

Decision-making processes in ecological risk assessment using copper pollution of macquarie harbour from Mt. Lyell, Tasmania, as a case study

J. R. Twining & R. F. Cameron

Australian Nuclear Science and Technology Organisation PMB 1, Menai, 2234

Received March 1997

Key words: Ecological risk assessment, copper, marine, estuarine

Abstract

Ecological risk assessment is increasingly being used to make decisions on the acceptability of industrial processes, as well as on the appropriate approach to take with remediation of contaminated sites. In this approach, the risks and costs must first be determined before decisions can be made.

In principle, the procedure for undertaking an ecological risk assessment for a site with existing contamination is fairly straight forward. Probability distributions are obtained for the concentration of the contaminant of concern and for the biological and/or structural impacts likely to occur in the affected habitat. The degree of overlap between these distributions determines the risk from the contaminant to the habitat. With water-borne contamination, the level of assessment can vary from a simple comparison with water quality criteria, through site specific literature surveys, to laboratory and field studies depending on the importance of the environment, the concentration and perceived nature of the contaminant, the resources available, and the likely benefit from the process to be developed.

However, a number of uncertainties make this process more difficult. These include the lack of a standard methodology, availability of appropriate data and agreed definitions of acceptable risk. Thus several arbitrary or considered decisions need to be made before and during such an assessment.

This paper discusses the application of an ecological risk assessment of copper pollution in Macquarie Harbour, Tasmania, using data from long-term monitoring of waters and literature searches on lethal and sub-lethal effects of copper in marine and estuarine environments. This study is part of a much larger program established to determine best methods for the remediation of the Mt. Lyell copper mine site as well as the freshwater and marine habitats downstream. The results of the assessment indicated that there was at present a probability greater than 0.9 of the occurrence of anodic stripping voltametry-labile copper water concentrations harmful to 5% of all species. For total dissolved copper the probability was higher than 0.98. The upper value of total dissolved copper in Macquarie Harbour that encompassed 90% of the probable concentrations would need to be reduced by a factor of approximately 30, without the inclusion of any additional application factors, to achieve (sub-lethal) protection for 95% of species.

Introduction

Ecological risk assessment is increasingly being used to make decisions on the acceptability of industrial activities, as well as on the appropriate approach to take with remediation of contaminated sites. It provides a framework for comparing the ecological effects with the acceptability criteria while including the uncertainty in determination of the risk parameters. Remediation strategies can then be assessed in terms of their poten-

tial for reducing risks as a function of cost. The use of ecological risk in this context is still developing, but the increasing use of risk based decision-making in other areas would imply that it will become increasingly important.

In principle, the assessment process is straightforward. A probability distribution for the concentration of the contaminant of concern is first derived by on-site monitoring or by some assessment of the source terms and dispersion. A distribution is also determined for

the biological and/or structural impacts likely to occur in the affected habitat. The degree of overlap between these distributions determines the risk from the contaminant to the habitat. With water-borne contamination, the level of assessment will increase as we move from simple comparisons with water quality criteria, through site specific literature surveys, to laboratory and field studies. The choice of which comparison to use depends on the importance of the environment, the concentration and perceived nature of the contaminant, the resources available, and the likely benefit from the process to be developed.

However, the process is made more difficult by the lack of key data and the need to incorporate the uncertainties which exist in data, in modelling and in representation of the actual environmental conditions. Some appreciation of the underpinning ecological structure and function of the environment in question must also be available in order to set minimal requirements for remediation. The degree of recovery to and beyond that level will depend on: the extent and severity of pollution; available resources in relation to treatments required and, from that, the *a priori* decisions as to what is adequate or acceptable; the natural resilience of the various systems; and time.

The Case study

Due to the mining of copper for a period in excess of 100 years, heavy pollution has occurred around the mine sites at Queenstown, Tasmania, as well as within the affected habitats downstream in the Queen and King Rivers and Macquarie Harbour (Figure 1). In addition to the problems that have arisen from the extraction and smelting processes of the past, acid rock drainage and consequent leaching of residual copper and other metals from the large waste rock heaps at the site continue to contribute to the presently poor condition of the affected area.

The area has a naturally high rainfall (2500 mm a^{-1}). Dissolved organics, particularly humic substances, persist in the fresh water of the system and give rise to values of 2–7 mg DOC l^{-1} in mid-salinity Harbour waters.

