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Appendix A

Macquarie Harbour, Tasmania: Environmental risk assessment of toxic effect

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1 Introduction

As part of the larger program, this report compares the measured copper contamination of Macquarie Harbour with literature values of significant biological impact under marine or estuarine conditions. Due to constraints on available resources, this study should be regarded as preliminary in nature. Many of the data were not critically assessed according to quality criteria prior to acceptance for the risk assessment. The water quality data by their nature can only give 'snapshots' of copper concentrations at the moments of sampling. The biological assessment endpoints selected are also somewhat arbitrary, although they do encompass both lethal and sub-lethal parameters. However, this report will provide a good approximation of the degree of improvement in harbour water quality required to attain acceptable low levels of biological impact.

The aim of this risk assessment was to determine the degree of overlap between the distribution of measured concentrations of copper in water samples from Macquarie Harbour and the distribution of concentrations of copper reported in the literature to have significant effects on biota in marine or estuarine environments. By comparing these distributions, the probabilities of exceeding critical values of copper in the environment relevant to selected endpoints, such as proportional lethality to a prescribed range of species across trophic levels, can be determined within set confidence limits. We can then assess the generic risk that copper, in waters of specific harbour habitats, presents to biota likely to inhabit those regions.

The water quality distributions can also be used for comparisons with site specific ecotoxicological data determined for algae, crustaceans and fish, discussed elsewhere in this report (see section 4.6). As these values will be based on actual Macquarie Harbour waters, they will give a better indication of any synergistic or antagonistic influences on copper toxicity when compared with the predicted effects from the literature.

2 Experimental

Data used in the analyses are available from the authors.

2.1 Macquarie Harbour water monitoring data

Monitoring data for various stations within Macquarie Harbour were provided by Dr Lois Koehnken (DELM). The data comprised a comprehensive but incomplete (for a variety of reasons) set over the period from May 1993–August 1995 at approximately 3 month intervals. The incompleteness is mainly due to poor weather or low water levels at the time of sampling. Quality assurance checks on the electronic transfer of the information indicated that the data arrived safely.

Missing data were ignored. Stations 35 and above were sampled on only one or a few occasions, so these stations were excluded for general consistency between dates.

The data were arranged by analysis type, ie anodic stripping voltammetry-labile copper (ASV), total dissolved copper (hereafter referred to as dissolved) (μg/L) and particulate copper (mg/L or ppm). The ASV labile and dissolved copper values were determined after filtration (0.45 μm), whilst the particulate copper was determined from that retained on the filter. The mid-water samples were taken at the point at which 20‰ salinity was measured in the profile. This represented the middle of the salt wedge boundary between the deeper, more dense, seawater and the shallower, less dense, river water.

Mid-water data were selected for modelling. This selection coincided with the choice of this salinity for the ecotoxicological studies carried out within the project. The use of this water quality was based on the assumption that the marine species to be tested could tolerate these salinity conditions and also that copper input from the fresh waters would be both more concentrated and more soluble, and hence bioavailable, under these conditions than in the deeper, saltier waters. It was thus inferred that these conditions would give the most conservative assessment of copper toxicity in the Harbour.

Within this category, ASV-labile and dissolved copper were selected for distribution analyses. Dissolved copper represents the upper extreme of measurable copper likely to be toxic. On the other hand, ASV-labile would more closely represent the bioavailable fraction, but by its nature this measure will still tend to overestimate toxicity (see following discussion) and as such is still an ecologically conservative estimate.

Total copper, the sum of dissolved and particulate copper, was also derived to compare with the ANZECC (1992) guideline values.

2.2 Biological data

Literature values were taken from this report and the pre-1980 review by Hodson et al (1979). Only criteria specific data were selected, that is, marine or estuarine, LC values for lethal endpoints and lowest or no observable effect concentrations (LOEC, NOEC) or EC values for sub-lethal effects. Algal toxicity data from experimental studies carried out in full nutrient media, containing compounds that absorb or complex copper, reduce copper toxicity and thus underestimate its effect (Stauber pers comm). These data were therefore excluded. Given the resource constraints on the study, no other quality criteria, such as listed in Emans et al (1993), were applied to reject literature data. Identical data from both review sources were included once only.

