Soluene-350) in g Cu/kg. The range of the latter concentration was 0.41-1.35 g Cu/kg, whilst the range of total copper in the sediment and the concentrations corresponding to the range of the organic fraction were 11.3-85 and 11.3-80 mg Cu/kg respectively. The concentration of organic matter was 2.1-10.8% but was not itself related to copper uptake. Manganese concentrations in the sediments were 6-75 mg Mn/kg with Mn:Cu ratios of between 0.69 and 1.27. The worms included a large proportion of immature Tubificidae and **Limnodrilus** spp. in the river stations and of Tubificidae and **Psammaryctes barbatus** among those in the lake. The results at the lower end of the range of total copper in the sediment correspond broadly with those of Mathis & Cummings (1973, **loc. cit.**), while those at the upper end correspond broadly with those of Gunn, Winnard & Hunt (in preparation) for sediments spiked with carbonate or sludge or iron hydroxide.

Chapman **et al.** (1979) measured the concentration of metals in the sediment and oligochaete worms (mainly **Limnodrilus hoffmeisteri** and **Tubifex tubifex**) at two stations on the Fraser River, British Columbia. The concentrations of copper at the two stations was similar for sediment (32.8 and 31.3 mg Cu/kg, respectively) but significantly different in the worms (9.5 and 15.7 mg Cu/kg, respectively). The latter values are somewhat lower than those found by other authora, including Greichus **et al.** (1977), who found 21 mg Cu/kg in unidentified oligochaetes and 22 mg Cu/ kg in aquatic insects in the presence of 15 mg Cu/kg in the sediment of Voelulei Dam, South Africa.

Hall & Bindra (1979) found a correlation between the uptake of copper by oligochaetes in British Columbia and a weakly-exchangeable fraction and, to a lesser degree, with an easily reducible fraction of copper in sediments.

Bonfonte **et al.** (1986) concluded from their work on the river Po that dissolved copper of the order of 10 ug/l (in contrast to some other metals) was more closely correlated with the concentration of copper in the bivalve mollusc, **Unio elongatulus** than was the concentration of copper in the suspended solids, but sediment concentrations were not given.

Tessier **et al.** (1983) stated that with the freshwater molluscs, **Elliptio complanata** and **Anodonta grandis** in lakes in Beauchastel, La Bruere and Montbeillard, Quebec, Canada, no statistically significant relations were found between organ or whole body burden of copper and the exchangeable fraction of copper in the sediment (using 1 N magnesium chloride at pH 7). Significant correlations were found between organ copper content and copper bound to carbonate (1 M sodium acetate/acetic acid at pH 5) and copper bound to iron-manganese oxides (0.04 M hydroxyl amine/hydrochoric acid in 25% v/v acetic acid at 96°C). Improved correlations were obtained using the sum of these three forms of copper and the ratio of these three to the corresponding concentration of iron.

The latter relations were:

$y = -0.02 + 6853.8\ x$ and

$y = 40.7 + 16731.5\ x$, for the two species, respectively,

where y = concentration of copper in soft tissue and

x = ratio of copper to iron.

More details of these results for **Elliptio** were provided by Tessier **et al.** (1984); the total concentration of copper in the sediments was 24-180 mg Cu/kg, that of the first three fractions, 6.5-59.3 mg Cu/kg and that of the first (exchangeable) fraction, only 0.1-0.3 mg Cu/kg. The relation between body burden and total copper in the sediment was significant (P = less than 0.05), though accounting for only 0.63 of the variance, trhe equation being:

$y = 0.46 + 6.81\ x$

where y = concentration in the soft tissues and

x = concentration in the sediment.

Marine

Neff, Foster & Slowey (1978, in Lewis & Cave, 1982), in measuring the accumulation of copper in 5 species of test organism, report that it did not correlate well with bulk metal analysis of the sediment, except in one case, the polychaete worm, **Neanthes arenacoelentata.**

Luoma & Bryan (1982), in studying the uptake of copper (and other metals) from sediment by the bivalve mollusc, **Scrobicularia plana** and the polychaete worm, **Nereis diversicolor**, found that a 1M hydrochloric acid extraction of the sediment gave a better measure of the bio-availabiliy of the metal than any other method.

Sandler (1984) examined the uptake of copper by benthic crustacea in the open part of the Bothnian Sea where anoxic conditions have not been recorded and the surface layers of the sediments are always oxidised. He found some indication of accumulation in older individuals of the isopod, **Mesidotea entomon**, but concentrations in this animal and in the amphipod, **Pontoporeia affinis**, were negatively correlated with total concentration in the sediments; this was probably because bio-availability was lower at the deeper water site because of scavenging by high concentrations of Fe and Mn. The concentration of total copper in water overlying the sediments was about 0.012 ug Cu/l and was not related to those in the sediments (in the range 10-40 mg Cu/kg dry wt), but the author cites other work at his Institute which demonstrated concentrations of 0.07 ug Cu/l in the interstitial water of the upper layers of the sediment, although this is a low concentration compared with data reported elsewhere for areas of copper mine tailings (Lewis & Cave, 1982).

Amiard **et al.** (1987) showed that the concentrations of copper in sediments in the Loire estuary and the nearby area of the Bay of Bourgreuf were 2 and 16 mg Cu/kg and were reflected by those in the burrowing worm, **Nereis diversicolor** (9 and 21 mg Cu/kg, respectively) and the burrowing bivalve, **Scrobicularia plana** (17 and 25 mg Cu/kg, respectively), but not in those of the shrimp, **Crangon crangon** (57 and 55 mg Cu/kg, respectively). No measurements were reported for concentrations in the overlying water.

Bryan & Hummerstone (1971) found a general relationship between the concentration of copper in **Nereis diversicolor** and those in the sediment they occupied in several estuaries in the UK. Mean concentrations ranged from 22 to 1142 mg Cu/kg in the worms and 41 to 3020 mg Cu/kg in the sediments. Their plot of individual sample data shows considerable scatter which is not readily explained, but which still indicates an asymptotic lower concentration in the worms which would be in line with the two data points of Armiard **et al.** (1987, **loc. cit.**). Bryan and Hummerstone (1971) found that correlation of body burden with concentration in the sediment extracted with an acetic acid/hydroxyl amine hydrochloride mixture (which does not extract metals incorporated into clay minerals) was similar to that obtained with total concentration in the sediment. The interstitial water contained concentrations of copper which varied considerably with depth of sediment; they ranged up to 5 ug Cu/l but were usually much less than 0.3 ug Cu/l and did not appear to be correlated with body burden.

Relationships between body burden and concentration in sediment, similar to that found by Bryan & Hummerstone (1971) for **Nereis diversicolor** have been found by Bryan & Gibbs (1983) for the errant polychaete species, **Perinereis cultrifera** and **Nephtys hombergi, Glycera convoluta, Cirriformia tentaculata** and **Tharyx marioni,** but not for **Melinna palmata.** For the bivalve mollusc, **Scrobicularia plana** the relationship was less marked than that for nereid worms, although the results are in accord with two data points of Armiad **et al.** (1987, **loc. cit.**). Bryan and Gibbs (1983) suggested that this lower uptake, compared with that of **Nereis,** might have been partly attributable to the animals choosing to filter-feed from the overlying water rather than from the sediment itself. The cockle, **Ceratoderma edule** showed similar but lower concentrations than those in **Nereis** and a rather more marked indication of an asymptotic low concentration at relatively low concentrations in the sediment (30-400 mg Cu/kg). The relationship for the plant, **Fucus vesiculosus** was very close to unity over the range studied in the sediment (200-1000 mg/Cu/kg).