Currently, the Mt Lyell Remediation Research and Demonstration Program is determining the extent of the pollution off site and its severity in terms of ecological impact. As part of the larger program, the aim of this risk assessment is to evaluate the probability of harm to aquatic populations in the marine environment downstream. This will be done by determining 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 similar environments. By comparing these distributions, the probabilities of exceeding critical values of copper in the environment relevant to selected end-points, 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 to compare with site specific ecotoxicological data yet to be determined for algae, crustaceans and fish. 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.

Data and assessment methods

Macquarie harbour water monitoring data

Monitoring data for various stations within Macquarie Harbour were provided by Dr Lois Koehnken of Tasmanian Department of Environment and Land Management in Hobart. 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 was 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 sampled on only one or a few occasions were excluded for general consistency between dates.

The data were arranged by analysis type, i.e. anodic stripping voltametry-labile copper (ASV), total dissolved copper (hereafter referred to as dissolved) ($\mu g\ l^{-1}$ or ppb) and particulate copper ($mg\ l^{-1}$ or ppm). The ASV and dissolved copper values were determined after filtration (0.45 μm), whilst the particulate copper was determined from that retained on the filter. For each station, samples were taken at the surface, at mid-water and immediately above the sediment. The mid-water samples were taken at the point at which 20 ppt salinity was measured in the profile. This repre-

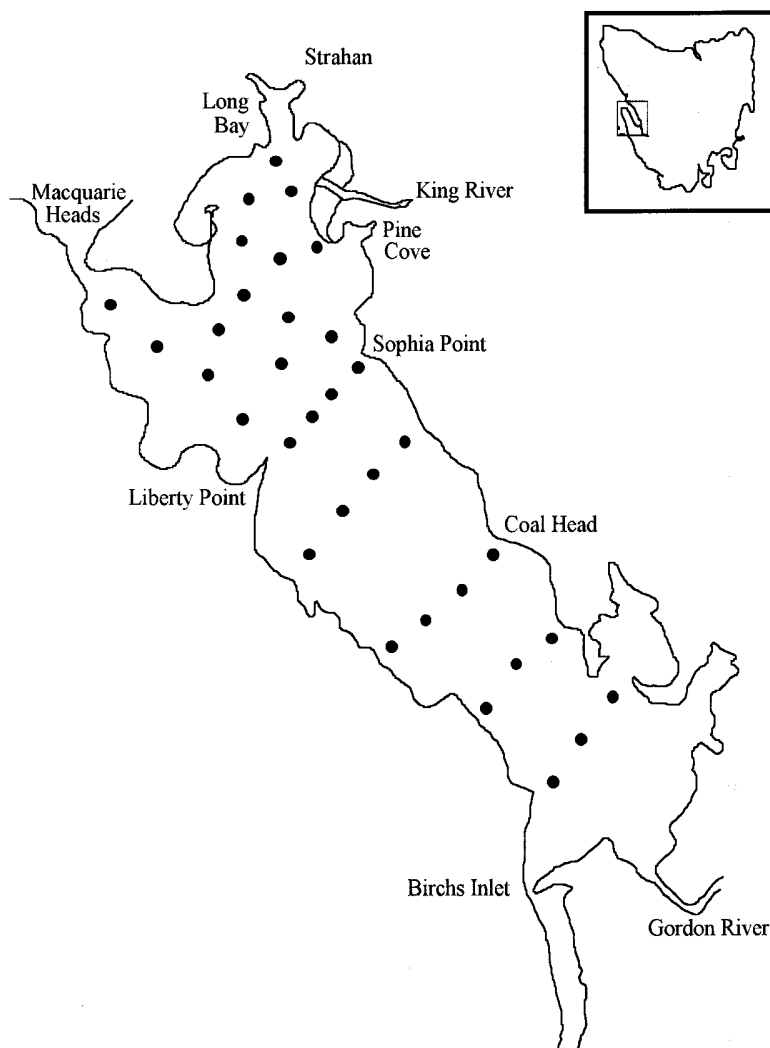


Figure 1. Map of Macquarie Harbour on the west coast of Tasmania, showing regularly monitored water sampling sites.

sented the middle of the salt wedge boundary between the deeper, more dense, sea water 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 assumption was 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 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 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.