The data were arranged by broad taxonomic group, ie algae, crustaceans, molluscs, and a few other smaller invertebrate groups, fish, and combinations of marine invertebrates and all marine taxa. The data within each category were separated into lethal (LD50 and LC50) and sub-lethal (EC50, LOEC and NOEC) criteria. In some categories not every criterion was available.

2.3 Statistical analysis

Preliminary observation showed that the water concentrations and subsets of the biological effect data were biased towards higher copper concentrations. In some cases this was extreme. Because of this, the data were assumed to be log-normally distributed and geometric means and standard deviations were derived. This form of distribution is typical for data of this nature (eg Kooijman 1987). Probability distribution functions were generated using these statistics within the STATISTICA software package (Statsoft Inc 1994). The goodness of fit of each derived log-normal distribution was determined using the Kolmogorov-Smirnov one sample test or the Chi-Squared test (Steel & Torrie 1981) at a significance level of 5%. The extreme high values mentioned earlier did not allow an adequate fit to the log-normal model. Thus, these values, which can be considered as outliers, were excluded in order to achieve statistically significant goodness of fit for the biota distributions. This action will make the assessed risk more conservative as the species most tolerant of copper pollution have been excluded in favour of more sensitive taxa.

Assuming that 5% of the representative population could be affected (ie a protection level of 95%), the critical hazardous copper concentrations (HC5%) for each of the subsets of biota distributions were derived (Wagner & Lokke 1991). The 95% and 50% confidence intervals around these estimates were also determined as per Aldenberg & Slob (1993). These values were then imposed on the distributions generated for the water sample copper concentrations (ASV and dissolved) to determine the prevailing probability of exceeding the critical water concentrations and also the degree by which water concentrations would need to be reduced in order to achieve the nominated degree of protection.

3 Results and discussion

3.1 Copper water concentrations

The selected water concentrations were observed for any seasonal and other temporal trends in their maximum, minimum and average values at stations for each sampling period (figs A3.1 a, b and c). Despite the occurrence of occasional high values, that may reflect sediment disturbance or increased pollutant inflow from the King River due to storm activity, there were no persistent patterns over the period of monitoring. These observations imply that copper concentrations, in this specific compartment of the areas affected by pollution from Mt Lyell, are currently relatively constant. On this basis, all further comparisons in this report used data combined from all sampling times.

3.2 Comparison with water quality guidelines

Figure A3.2 shows the degree of overlap between measured Macquarie Harbour copper concentrations and the ANZECC (1992) guideline values of total copper (dissolved plus particulate) for the protection of marine ecosystem health. None of the measured total copper concentrations were less than the guideline value of 5 ppb (0.7 on the log10 scale) which is commonly taken as the default regulatory limit. Even dissolved copper (the typical measure of environmental copper concentrations in water) and ASV-labile copper (a value more closely approximating bioavailable concentrations) were in excess of the guideline value most of the time. More than 95% of the measured dissolved copper values and 75% of the ASV-labile values were greater than the guideline at all times.

Total copper is not a good measure of environmental hazard as most of the measured metal is not biologically available and as such will not directly contribute to toxic effect. Indirect contribution is possible depending upon the degree to which the particle associated copper can be mobilised into a bioavailable form. Exceptions to this generalisation include toxicity from particulate copper to members of the ecological community that are filter feeders, detritivors that ingest particles containing copper, and plants that use the copper bearing particulates as a nutrient substrate. These exposure pathways can be especially significant if the affected taxa include keystone species.