Batley (1987) found copper present in the hairy mussel, **Trichomya hirsuta** and the cockle, **Anadara trapezia** at concentrations of 2.6 and 1.7 mg Cu/kg, resepectively, at a site in Lake Lacquarie, Australia where the concentrations in the sediment and water were 34.3 mg Cu/kg and 2.6 ug Cu/l, respectively.

2.2.2. Effects on populations

Freshwater

Norris (1978) found a tendency for numbers of invertebrates at 8 sites in the South Esk river, Tasmania, to be reduced with increase in concentration of copper, zinc and cadmium in both the water and sediments and with reduction in concentration of iron in the sediments. The concentration of copper in the sediments ranged from 7.6 to 336 mg Cu/kg, but examination of the data shows that the only significant correlation is found with cadmium; excluding station 8 (which is considered anomalous) cadmium in the sediment and water accounted for 0.9 and 0.92 of the variance of the logarithm of numbers of the most sensitive group of organisms against log concentration, at P values of 0.01 and 0.001, respectively.

Hall & Merlini (1979a, 1979b) measured the abundance of oligochaetes at 9 sites where the concentrations of copper in the sediments ranged 11.3 to 80 mg Cu/kg and numbers of worms ranged from 490 to 38,700; although numbers tended to fall with increase in copper content at a rate similar to those in other studies (Malueg **et al.**, 1984a; Kraft, 1979) the correlation was of low statistical significance (P = 0.1-0.05).

Eyres and Pugh-Thomas (1978) found that the macro-invertebrate community in the River Irwell, UK was poorer than might be expected from water quality alone; the only details given were that only six species of tubificids occurred thoughout and only two species were present in the upper reaches. Taking the upper five stations, the concentrations of metals in the water were less than 5 ug Cu/l, 20 ug Zn/l and 0.6 ug Pb/l, whilst those in the substrate (scapings from stones) were 24-145 mg Cu/kg, 112-702 mg Zn/kg and 37-330 mg Pb/kg. More details of the invertebrate species composition and abundance were given by Eyres (1976) for seven bi-monthly samples from ten stations; these showed that the fauna was dominated by oligochaetes (84%) and chironomids (13%). Neglecting the uppermost, control station, which was low in copper, but also low in number and variety of invertebrates, there was a significant reduction in number of species with increase in concentration of copper in the substrate (P = 0.0-0.001), accounting for 0.78 of the variance, according to the equation:

$$\log y = 2.2 - 0.41 \log x,$$

where y = average number of species and
x = concentration of copper in substrate in mg Cu/kg.

The range of copper concentrations was 107-504 mg Cu/kg. A similar reduction in average abundance of invertebrates was not statistically significant.

Kraft (1979) found that the benthic invertebrates at 258 sites on the shore of Lake Superior, USA, where copper was present from mine tailings was dominated by the amphipod, **Pontoponeia hoya**, although it was absent from areas where the concentration of copper in the sediments ranged from 395 to 1310 mg Cu/kg. The highest concentrations occurred nearest to the shore at depths down to 25 m (25-928 mg Cu/kg) and, within this zone, examination of the author's summarised data for 5 sites shows that the abundance was reduced significantly (P = 0.05) with increase in log concentration; at 30 mg Cu/kg, it was 170/m^2 and at 300 mg Cu/kg it was 17/m^2. Concentrations were lower (8-140 mg Cu/kg) at depths greater than 25 m and in this region there was no relationship between them and the abundance of amphipods.

Kraft & Sypniewski (1981) found significant effects of copper on benthic macro-invertebrate density, and number of taxa present in the northern area of Keweanaw Waterway, Michigan (which was polluted by copper tailings) where sediment concentrations of copper ranged from 39 to 1229 mg Cu/kg (mean 589 mg Cu/kg) compared with a range of 6 to 54 mg Cu/kg (mean 33 mg Cu/l) in the southern area. **Hexagenia** sp. were very sensitive to copper, as were molluscs, amphipod crustaceans (including **Gammarus**), caddisfly larvae, oligochaetes and several chironomid midges; however, no details of the aqueous concentrations are given. Later work there by Malueg **et al.** (1984a) amplified some of the information on macro-invertebrates in the Southern and Northern Waterways: sediment concentrations of copper were given as 33 and 425 mg Cu/kg, respectively; and the respective numbers of invertebrates were 491 and 110/m^2; the number of taxa, 13.4 and 3.8; and the biomass, 3.72 and 0.41 g/m^2. Thus the abundance, diversity and biomass were all reduced by increased copper in the sediments. However, again, no data were included on concentrations of copper in the overlying water.

Malueg **et al.** (1984b) examined the fauna from 3 different locations in the United States and, at the majority of stations, also measured the concentration of copper. Examination of their data at 6 sites at the Phillips Chain of lakes, Wisconsin, shows a significant reduction in number of taxa, diversity and biomass, but no apparent trend in density of animals (mean, 1014/m^2), over the range 30 to 540 mg Cu/kg. At a site in Torch lake, Michigan, where the concentration was 1800 mg Cu/kg, only one taxon was found and at a density of only 14/m^2. At several sites in the Little Grizzly Creek system, California, there were also marked reductions in number of species and biomass (based on data of Sheehan, 1980, in Malueg **et al.**, 1984) over the range, 20 to 2700 mg/Cu/kg.

Marine

Bryan & Hummerstone, (1971) found copper-resistant **Nereis diversicolor** living in heavily contaminated parts of Restronguet creek, UK where concentrations of copper in the sediment averaged 3020 mg Cu/kg; other organisms present included the deposit-feeding bivalve mollusc, **Scorbicularia plana**, the polychaete, **Nephthys hombergi**, the amphipod, **Corophium volutator** and the brown seaweed, **Fucus vesiculosa**, but no quantitative data are available (G. W. Bryan, personal communication).

Increased tolerance to copper was also reported by Bryan and Gibbs (1983) for all these species and also for the crab, **Carcinus maenus.** The increase was 2.8-fold and 2-fold for the 96-h LC50 of **Nephtys hombergi** and **Scrobicularia plana**, respectively, compared with animals from the Tamar and Avon estuaries, respectively, and 1.6-fold for the 168-h LC50 of **Corophium volutator** taken from the Avon estuary. The authors suggest that for **Nereis diversicolor** and **Fucus vesiculosus** the increased tolerance has a genetic basis, especially for the former in which much of the resistance is retained after being grown for 4 months in acid-washed sand and fed on a diet of yeast. The areas studied by these authors have a history of mining pollution going back some 200 years.