Biotic data

Literature values were taken from the recent marine-specific review by Ahsanullah et al. (1995) and the more comprehensive pre-1980 review by Hodson et al. (1979). Only criteria specific data were selected, that is, marine or estuarine, LC or LD values for lethal end-points and Lowest or No Observable Effect Concentrations 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, Fish, and combinations of all Marine Invertebrates and All Marine taxa. Significant variability was encountered within each criterion. For example: exposure periods for experimental tests ranged between 2–720 hours; salinity varied between 5–36 ppt; temperature ranged from 5–35 °C; and the end-points ranged across all life-stages encompassing metabolic activity, physiological and behavioural responses, growth rates and mortality. The data within each category were separated into lethal (LD_{50} and LC_{50}) and sub-lethal (EC_{50} ; LOEC and NOEC) criteria. In some categories not every criterion was available.

Despite the fact that some species were more heavily represented than others and that the endpoints within the different effect categories varied considerably, all individual results were included separately to ensure that the total variability inherent in the data was included. This was to allow for a more accurate uncertainty estimate when calculating the critical values.

Statistical analysis

When relatively large sets of data are available (usually 8 or more sets), it is possible to derive a species sensitivity model from fitting a distribution function to the frequency distributions of the test data and deriving a criterion using a prescribed percentile of that distribution (OECD, 1992). In using this approach, it is assumed that the species have some distribution of sensitivity with a few very sensitive species and many moderately sensitive species. This approach is

not, however, able to account for interactions between species and is based on an assumption that differences in toxicity only arise because of differences in sensitivities between species. In general, the models have been developed to arrive at a concentration which protects 95% of the aquatic genera.

In deriving these models, the major issues are the choice of the distribution, the choice of the protection level and the statistical evaluation of the uncertainties due to the limited number of toxicity data. The former issue relates to the error in fitting the actual data by distributions and the latter to using samples to estimate population parameters.

In deriving values for protection of the ecosystem, there are various approaches in current use. The method of Stephan et al., (1985) estimates a Final Chronic Value (FCV) to protect 95% of the species, based on the geometric means of the species chronic values. A triangular distribution is used to estimate the FCV from the 4 lowest genus means. In the method of Aldenberg and Slob (Aldenberg & Slob, 1993), an extrapolation factor, T, is estimated and used to derive a concentration expected to be harmful to no more than 5% of the community. This method takes into account the uncertainty caused by using estimated parameters to represent a population and is based on the use of a log-logistic distribution. The method of Wagner and Lokke (Wagner & Lokke, 1991) is similar to Aldenberg and Slob in estimating a parameter to protect p% of the community, but these authors base their results on a lognormal distribution.

In comparisons made with the various methods (OECD, 1992), it was noted that:

- the choice of distribution did not have a marked effect on the protection level calculated.
- the level of confidence of the estimate (from 50% to 95%) altered the protection level by around a factor of six. (for relatively small numbers of test results).
- larger differences arose when the number of data were small.
- the use of acute values divided by 100 gave similar results to using the NOEC values divided by a factor of 10.

Thus the choice of a distribution should be determined by the data themselves, especially where larger data sets are available. The distributions differ in how extreme the tailing is at the lower and upper ends. Clearly, a lowest level of zero is a requirement.

In general, the use of chronic values is more appropriate as a protection level, for species exposed to

pollutants over a long period. LC_{50} values are, however, appropriate to use for uncommon exposures of short duration, where some level of mortality would be acceptable. Since large kills may not be acceptable, it may be desirable to use a lower percentage than 50 in the LC criterion. This may be a better approach than application of an arbitrary factor to the LC_{50} value. The difficulty with use of NOEC or LOEC values is that measurement of the effect is more difficult because of the variability in magnitude of the type of effect chosen and the greater variability among individual members of the species.

Most approaches use the 95% level as the appropriate protection level for most species. It is, however, justifiable to use a lower level for distributions of algae and bacteria in consideration of the higher diversity, functional redundancy, highly variable structure and low public concern for these communities. Generally, there is no consensus on what level of confidence should be applied to the protection level with some groups favouring the 95% level and others the 50% value. Those groups favouring the 95% level, calculate the bounds using methods based on random sampling. These can add uncertainty since the data set variability is often systematic rather than random. The US EPA does not have a provision for specifying this level of confidence and hence its methods should be compared with the 50% levels used by others. Because of the emphasis on determining a parameter at the lower end of the data (the 5% level), some censoring of the very high values is also considered appropriate. This will prevent distortion of the 5% level, from either being too high or too low.