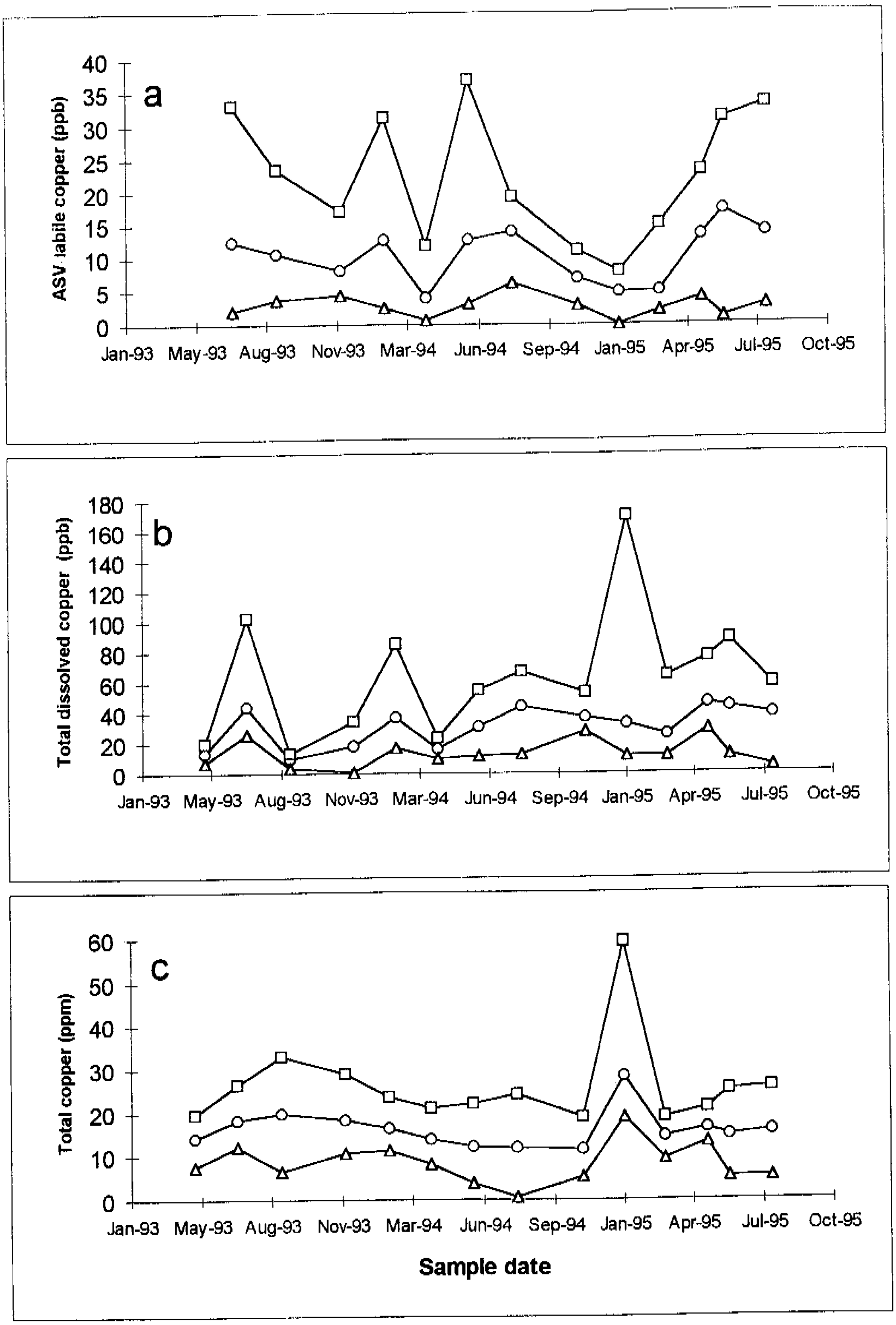

Figure A3.1 Maximum (□), average (O) and minimum (Δ) copper concentrations in mid-salinity Macquarie Harbour waters at each sampling period as measured by: a) anodic stripping voltammetry-labile copper; b) total dissolved copper (0.45 μm) (both in μg/L); and c) total copper (dissolved plus filterable) (mg/L)