Bryan & Gibbs (1983) showed that **Scrobicularia plana** was present at the limit of its distribution in Restronguet creek at a point furthest from the main river channel where the concentrations of copper in the sediment extracted in four different ways (with nitric acid, 1N hydrochloric acid, 25% acetic acid and 1N ammonium acetate) were 2541, 1920, 1534 and 90 mg Cu/kg, respectively. This species was absent from a point nearest the central channel where the corresponding concentrations were 2568, 2110, 2039 and 239 mg Cu/kg, respectively. This suggests that the ammonium acetate extraction yielded a better measure of the bioavailablity and toxicity of the copper in the sediment than the other methods used. Concentrations in the interstitial water at these two points in the creek were 66 and 83 ug Cu/l, respectively, whilst that in the supernatant water at the first of these two points on two occasions as the tide advanced was 6 and 22 ug Cu/l; these should be compared with the threshold LC50 of 50 ug Cu/l and the 12-d LC50 of 325 ug Cu/l found for specimens collected from a less contaminated creek in the Fal estuary where concentrations in the sediment were in the range, 150-300 mg Cu/kg.

No quantitative data on the distribution of benthic organisms are available for the Fal estuary, but the species listed at 18 sites (Bryan and Gibbs, 1983) have been grouped into 1) the two sites nearest the mouth of Rostronguet creek, 2) 8 sites in the western half of the Fal, adjacent to Rostronguet creek and 3) and 8 sites in the eastern half. In these three areas, the average number of species per site among the 31 common species found in the Fal are 9.5, 9.1 and 13.5, respectively, and among the 27 rare species, the corresponding figures are 0, 1.6 and 2.8, respectively. The corresponding ranges of concentration of copper in the sedimens (taken from distribution maps) are 1000-2000, 500-1000 and 150-500 mg Cu/kg, respectively. The regression of log number of species on log median concentration of copper is significant (P = 0.05).

Oyenekan (1983) sampled sediment and benthic organisms over a period of 20 months at two sites in the south-western region of Southampton water, UK. From the graphs presented, the mean concentrations of copper in the sediments were calculated to be 215 and 430 mg Cu/kg, respectively and the species' diversity (Sannon-Wiener Index) was 1.44 and 0.59, respectively. Populations of the polychaete, **Capitella capitata** were 37 and 2188/m^2, respectively, their total production was 0.38 and 1.62 g/m^2/y, respectively, but the total macro-faunal production was 5.4 and 3.5 g/m^2/y. respectively. Thus, although **Capitella** was not adversely affected by increased copper, both diversity and overall production appeared to have been reduced. Hydrocarbons were also said to be present but no data on them were presented.

Rygg (1985) analysed data from 63 fijord areas and found significant negative correlations between the logarithm of diversity (expressed as relative number of species) and the logarithm of concentration of copper, lead, zinc and organic content in the sediment, each tested separately. A multiple correlation was carried out by Rygg, but the largest correlation coefficient and the largest effect was found with copper (P less than 0.001), the equation for which was:

log relative no. of species = 1.79 - 0.32 log x

where x = concentration of copper (mg Cu/kg)

(The intercept was read from the author's graph (Fig. 1) because the printed figure was incorrect). Thus, ignoring the possible interaction of copper uptake with organic matter and the presence of other metals, the number of species was roughly halved for each 10-fold increase in copper concentration. Among the resistant species was the majority of carnivores compared with the others which were mainly deposit feeders. The range of concentration of copper studied was from 15 to 3,000 mg Cu/kg.

Analysis of data from Powell (1987) has shown that biomass, as well as diversity of benthic organisms, can be reduced significantly (P = 0.01) with increase in concentration of copper in sediments in coastal conditions; over the range 30 to 1522 mg Cu/kg reductions in biomass of between 68 and 93% were found in two different years for a 10-fold increase in copper concentrat-ion (but fish catches appeared not to be affected).

McGreer (1979, in Lewis & Cave, 1982) found no evidence that copper in sediments in the vicinity of a sewage outfall was toxic to the adult of the bivalve, **Macoma balthica**, but suggested that it might have had an effect on the settlement of the larvae.

Long & Chapman (1985) found a general difference in the abundance of benthic organisms in Puget Sound, United States, between control stations and those contaminated by heavy metals and organic chemicals which was generally related to toxicity (as measured in the laboratory; **loc. cit.**, Section 2.1.2)); at contaminated stations there was an increase in the percentage contribution of polychaetes and molluscs and a decrease in phoxocephalids, arthropods and echinoderms, and although mean copper concentrations increased from 34 to 145 mg Cu/kg, this is not necessarily the cause. However, multiple regression analysis of the data shows that the log concentration of copper alone, rather than the combined concentration of copper, zinc and lead, accounts for much (0.5) of the variance in results for ploychaetes and molluscs. Nevertheless, analysis of that part of the data that includes PCB's and other organic chemicals shows that the former accounts for most of the variance.

Brown (1977) recorded the number of species of invertebrates in the River Hayle, Cornwall, UK and also measured the concentrations of copper in water and sediments. Analysis of her data show that the number of speies is significantly correlated with the concentration of 'soluble' copper in the water (in the range, 1-18 ug Cu/l), rather than with that of copper in the sediment (range, 133-4500 mg Cu/kg); the pH ranged from 5.5 to 7 and the proportion of 'available' copper averaged 0.18 (analysed by shaking for 15 minutes with 2.5% acetic acid and then left for 24 hours).

Halcrow **et al.** (1973) examined the distribution of metals and organisms in sediments in the Firth of Clyde, UK. Maximum concentrations were 269 mg Cu/kg in an area used for dumping sludge, compared with 16 mg Cu/kg in control areas. Aqueous concentrations were 0.5-5 ug Cu/l. A full account of the organisms was not given, but the centre of the disposal area was dominated by polychaetes, mainly Cirratulidae and large numbers of **Capitella capitata** and oligochaetes, **Peloscolex** sp., but only one species of mollusc, **Phacoides borealis**; species such as the cnidarian, **Cerianthus lloydi** and the polychaete, **Pyospio elegans** flourished only at the perifery of the most contaminated zone. These results are not necessarily attributable to copper; of the total extracted with nitric/perchloric acid, only a small portion was extracted by 0.5 M ammonium acetate (0.2%), 0.5 M ammonium nitrate (also 0.2%), 0.1 M sodium EDTA (11%) and 2.5% acetic acid (2.5%).

2.3 Comparison of field survey data and laboratory toxicity

The number of parallel studies that have compared field survey data with toxicity are few, though consistent in their conclusions. Sediment samples collected from areas depleted of natural benthic populations and dominated by tolerant species have been found to be toxic to representative benthic organisms in the laboratory. Malueg **et al.** (1984a, **loc. cit.**) showed this for the Keweenan waterway, Michigan and similar results have been obtained in other contaminated sites in Elk lake in Wisconsin, Torch Lake in Upper Michigan and Little Grizzly Creek in California (Malueg **et al.**, 1984b), although in some cases the toxicity has been shown to be related to aqueous, rather than to sediment concentrations. Similar results have been obtained by Bryan and Gibbs (1983, **loc. cit.**).

Tsai **et al.** (1979) showed that there was a close correlation between the toxicity of suspended sediments to mummichog, (**Fundulus heteroclitus**) and the diversity of benthic macro-invertebrates, but analysis of theit results indicates that organic chemicals, rather than copper were mainly responsible for the toxicity.

Swartz **et al.** (1982) also showed a correlation between the toxicity of settled sediments to the amohipod, **Rhepoxynius abronius** and log number of species and mean diversity of amophipods in Commencent Bay, Washington, USA and, although chemical analyses were not carried out, there was evidence for the presence of a variety of contaminants.

3. FISH

3.1. Laboratory data

3.1.1. Uptake of copper

Bryan and Gibbs (1983) found slight evidence of accumulation of copper by the gurnard (**Trigla lucerna**) when fed over a period of 22 days with **N. diversicolor** containing 2 mg Cu/kg; concentrations in livers were 11.3 mg Cu/kg compared with 3.9 mg Cu/kg in those of fish fed on a low-copper diet, although the result might be explained in part by the relatively small size of the livers of the test group.

3.1.2. Sub-lethal effects

Xie **et al.** (1986) exposed bighead carp (**Aristychthys nobilis**) for 10-20 days to sediments taken from the River Xiang and spiked with copper chloride at a concentration of 138.3 mg Cu/kg; they found significant changes in protein content and in the activity of the enzyme, lactate dehydrogenase. However, concentrations of copper in the supernatant water averaged 58 ug Cu/l compared with 9 ug Cu/l in the controls and were also very variable (12-100 ug Cu/l).

Ou **et al.** (1986), working with the same species exposed for 3 months to sediment from the same source and spiked with up to 1200 mg/kg copper chloride found that the chromosomes of the blood cells were damaged. Concentrations of copper varied over the test period, but average values were 50 mg Cu/kg in the natural sediment and 298 mg Cu/kg (maximum, 433 mg Cu/kg) where a significant effect was found after 3 months (P = 0.05). The average incidence of micronuclei and nuclear fragmentation was increased from 0.06% in the controls to 0.33% and the maximum incidence (at 3 monthds) was 0.79%. On average only about half the added copper chloride is accounted for in the sediments and, although concentrations in the overlying water were measured, they were not reported; it seems likely, however, that they were identical to those reported by Xie **et al.** (1986, **loc. cit.**) because other experimental variables match. Iron, manganese and organic matter in the sediment were not measured.

Chen **et al.** (1986), using **Monopterus albus,** examined nuclear anomalies in peripheral erythrocytes and the mitotic index of renal cells of fish exposed to sediment containing copper. There was considerable scatter in the results and, while there was some indication of an increased micro-nuclear rate from about 2% in the controls at 62 mg Cu/kg to nearly 6% by the end of the experiment after 16 weeks at 618 mg Cu/kg, there appeared to be no effect at 777 mg Cu/kg. The erythrocyte nuclear malformation rate also showed considerable scatter, but tended to be higher than control values in the presence of 444 to 777 mg Cu/kg; control values were about 10% at the beginning and end of the 5-month test, but peaked to about 27% after one month: values at the two highest test concentrations (618 and 777 mg Cu/kg) were about 40% after one month and about 20% at 5 months. The mitotic index of renal cells increased steadily in controls from an initial value of about 0.125 to 0.3 over the 4-month test, while in the test fish it started at less than 0.03 and increased to 0.2 in those exposed to 444 mg Cu/kg, and showed a similar increase initially in those exposed to 618 mg Cu/kg but then dropped to 0.03, and remained at less than 0.01 throughout the test at 777 mg Cu/kg. Concentrations of copper in the overlying water were measured, but no data were presented.

Whether these biochemical and nuclear changes can be regarded as adaptive, or as indicating that the fish are under a stress that would be ecologically damaging, is not known. For one of these three studies (Xie **et al.**, 1986) it is likely that the result was largely attributable to copper in solution in the water overlying the sediments and the same may well be true of one of the others (Ou **et al.**, 1986).

3.2. **Field studies**

3.2.1. Uptake of copper

Freshwater

Mathis & Cummings (1973) in a study of several metals in the Illinois river, USA found mean concentrations of about 1.0 ug/l in the water, 19 mg Cu/kg (dry wt.) in the sediment and 0.13 mg Cu/kg (et wt.) in the muscle of carnivorous fish - pike (**Esox lucius**), 0.07 mg/kg; **Micropterus salmoides**, 0.1 mg/kg; **Morone chrysops**, 0.19 mg/kg; **Lepisosteus platostomus**, 0.16 mg/kg; and smallmouth bass (**Micropterus dolomieui**), 0.15 mg/kg - and significantly higher values of 0.21 mg Cu/kg in omnivorous fish - **Ictiobus cypsrinellus**, 0.18 mg/kg; shad (**Dorosoma cepidianum**), 0.26 mg/kg; **Moxostoma maroleidotum**, 0.18 mg/kg; **Carpoides cyrinus**, 0.17 mg/kg; and common carp (**Cyprinus carpio**), 0.24 mg/kg.

Boyer (1982) studied several stations on the Mississippi river near Mineapolis and one site on a nearby tributary, the St. Croix river, USA. Concentrations of copper in the two rivers were: 24.6 and 23 mg Cu/kg, respectively in the sediment (which was silt and clay); 0.4 and 0.39 mg Cu/kg (wet weight), respectively in the muscle of common carp (**Cyprinus carpio**); 0.29 and 0.32 mg Cu/kg, respectively in that of smallmouth bass (**Micropterus dolomieui**); and 5.9 and 2.4 ug Cu/l, respectively in the water. All the values are somewhat higher than those found by Mathis & Cummings (1973, **loc cit.**). Values in the sauger (**Stizostedion canadense**) were similar to those of the other two species. Values in other organs of carp were higher than those in the muscle; they were 3.43 and 1.96 mg Cu/kg (wet weight), respectively in the liver of these two species and 7.06 and 2.94 mg Cu/kg (wet weight) respectively in the kidney; although there appeared to be an increase in these with increase in copper in the sediment and with decrease in fish weight, this was not statistically significant.

Johnson (1987) measured concentrations of heavy metals in whole fish in lakes in Ontario, Canada and, while he found that some were positively correlated with inputs to sediments, those for copper were not. They were relatively constant among 6 species of fish (lake trout, whitefish, common sucker, yellow perch, northern pike and walleye) at about 1.0 mg Cu/kg wet wt. (range 0.6-1.2 mg Cu/kg wet wt.) and were associated with sediment concentrations of about 30 mg Cu/kg (range: about 25-50 mg/kg Cu/kg) dry wt., as judged from the author's graphs. There were no data on aqueous concentrations.

Greichus **et al.** (1977) measured concentrations of copper, amongst other water characteristics, in water, sediment and composite samples of ten (presumably whole) fish in two dams, Hartbeespoort and Voelvlei in South Africa. The results were 3 ug Cu/l, 41 mg Cu/kg and 2.9 mg Cu/kg, respectively in the first dam and 13 ug Cu/l, 15 mg Cu/kg and 3.8 mg Cu/kg in the second; two species of fish were involved in each case: canary kurper (**Chetia flaviventus**) and blue kurper (**Saarotheron mossambicius**) in the first and bluegill (**Lepomis macrochirus**) and largemouth bass (**Micropterus salmoides**) in the second.

Hakanson & Uhrberg (1981) measured the concentrations of copper in fish and sediments in Sweden. Examination of their data reveals no relation between concentrations in fish liver of pike, (**Esox esox**) and perch (**Perca fluviatilis**) and concentrations in the sediments (range 11-360 mg Cu/kg) although about 0.2 of the variance of log concentration in pike was significantly related ($P = 0.01$) to log fish length (22.6 mg/kg at 20 cm and 80 mg/kg at 80 cm). It is not possible to relate these data to those of Johnson (1987, **loc. cit.**) who analysed only whole fish, or to those of Mathias & Cummings (1973, **loc. cit.**) who analysed only the muscle.