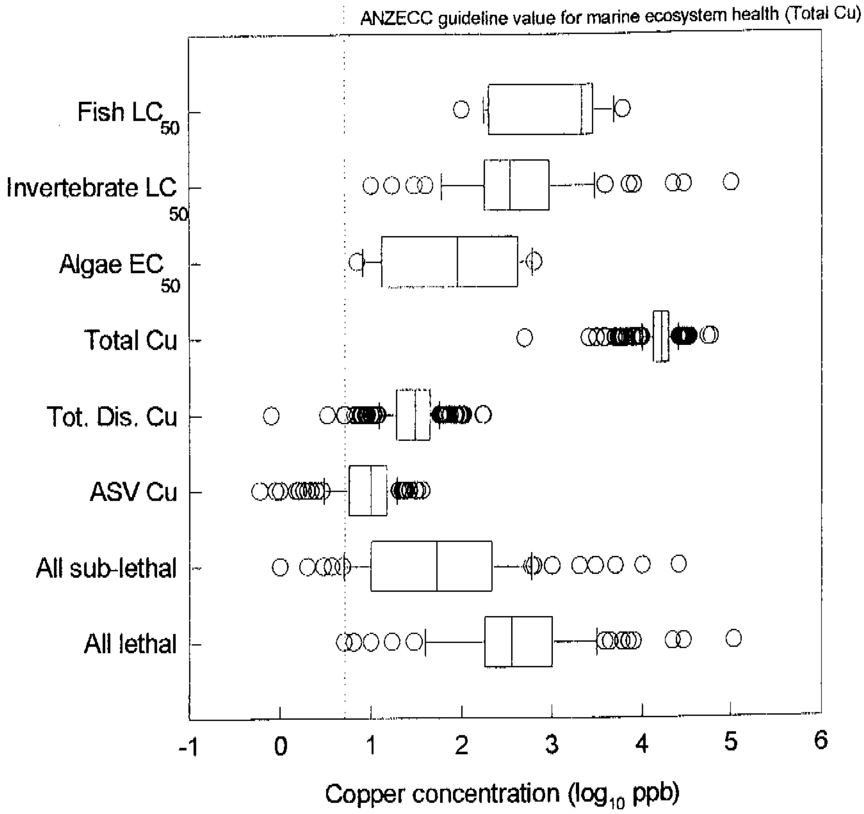

Figure A3.2 Box plots of measured copper concentrations at mid-salinity depths of selected Macquarie Harbour sampling stations (see text) and sub-sets of raw ecotoxicity data (lethal and sub-lethal) from the literature in relation to the ANZECC guideline copper concentration for marine ecosystem health (dotted line). The boxes extend from the 25th–75th percentiles with the median as a mid-line. The capped bars indicate the 10th and 90th percentiles and symbols indicate data outside these values.

3.3 Biological data

It is generically assumed that the concentrations for each of the biological endpoints used in the data sorting will decrease in the order LC50>LD50>EC50≥LOEC>NOEC. Chronic NOECs were found to be 10–30 times lower than acute median lethal values on average by Hendricks (1995) when studying organic toxicants. This general pattern could be observed in the raw data of our current study, particularly where results for a single species or within closely related taxa were examined. However, this was not always found to be the case as some of the observed sub-lethal criteria were less sensitive than others and there were wide ranging degrees of tolerance between species. That is, some very tolerant organisms showed no or low observed response to very high concentrations of copper (high NOEC/LOEC) whilst some extremely sensitive organisms died at low concentrations or exposures (low LC50, LD50).

In fig A3.2 the measured copper concentrations in Macquarie Harbour waters are compared with sub-sets from the literature data indicating the biological effect of copper. Both lethal and sub-lethal parameters are represented. The plots of All lethal and All sub-lethal data include information in addition to that given for the sub-sets at the top of the page.

The available literature data cover several trophic levels. The information density varies between these levels but the discrepancies are minor. Also, the biological effects within any category occur over orders of magnitude differences in copper concentrations. From these observations it is apparent that the data have provided a representative spread of effect levels for both sensitive and insensitive species across most trophic levels and, as such, they provide a reasonable basis for ecosystem scale assessment.

The boxplots representing all lethal and sub-lethal data show a substantial overlap (fig A3.2). However, sub-lethal effects may be seen to generically occur at copper concentrations an order of magnitude lower than those observed for lethal effects.

The probability distribution functions of combined taxa lethality data (LC50 and LD50 values) and sub-lethality data (EC50, LOEC and NOEC values) are shown in figs A3.3a and b respectively. The most sensitive comprehensive subset, algal EC50 data, could not be adequately fitted by a log-normal model.

From the raw data, the copper concentrations likely to be hazardous to 5 and 10% of the biota at the given endpoint are given in table A3.1. Also given are the parameters derived from the fitted distributions. These are the HC5% and the lower limits of the 50% and 95% uncertainty, or confidence, ranges about the critical value.