Norris & Lake (1984) found a strong indication of a direct relation between aqueous concentrations of copper in different parts of the R. South Esk, Australia and the corresponding concentrations in the liver of perch (**Perca fluviatilis**) and appear to have ignored the possible role of sediment concentrations. Their data for trout (**Salmo trutta**) are few, but these also suggest an increase in concentrations in liver with increase in aqueous concentrations; they are compatible with those of Howells **et al.** (1983). Their data also indicate that concentrations in fish may asymptote down to a low normal background value, which is close to the threshold at which Howells **et al.** (1983) found that trout populations are not adversely affected by copper.

Data are available for Lake Biwa, Japan (Anon, 1983); they cover a range of concnetrations of copper in sediment of 8.7-129 mg Cu/kg at different locations in May, 1977 and also of copper in individual or batches of fish in June, 1975 to August, 1976. There was a significant positive correlation for the cyprinid fish, yarutanago (**Acheilognathus lacnceolata**) (Mori & Miura, 1980) which accounted for 0.66 of the variance, the equation being:

$$y = 0.9 + 0.017\ x$$

where y = concentration of copper in whole fish in mg Cu/kg (wet wt.)
and x = concentration of copper in sediment in mg Cu/kg (dry wt.).
No significant correlations were found for 6 other species for which 3 or more pairs of data were available.

Estuarine

Rozhanskaya & Spirandi (1981) collected fish (and invertebrates) at the mouth of the R. Danube and the North-western Black Sea and, although they contended that the content of copper in the tissues and whole organisms was related to various factors, including environmental concentrations, the data do not support the conclusion and the relative importance of aqueous, and sediment concentrations was not considered.

Marks **et al.** (1980) examined the concentration of metals in the muscle of several species of fish in the Swan-Avon estuary, Western Australia and found that generally the mean concentration in fish which had ingested sediment was greater than that in those which had fed on aquatic organisms. However, this was not clearly demonstrated for copper, except, possibly, for one species, black bream (**Acanthopagrus butcherii**) which, in common with some of the other species, apparently feeds to varying degrees on invertebrates such as polychaetes, molluscs and crustacea; it had the lowest concentrations (0.29 mg Cu/kg wet wt.) compared with sea mullet (**Mugil cephalus**) (0.35 mg/kg), yellow-eyed mullet (**Aldrichetta fosterii**) (0.34 mg/kg), yellow-tailed trumpeter (**Amnialaba caudavittatus**) (0.37 mg/kg) and Petts herring (**Nematolosa vlaminghi**) (0.39 mg/kg). No data were given on concentrations of copper in the sediments or the overlying water. Other data, from Bebbington **et al.**, 1977 (in Lewis & Cave, 1982) for New South Wales, Australia show differences in the same direction for **Acanthopagarus australis** (0.1-2.0 mg Cu/kg) and **Mugil cephalus** (0.2-2.8 mg Cu/kg). It should be noted, however, that concentrations of copper in the mullet decrease significantly with increase in fish weight (Marks **et al.**, 1980).

3.2.2. Other studies

Wright (1987) showed that in Chesapeake Bay, USA where there has been a decline in the striped bass (**Marone saxatilis**), sediment concentrations of copper were in the range 20 to 60 mg Cu/kg. However, concentrations of soluble copper and cadmium were, on occasion, within the lethal range for this species and are, therefore, likely to account for the results.

Thus, there appear to be no data on the effect of sediment concentrations of copper on the abundance, growth, reproduction and behaviour of fish, other than the single study already referred to in Section 2.2 which indicates that, even where the biomass and diversity of invertebrates was affected, the catches of fish were not. = (p.11) (Powell 1987)

4. OTHER ORGANISMS

Buhl & McConville (1982) sampled sediment and aquatic macrophytes in the upper Missippippi river, USA; concentrations of copper (in mg Cu/kg dry wt.) were 14 in the sediment, 13.1 and 4.6 respectively in the roots and shoots of broadleaf arrowhead (**Sagittaria latifolia**), 6.2 and 4.0

respectively in the rhizomes and shoots of white water lily (**Nymphae tberosa**), 6.2 in broadleaf pondweed (**Pomogeton americanus**) and 8.6 in coontail (**Ceratophyllum demersum**).

Batley (1987) demonstrated similar concentrations of copper in the leave and rhizomes of seegrass (**Zostera caprinicorna**) from two sites in Lake Macquarie, Australia, despite differences in concentrations in the sediment; they were 18 mg Cu/kg in leaves and rhizomes at one site where the sediment concentration was 94 mg Cu/kg and 16 and 23 mg Cu/kg in these two tissues, respectively at another site where the sediment concentration was only 33.8 mg Cu/kg. Aqueous concentrations were of the order of 2 ug Cu/l at both sites.

Bryan & Hummerstone (1971) recorded the presence of the brown seaweed (**Fucus vesiculosa**) in Rostronguet creek, UK where the mean concentration of copper in the sediment was 3020 mg Cu/kg (see Section 2.2.2). Bryan & Gibbs (1983) presented extensive data for **F. vesiculosus** from the Fal estuary indicating a linear relation between concentrations of copper in the plant and those in the sediment, the slope of the line being close to 1.0. Bryan & Hummerstone (1973, in Bryan & Gibbs, 1983) had concluded that concentrations in this organism reflected those in the water, but later work (Lucoma, Bryan & Langstone, 1982, in Bryan & Gibbs, 1983) suggested that copper might also be scavenged by the weed directly from suspended particles because of the high selectivity coefficients possessed by fucoid polyphenols. Limited data for **Ascophyllum nodosum** (Bryan and Gibbs, 1983) fit those for **F. vesiculosus.**

5. SUMMARY AND CONCLUSIONS

5.1. Bioavailability of copper in sediment

A variety of chemical extraction methods has been used to estimate the bioavailable fractions of copper in sediment and some have related the results to bioavailability as measured by the responses of organisms. The uptake of copper by tubificid worms under laboratory conditions has correlated best with the more easliy extracted phases of copper (Diks and Allen 1983; Gunn **et al.**, in preparation). Also the body burden of copper in other organisms, including nereid worms collected from the field has correlated better with acid extracted, rather than with total copper (Luoma and Bryan, 1982) and best when the sum of the exchangeable, carbonate and easily reducible phases of copper are expressed as a fraction of the reducible iron. One study (Bryan and Gibbs, 1983) also indicates the probable relevance of the exchangeable cation phase, rather than other phases of copper, in determining the presence or absence of a deposit-feeding bivalve mollusc under field conditions.

Under laboratory conditions, the presence of organisms in sediments can lead to an increase in the proportion of copper in the more biologically available phases and to an increase in concentration in the overlying water (Krantzberg and Stokes, 1981; Malueg **et al**,. 1983) which, in some cases, can account for its toxicity to free-swimming organisms.

It is notable that, in many of the studies reviewed here, soluble copper in the overlying water was not measured. This applies to more than a score of studies involving invertebrates and to half a dozen studies involved with fish. The interpretation of the results of these studies in terms of sediment concentrations must, therefore, remain equivocal.