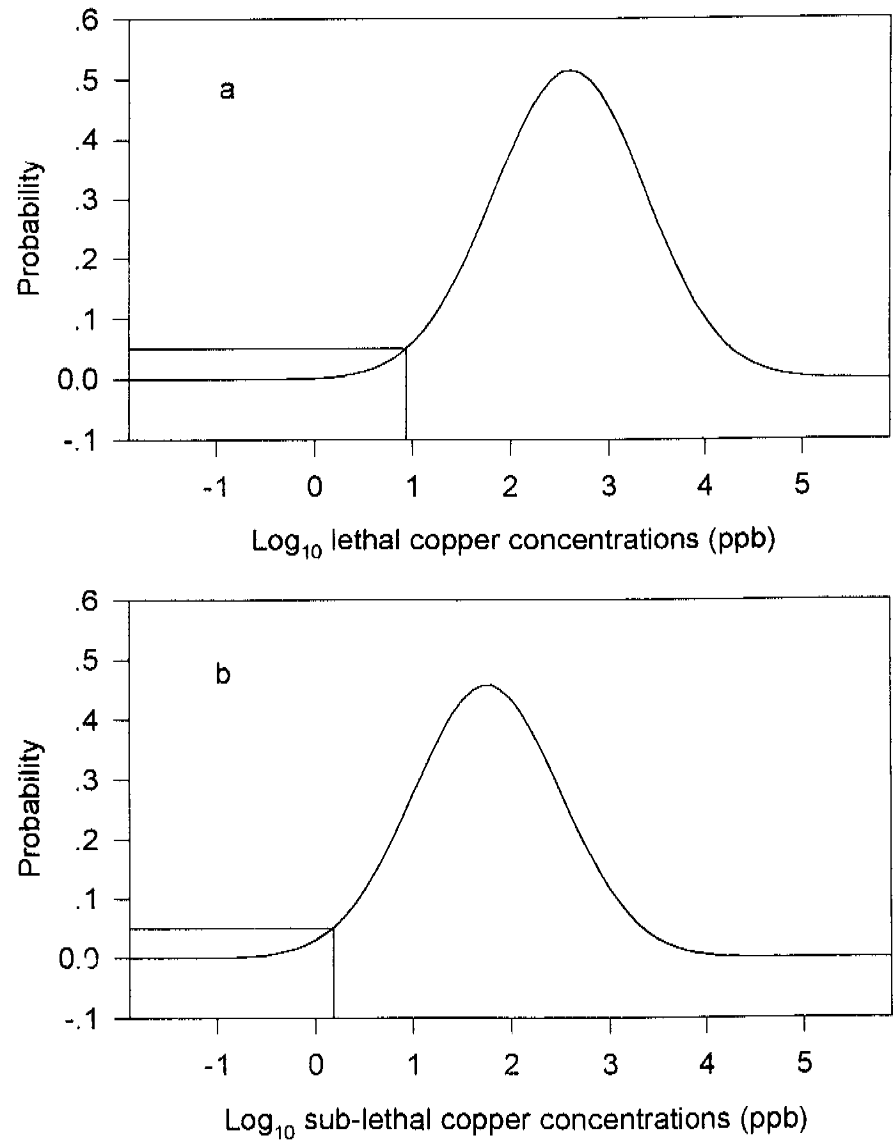

Figure A3.3 Probability distribution functions of copper toxicity data for a) lethal and b) sub-lethal end-points taken from the literature. Extreme (high) values were excluded to allow statistically adequate fit of the distributions. The intercepts indicate the copper concentrations below which only 5% of species are predicted to show a response.

Table A3.1 Critical values of copper concentrations (ppb) that have lethal and sub-lethal effects on biota. Outliers were high values which were removed from the data sets to allow for statistically adequate model fitting.

		Raw data			Fitted distribution	
Taxonomic group	Criteria	5%	10%	$HC_{5\%}$	50% conf. value	95% conf. value
All	lethal	30	60			
All (- outliers)	lethal	17	40	21.1	20.8	9.4
All	sub-lethal	4.9	5			
All (- outliers)	sub-lethal	3.7	5	2.1	2.1	0.9
algae	sub-lethal	15	15			
invertebrates	lethal	17	40	23	21	5.1
fish	lethal	100	200	93.8	84.9	18.1

3.4 Comparison of the water and biota distributions

Predominantly the literature data refer to soluble or dissolved copper concentrations, particularly when dealing with determination of lethal endpoints. Hence total copper concentrations (dissolved + particulate) provide a poor basis for comparison. Field data in particular refer mainly to dissolved copper concentrations. Experimental data are generally concerned with ionic copper species and therefore more closely correspond to the ASV-labile values.

Thus, for comparison of likely toxic effect, dissolved copper will give the upper limit to possibly toxic copper concentrations in Macquarie Harbour. However, Macquarie Harbour waters are known to have a very high complexation capacity, predominantly from the levels of organics input from the surrounding freshwater catchments. From this, it is reasonable to refer to the ASV-labile copper distribution for a more realistic appraisal of ecological risk. This assessment will still be conservative as the copper measured as ASV-labile will include species such as carbonates that are non-toxic (Hunt 1987) and copper that is moderately bound to some organic ligands within the water column (Batley pers comm). These components of the measured copper are not considered to be biologically available. The cumulative probability distributions of ASV-labile and dissolved copper in Macquarie Harbour mid-salinity water samples are shown in figs 3.4a and b respectively.

Using the 5% value in the raw data across all species (less outliers) for comparison with the distributions derived from the monitored copper concentrations in Macquarie Harbour, it can be seen that the current probability of exceeding the lethal critical concentration is 0.76 based on the dissolved copper and 0.19 based on the ASV-labile copper. The lower 50% confidence interval of the HC5%, based on the distribution with outliers removed, is less restrictive. The likelihood of exceedence in these cases reduces to 0.66 and 0.12 for the two measures of copper concentration respectively.

The sub-lethal HC5% lower 50% confidence limit, derived excluding outliers, is exceeded with a probability of 0.98 (almost all the time) based on the ASV-labile distribution and of approximately 1 (ie at all times) using the dissolved copper. The 5% point in the raw data is exceeded with a probability of 0.90 and 1.00 by the two measured copper distributions respectively. If Macquarie Harbour is assumed to have similar proportions of copper in biologically available forms to waters tested in the literature then the 0.90 probability concentration of total dissolved copper in Macquarie Harbour would need to be reduced by a factor of approximately 30 to achieve adequate protection based solely on this criteria without application factors.

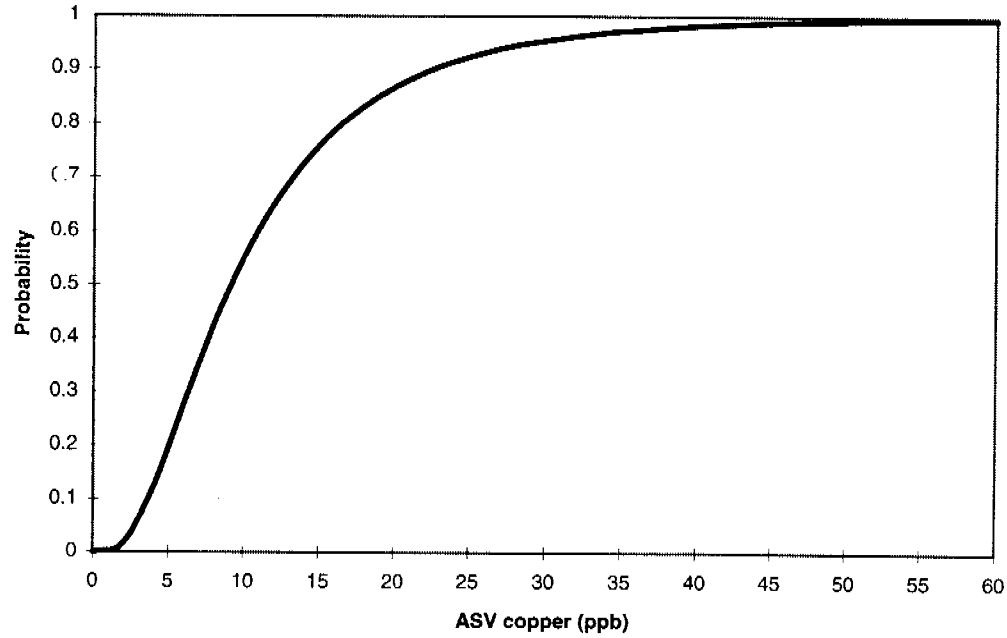

Figure A3.4a Cumulative probability distribution of ASV-labile copper in mid-salinity waters of Macquarie Harbour. The curve indicates the probability of measuring a concentration less than any specified value, based on monitoring data.