5.2. **Uptake of copper**

Many animals show increased concentrations of copper in their tissues in the presence of enhanced concentrations of copper in sediments. The relation between the logarithms of these two variables usually has a slope of less than unity, especially at relatively low environmental concentrations (e.g. Hall and Merlini, 1979a; 1979b), indicating the likely presence of asymptotic low concentrations at the low end of the range of sediment concentrations (Bryan and Hummerstone, 1971; Bryan and Gibbs, 1983; Amiard **et al.**, 1987).

The uptake of copper by **Asellus** appeared to be associated with copper in the water, whereas the uptake by a leech and oligochaetes appeared to be related to copper in the sediment (Eyres & Pugh-Thomas, 1978).

The relationship between the logarithm of concentration of copper in tissues and log concentration in sediments may be close to unity for some plants (Bryan and Gibbs, 1983).

5.3. **Toxicity of copper**

Laboratory tests show that copper in sediments may not be harmful at concentrations up to 131 mg Cu/kg (for the development and survival of the amphipod **Capitella capitata**) or even up to 581 mg/Cu/kg (for the short-term survival of the amphipod **Rhopxynius abronius.**

Concentrations in excess of 91 mg Cu/kg have been associated with adverse effects on the survival and reproduction of benthic organisms but in many cases the interpretation of such results is equivocal because other factors could have been involved. However, abnormal surfacing behaviour of **Nereis** transferred to sediment containing 3020 mg/Cu/kg (Bryan and Hummerstone, 1971) was associated with a body burden of 200 mg Cu/kg, which is close to that (220 mg Cu/kg) found in specimens killed in the presence of copper.

In several studies, toxicity does not appear to be associated with soluble copper in the overlying water (Bryan & Gibbs, 1983; Sandler, 1984; and Bonfonte **et al.**, 1986) or with copper in the interstitial water (Bryan & Hummerstone, 1971). In others, the causal factor appears to be copper in the supernatant water (Malueg **et al.**, 1984a, Malueg **et al.**, 1984b; Cairns **et al.**, 1984).

Sublethal effects have been observed on the enzymes of fish kept in water overlying sediments containing copper in excess of 138 mg Cu/kg (Xie **et al.**, 1986), on the chromosomes of blood cells at concentrations in excess of 298 mg Cu/kg (Ou **et al.**, 1986) and in causing nuclear anomalies at concentrations greater than 618 mg Cu/kg (Chen **et al.**, 1986) but it is not known whether and to what extent such effects are attributable to aqueous concentrations or whether they are ecologically damaging.

5.4. **Effects on populations**

A number of studies has been made of the association between various characteristics of animal populations in the field and concentrations of total copper in sediments. They are summarised in Figs. 1 & 2 for diversity in fresh and saline water, respectively, and in Figs. 3 & 4 for abundance in these two media, respectively. The lines include some which are drawn between only two observational points and may or may not be statistically significant, as well as others which represent a large number of observations and are significant, as indicated in Section 2.2.2. In general, both diversity and abundance are reduced with increase in concentration of copper in sediment. Excluded from these figures are data where factors other than copper in sediment are likely to have been involved (Norris, 1978; Halcrow **et al.**, 1973; Long & Chapman, 1955; Tsai **et al.**, 1979; Swartz **et al.**, 1982; Wright, 1987) and where copper in the overlying water appears to be the causal agent.

5.5. Adaptation to copper

Adaptation of some organisms to high concentrations of copper in sediment has been shown by Bryan & Gibbs (1983) working on the Fal estuary and by others, by tests both in sediments and in solutions containing copper. The differences in sensitivity are between 1.6- and 2.8-fold in terms of aqueous concentrat-ions. The subject has been recently reviewed by Klerks & Weis (1987) who point out that evidence for species failing to adapt is scarce, simply because most studies have compared the resistance of populations surviving in a polluted environment with that of the same species elsewhere, whereas evidence for the failure to adapt is supported by the results of selection experiments and the often repeated reduction in diversity found in polluted environments.

Where adaptation to copper has been demonstrated there is good evidence that, in the case of bacteria and algae, it has a genetic component which is to be expected in view of the relativley short generation times of these groups. The same is not necessarily also true of other groups, including invertebrates and fish with longer life histories, although some physiological adaptation to copper may occur on exposure to sub-lethal concentrations of copper.

Fig. 1. Summary of the relation between diversity of invertebrates (expressed as a percentage of the value extrapolated at 10 mg Cu/kg in the sediment) and copper in sediment in fresh water. Lines indicate, from the upper to the lower:
1, number of taxa and diversity index H; 2, number of species in top 75% and diversity index H; 3, number of taxa; 4, number of species in top 75%; 5, number of taxa; 6, proportion of chironomids (Malueg **et al.**, 1984a and 1984b); 9, number of species (Eyres, 1976; Eyres & Pugh-Thomas, 1978).

Fig. 2. Summary of the relation between diversity of invertebrates (expressed as a percentage of the value extrapolated at 10 mg Cu/kg in the sediment) and copper in sediment in saline water. Lines indicate, from the upper to the lower:
1 and 2, diversity index H (from Powell, 1987); 3, number of species (from Rygg, 1985); 4, Shannon Weaver Index (Oyenekan, 1983).

Fig. 3. Summary of the relation between abundance of invertebrates (expressed as a percentage of the value extrapolated at 10 mg Cu/kg in the sediment) and copper in sediment in fresh water. Lines indicate, from the upper to the lower;
1 and 3, number/m^2 (Malueg **et al.**, 1984a and 1984b); 2 and 5, average abundance of all species (Eyres, 1975; Eyres & Pugh-Thomas, 1978); 4 and 6, g/m^2 (Malueg **et al.**, 1984b); 7, number/m^2 (Hall & Merlini, 1979a and 1979b); 8, mg/m^2 (Kraft, 1979).

Fig. 4. Summary of relation between abundance or production of invertebrates (expressed as a percentage of the value extrapolated at 10 mg Cu/kg in the sediment) and copper in sediment in saline water. Lines indicate, from the upper to the lower:
1 and 3, g/m^2 (from Powell, 1987); 2, number/site of the common species; 4, number/site of the rare species (from Bryan & Gibbs, 1983). 5, g/m^2/year (Oyenekan, 1983).

6. REFERENCES

Alabaster, J. S. (1982) **Water Quality Criteria for Freshwater Fish.** Butterworths for FAO, 2nd Ed. 361pp.

Amiard, J. C., Amiard-Triquet, C., Bertlet, B, & Metayer, C. (1987) Comparative study of the patterns of bioaccumulation of essential (Cu, Zn) and non-essential (Cd, Pb) trace metals in various estuarine and coastal organisms. **J. exp. Mar. Biol. Ecol., 106**: 73-89

Anon (1983) Research Report on Heavy Metals in Fish, Shellfish, Aquatic Plants and Sediments in Lake Biwa, 1975-1978. 34pp. Shiga Prefectural Institute of Public Health and Environmental Science (In Japanese)

Batley, G. E. (1987) Heavy metal speciation in water, sediments and biota from Lake Macquarie, New South Wales. **Aust. J. Mar. Freshw. Res., 38**: 591-606

Bonforte, G., Guzzi, L., Martinotti, W. & Quierazza, G. (1986) Identification and choice of a biological indicator for the study of the contamination of a river environment by heavy metals. **Chemistry in Ecology, 2**: 199-204

Boyer, H. (11982) Trace elements in the water, sediments and fish of the upper Mississippi river, Twin Cities Metropolitan Area. Chapter 9: 195-230. In **Contaminants in the Upper Mississippi River.** Proc. 15th Annual Meeting of the Mississippi River Research Consortium. eds. J. G. Weiner, R. V. Anderson & D. R. McConville. Butterworths. An Ann Arbor Science Book. 368 pp.

Brown, B. E. (1977) Effects of mine drainage on the river Hayle, Corneall. A) Factors affecting concentrations of copper, zinc and iron in water, sedimemnts and dominant invertebrate fauna. **Hydrobiologia, 52**: (2-3): 221-233

Bryan, G. W. & Hummerstone, L.G. (1971) Adaptation of the polychaete **Nereis diversicolor** to estuarine sediments containing high concentrations of heavy metals. I. General observations and adaptation to copper. **J. Mar. biol. Assn., UK, 51**: 845-863

Bryan, G. W. & Gibbs, P. E. (1983) Heavy metals in the Fal estuary, Cornwall: a study of long-term contamination by mining wastes and its effects on estuarine organisms. Occasional Publications No. 2. March, 1983. Marine Biological Association. 111pp.

Buhl, K. J. & McConville, D. R. (1982) Heavy metal accumulation in selected sessile components of Fountain City Bay, Pool 5A of the Upper Mississippi river. Chapter 8: 171-194. In **Contaminants in the Upper Mississippi River.** Proc. 15th Annual Meeting of the Mississippi River Research Consortium. eds. J. G. Weiner, R. V. Anderson & D. R. McComville. Butterworths. An Ann Arbor Science Book. 368 pp.

Cairns, M. A., Nebeker, A. V., Gakstatter, J. H. & Griffis, W. L. (1984) Toxicity of copper-spiked sediments to freshwater invertebrates.

Environ. Toxicol. Chem., 3 (3): 435-445

Campbell, P. G. C., Lewis, A. G., Chapman, P. M., Crowder, A. A., Fletcher, W. K., Imber, B., Luoma, S. N., Stokes, P. M. & Winfrey, M. (1988) Biologically available metals in sediments. Publication No. NRCC 27694, National Research Council of Canada, Ontario. 298 pp.

Chapman, P. M., Churchill, L. M., Thomson, P. A. & Michnowsky, E (1979) Heavy metal studies with oligochaetes. In **1st Int. Symp. Aquatic Oligochete Biology**. Eds. R. D. Brinkhurst & D. G. Cook. Plenum Press, 477-502

Chapman, P. M. & Fink, R. (1984) Effects of Pugebt Sound sediments and their elutriates on the life cycle of **Capitella capitata. Bull. Environ. Contam. Toxicol. 33**: 451-459

Chen, Y. Zou, L., Peng, M., Han, F., Liv, V., Li, B. & Chen, C. (1986) Effect of heavy metal pollution in sediments on cytogenetic damage to three kinds of fish. **Hunan Shiftan Daxue Xuebao, Ziran Kexueban, 9** (2, Suppl.); 85-91 (in Chinese)

Diks, D. M. & Allen, H. E. (1983) Correlation of copper distribution in a freshwater-sediment system to bioavailability. **Bull. Environm. Contam. Toxicol., 30**: 37-43

Dixit, S. S & Witcomb, D. (1983) Heavy metal burden in water, substrate and macroinvertebrate body tissue of a polluted River Irwell (England). **Environ. Pollut. Series B., 6**: 161-172

Eyres, J. P. (1976) Studies on the macroinvertebrates fauna of the Irwell, a polluted river. Ph.D. thesis. University of Salford, England. 285 pp.

Eyres, J. P. & Pugh-Thomas, M (1978) Heavy metal pollution of the river Irwell (Lancashire, UK) demonstrated by analysis of substrate materials and macroinvertebrate tissue. **Environ. Pollut.**, (16): 129-136

Greichus, Y. A., Greichus, A., Amman, B. D., Call, D. J., Hamman, D. C. D. & Pott, R. M. (1977) Insecticides, polychlorinated biphenyls and metals in African lake ecosystems. I Haartbeespoort Dam, Transvaal and Voelvei Dam, Cape Province, Republic of South Africa. **Arch. Environ, Comtam. Toxicol. 6**: 371-383

Gunn, A. M., Winnard, D. A. & Hunt, D. T. E. (1988) Trace metal speciation in sediments and soils - an overview from a water industry point of view. 261-294. In **Metal Speciation - Theory, Analysis, and Application.** (eds. J. R. Kramer & H. E. allen). Lewis Publishers.

Hakanson, L. & Uhreberg, R. (1981) Metals in fish and sediments. Naturvardsverket Papport SNVPM 1408, Statens naturvardsverk Vatten-laboratoriet, Uppsala. 215pp. (in Swedish)

Halcrow, W., Mackay, D. W. & Thornton, I. (1973) The distribution of trace metals and fauna in the Firth of Clyde in relation to the disposal of sewage sludge. **J. mar. biol. Ass. U.K. 53**: 721-739

Hall, K. J., & Bindra, K. S. (1979) Geochemistry of selected metals in sediments and factors affecting organism concentration. in **Management and Control of Heavy Metals in the Environment,** London. CEP Consultants: 337-340

Hall, T. M. & Merlini, L. (1979a) Concentration of Cr, Pb, Cu and Mn in some biotic and abiotic components of the benthic ecosystem of the Toce river and Osole Borromee basin (Lake Maggiore, Italy). I. Abiotic components. **Mem. Ist. Ital. Idrobiol., 37**: 1-22

Hall, T. M. & Merlini, L. (1979b) Concentration of Cr, Pb, Cu and Mn in some biotic and abiotic components of the benthic ecosystem of the Toce river and Osole Borromee basin (Lake Maggiore, Italy). II. Oligochaetes and other invertebrates. **Mem. Ist. Ital. Idrobiol., 37**: 23-32

Hall, T. M. & Merlini, L (1979c) An attempt to determine the influence of the gut content on the determination of heavy metals in aquatic oligochaetes. **Mem. Ist. Ital. Idrobiol., 37**: 33-49

Howells, E. J., Howells, M. E. & Alabaster, J. S. (1983) A field investigation of water quality, fish and invertebrates in the Mawddach river system, Wales. **J. Fish Biol., 22**: 447-469

Hunt, D. T. E. (1987) Trace metal speciation and toxicity to aquatic organisms - a review. TR 247, Water Research Centre, UK., 51 pp.