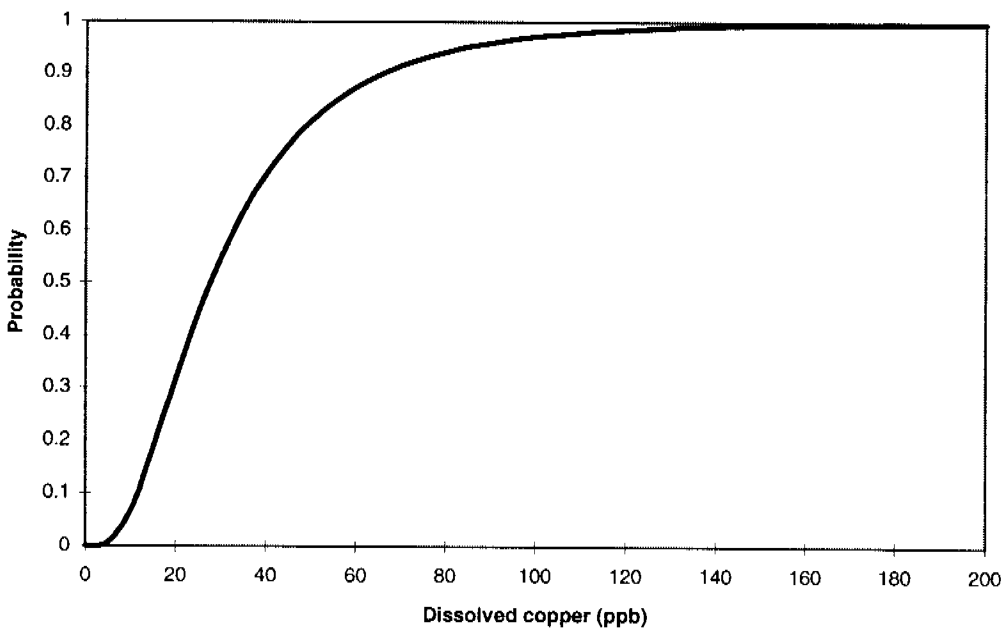

Figure A3.4b Cumulative probability distribution of total dissolved copper in mid-salinity waters of Macquarie Harbour. The curve indicates the probability of measuring a concentration less than any specified value, based on monitoring data.

The most sensitive 5% of algae are currently exposed to sub-lethal concentrations with a probability of 0.24 based on the raw data and ASV-labile water concentrations. To protect 95% of the algal species 90% of the time a reduction in ASV-labile copper concentrations by a factor of approximately 2 is required.

When making assessments of the degree of reduction in copper required to achieve this type of end-point, the degree of dissolution from sediment must also be taken into account in addition to reductions in input via the King River.

The lethal parameters for invertebrates and fish are included in table A3.1. The raw data are also shown in fig 3.2. It can be seen that invertebrates are relatively comparable to the generic lethal data and, as such, sub-sets of crustacean data may be a reasonable surrogate for more extensive biological data in other comparisons. The fish data are relatively insensitive when compared with the endpoints derived for combined taxa lethal data or any sub-lethal parameters.

3.5 Factors that affect the relative degree of safety implicit in the risk analysis

The following factors provide inherent conservatism (safety) to the risk assessment:

Use of measured values that overestimate the biologically available copper water concentrations.

The labile copper measured by ASV as well as the dissolved concentrations include some chemical species that are less, or not, bioavailable. These chemical species are less toxic than the free ionic form of copper.

Use of mid-salinity water quality data maximised the measured copper concentration in the marine waters of Macquarie Harbour and, hence, the perceived risk to marine organisms.

Use of all water measurements rather than averages for any period.

There is little likelihood of all sites being simultaneously contaminated to high levels. The average values at any particular sampling period (fig A3.1) indicate a distribution about a factor of two lower than the maximum values measured at the same time. This provides an additional safety factor in the assessment given that motile species will be at an advantage in that they may avoid or move out of highly contaminated zones to other depths or locations, and widely distributed species will be able to recolonise affected areas.

The data from the literature studies represent effects to proportions of individuals within populations rather than to populations as a whole.

Higher concentrations would be required to affect all individuals within the tested populations.

Probable bias in the literature data towards sensitive species.

Research workers will tend to select species that are most likely to show a significant response to any test. Sensitive species are also likely to have been chosen for testing or monitoring on the basis of their relative response in field surveys. In addition, the exclusion of extremely tolerant species from the biota data to achieve normal distributions has biased the data towards more sensitive taxa.

The use of laboratory studies to estimate environmental risk.