Johnson, M. G. (1987) Trace element loadings to sediments of fourteeen Ontario Lakes and correlations with concentrations in fish. **Can. J. Fish. Aquat. Sci., 44** (1):3-13

Klerks, P. L. & Wais, J. S. (1981) Genetic adaptation to heavy metals in aquatic organisms: a review. **Environ. Pollut. 45**: 173-205

Kraft, K. J. (1979) **Pontopoeia** distribution along the Keweenaw shore of Lake Superior affected by copper tailings. **J. Great Lakes Res., 5** (1): 28-35

Klerks, P. L. & Weis, J. S. (1987) Genetic adaptation to heavy metals in aquatic organisms: a review. **Environ. Pollut., 45**: 173-205

Kraft, K. J. & Sypniewski, R. H. (1981) Effect of sediment copper on the distribution of benthic macroinvertebrates in the Kaweenaw Waterway. **J. Great Lakes Res., 7** (3): 258-263

Krantzberg, G & Stokes, P. M. (1981) The influence of benthic biota on copper speciation and distribution in freshwater-sediment systems. **Wat. Pollut. Res. J. Canad., 16**: 45-58

Lewis, A. G. & Cave, W. R. (1982) The biological importance of copper in oceans and estuaries. **Oceanogr. Mar. biol. Ass. Rev., 20**: 471-695

Long, E. R. & Chapman, P. M. (1985) A sediment quality triad: measures of sediment contamination, toxicology and community composition in Puget Sound. **Mar. Pollut. Bull., 16** (10):405-415

Malueg, K. W., Schuytema, G. S., Gakstatter, J. H. & Krawczyk, D. F. (1983) The effect of **Hexagenia** on **Daphnia** response in sediment toxicity tests. **Environ. Toxicol. Chem.**, 2: 73-82

Malueg, K. W., Schuytema, G. S., Krawczyk, D. F. & Gakstatter, J. H. (1984a) Laboratory sediment toxicity tests, sedimentary chemistry and distribution of benthic macroinvertebrates in sediments from the Keweenaw Waterway, Michigan. **Environ. Toxicol. Chem.**, 3 (2): 233-242

Malueg, K. W., Schuytema, G. S., Gakstatter, J. H. & Krawczyk, D. F. (1984b) Toxicity of sedimants from three metal-contaminated areas. **Environ, Toxicol. Chem., 3: 279-291**

Marks, P. J., Plaskett, D., Potter, I. C. & Braddley, J. S. (1980) Relationship between concentration of heavy metals in muscle tissue and body weight of fish from the Swan-Avon estuary, Western Australia. **Austral. J. Mar. Freshwat. Res.**, **31** (6): 783-793

Millbrink, G. (1987) Biological characteristics of sediments by standard tubificid bioassays. **Hydrobiologia, 155**: 267-275

Namminga, H. & Wilhm, J. (1977) Heavy metals in water, sediments and chironomids. **J. Wat. Pollut. Control Fed., 49**: 1725-1731

Mori, S. & Miura, T. (1980) List of plant and animal species living in lake Biwa. Contribution No. 265 Otsu Hydrobiological Station, Kyoto University, **Series of Biology,** 8: 1-33. In **An Introduction to Limnology of Lake Biwa. (ed. S. Mori). August, 1980. Kyoto.**

Norris, R. H. (1978) The ecological effects of mine effluents on the South Esk river (North East Tasmania). Ph.D Thesis, University of Tasmania, Hobart.

Norris, R. H. & Lake, P. S. (1984) Trace metal concentrations in fish from the South Esk river, northeastern Tasmania, Australia. **Bull. Environ. Contam. & Toxicol.**, **33** (3): 348-354

Ok Tedi Mining Ltd. (1987) Environmental Study Progress Report No. 3. Rept. No. ENV/87-16, Dec., 1987. 170 pp.

Ou, D., Guo, Y, Zhou, Q & Xie, J. (1986) Micronucleus test for studying the toxic effect of copper in the bottom sediment of the Xiang River on fish blood cells. **Hunan Shifan Daxue Xuebao, Ziran Kexueban,** 9 (2): 55-58 (in Chinese)

Oyenekan, J. A. (1983) Production and population dynamics of **Capitella capitata. Arch. Hydrobiol.**, **98** (1): 115-126

Pavlou, S. P. (1987) The use of the equilibrium partioning approach in determining safe levels of contaminants in marine sediments. Chapter 25, 388-412. In **Fate and Effects of Sediment-bound Chemicals in Aquatic Systems,** (eds. K. L. Dickenson, A. W. Maki & W. A. Brungs). Proc. 6th Pellston Workshop, Florissant, Colarado, August 12-17, 1984. Pergamon Press, 447 pp.

Powell, J. H. (1987) The effect of mine tailings disposal on shallow coastal benthos and tropical fish assemblages. Ph.D. Thesis, 5/8/87, University of Queensland, Australia

Prosi, F. & Back, H. (1985) Indicator cells for heavy metal uptake and distribution in organs from selected invertebrate animals. **Heavy Met. Environ., Int. Conf., 5th, 2**: 242-244. Ed., T. D. Lekkas. CEP Consult., Edinburgh, UK.

Rozhanskaya, L. I. & Spirandi, O. B. (1981) Manganese, Zinc and Copper in Hydrobionts in the Danube and the Northwestern Black sea. **Hydrobiol. J., 17** (1): 78-83

Rygg, B. (1985) Effect of sediment copper on benthic fauna. **Mar. Ecol. Prog. Ser., 25**: 83-89

Salomans, W., Kerdijk, H., van Pagee, H., Kiomp, R. & Schreur, A. (1987) Behaviour and impact assessment of heavy metals in estuaries and coastal waters. Delft Hyrdaulics Communication No. 875, 47 pp.

Sandler, H. (1984) Zinc and copper concentrations in benthic invertebrates considered in relation to concentrations in sediments and water in the Bothnian Sea (Northern Baltic). **Finn. Mar. Res.**, (250): 19-32

Tessier, A., Campbell, P. G. C, & Auclair, J. C. (1983) Relationships between trace metal partitioning in sediments and their bioaccumulation in Pelecypods. **Proc. 4th. Int. Conf. Heavy Metals in the Environment.** Heidelburg, CEP Consultants Ltd., (ed), Edinburgh, UK: 1086-1089

Tessier, A., Campell, P. G. C., Auclair, J. C. & Bisson M. (1984) Relationships between the partitioning of trace metals in sediments and their accumulation in the tissues of the freshwater mollusc **Elliptio complanata** in a mining area. **Can. J. Fish Aquat. Sci., 41**: 1463-1472

Tsai, G.-F., Welch, J., Chang, K.-Y. & Shaeffer, J. (1979) Bioassay of Baltimore harbour sediments. **Estuaries, 2**, (3): 141-153

Ward, T. J. & Young, P. C. (1982) Effect of sediment trace metals and particle size on the community structure of epibenthic seagrass fauna near a lead smelter, South Australia. **Mar. Ecol. Prog. Ser., 9**: 137-146

Wiederholm, T Wiederholm, A-M, & Milbrink, G. (1987) Bulk sediment bioassays with five species of freshwater oligochaetes. **Wat. Air & Soil Poll., 36**: 131-154

Wright, D. A. (1987) Dose-related toxicity of copper and cadmium in striped bass larvae from the Chesapeake Bay: field considerations. **Proc. Conf. Coastal & Estuarine Pollution.** Kyushu University, IAWPC/JSWPR., Oct. 19-21, 1987: 42-51

Xie, J., Guo, Y., Zhou, Q., Ou, D., Yang, C. & Lai, Q. (1986) Relation between toxicity of heavy metals, cadmium, lead and copper in sediments and some biochemical alterations in fish. **Hunan Shifan Daxue Xuebao, Ziran Kexueban, 9** (2, Suppl.): 2-14 (in Chinese)