Most controlled laboratory studies constrain the experimental parameters to minimise variability. Many natural water quality parameters that reduce toxicity (eg complexation capacity) are thereby excluded from these studies. Hence, this may lead to an overestimate of toxic effect when the results of laboratory studies are applied to natural systems.

The use of the lower limit of the uncertainty estimate of the critical hazardous concentration is inherently conservative.

The likelihood of the occurrence of tolerant populations of species within the Harbour brought about by over a century of natural selection pressure.

The following factors are of unknown significance or could contribute to an estimate of greater risk from copper to biota in Macquarie Harbour:

The magnitude of significant water quality parameters

This study has looked solely at copper concentrations in the mid-salinity habitat of Macquarie Harbour. There has been no specific attempt in this study to address the other habitat parameters that can influence copper toxicity. These include possible synergistic effects from other toxic materials (eg zinc) and antagonistic effects such as complexation by organic ligands or the formation of non-toxic metal species.

The keystone species for ecological sustainability have not been identified.

At present too little is known of the local biological communities, either within Macquarie Harbour or in similar habitats unaffected by the pollution from Mount Lyell. As such the keystone or indicator species have yet to be adequately identified for the overall study. The successful identification and re-occurrence of these species within Macquarie Harbour is certain to be one of the criteria for success of the overall remediation process.

The impact of copper concentrations in the upper water layer habitat of Macquarie Harbour has not been addressed.

Very high levels of copper are present in the less dense river water suspended above the saline wedge within the Harbour. The copper levels are well in excess of the ANZECC guidelines for freshwaters. The impact on euryhaline, migratory or freshwater species could be significant at the measured concentrations. Any assessment of this habitat should include toxicity to water fowl including bioaccumulation pathways.

Bioaccumulation pathways and their associated risk, to other biota or humans, have not been addressed.

Quality criteria have not been applied to the selection of literature data used for the models. Exclusion of data will lead to changes in the probability distributions but the significance of these changes cannot be assessed at present.

Sediment effects

Estimations on the degree of copper concentration reductions required will need to include an assessment of the likely remobilisation of sediment bound copper as well as reductions in riverine input. It must also be recognised that some keystone organisms, environmentally critical to the remediation, may occupy a benthic habitat. As such, these species will be at risk from current and future sedimentary copper.

4 Conclusions

When compared with the ANZECC (1992) water quality guidelines, copper concentrations in Macquarie Harbour waters are too high. This preliminary comparison justifies the need for a more comprehensive risk assessment.

When alternate, less restrictive, criteria are used to compare concentrations of copper in Macquarie Harbour water with literature data on the biological effects of copper in marine systems, the monitored water concentrations still exceed the critical hazard levels using both lethal and sub-lethal endpoints. Based on these more realistic evaluations the prevailing total dissolved copper water concentrations have a probability of 100% of exceeding the sub-lethal critical limit and of 66% of exceeding the critical limit for lethality.

If Macquarie Harbour is assumed to have similar proportions of copper in biologically available forms to waters tested in the literature, then to achieve water concentrations that have an adequately low probability (eg 10%) of exceeding the critical sub-lethal limit across all taxa, a reduction in total dissolved copper water concentrations by a factor of at least 30 would be required. However, the results obtained for Macquarie Harbour waters indicate that the actual toxicity is considerably lower than would be expected from the copper concentrations measured. For algae, important as the autochthonous primary producers of the ecosystem and the most sensitive taxonomic group, the reduction of the ASV-labile copper concentration in water that is required to protect 95% of species is an approximate factor of only 2 based on the available literature.

It must be stressed that the risk assessment is reasonably conservative for a variety of reasons (see 3.5). Predominant amongst these are that a relatively low risk of hazard (5%) was chosen as the critical assessment level; that sub-lethal endpoints were considered; and that bioavailable copper was over estimated. Use of toxicity data from bioassays carried out in Macquarie Harbour waters should enable better prediction of the copper concentrations able to be tolerated by aquatic organisms in this harbour.

Factors that may contribute to risk but which have not been addressed in this study include the possible presence of metals such as zinc that act synergistically with copper. It is also imperative that a biological survey be undertaken to identify, if possible, potential keystone species in equivalent environments with particular note of any filter feeders or benthic species that may be affected by the high concentration of copper in the Harbour sediment.

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