In this study, preliminary data analysis 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 (e.g. 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 at 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 (i.e. a protection level of 95%), the critical hazardous copper concentrations ($HC_{5\%}$) 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 (1994). 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.

Results and discussion

Copper water concentrations

The selected water concentration monitoring data were observed for any seasonal and other temporal trends in their maximum, minimum and average values at stations for each sampling period (Figures 2a, 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.

Comparison with water quality guidelines

Figure 3 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 \log_{10} scale) which is commonly taken as the default regulatory limit. Even dissolved copper (the typical measure of environmental copper concentrations in water) and ASV copper (a value more close-

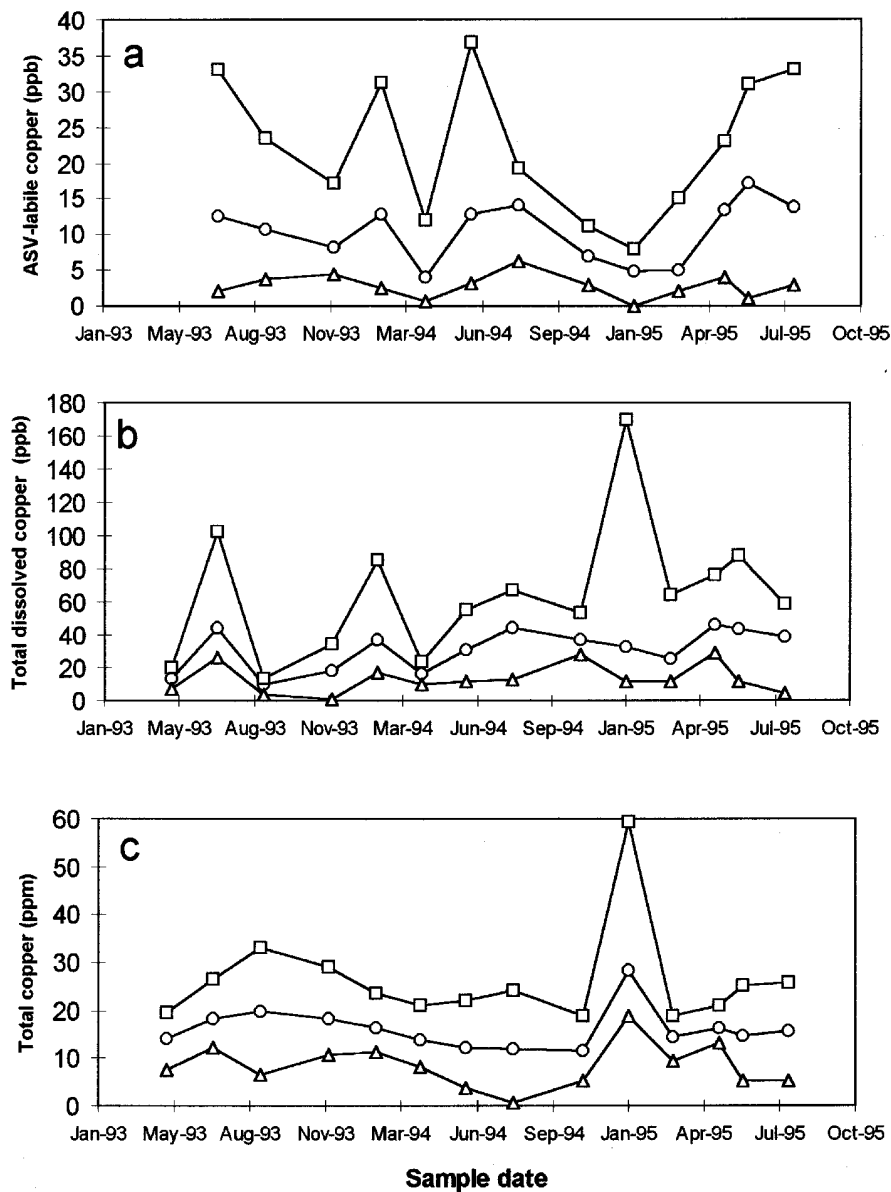


Figure 2. Maximum (\square), average (\circ) and minimum (\triangle) copper concentrations in mid-salinity Macquarie Harbour waters at each sampling period as measured by: (a) anodic stripping voltametry-labile copper; (b) total dissolved copper ($0.45 \mu\text{m}$) (both in $\mu\text{g l}^{-1}$); and (c) total copper (dissolved plus filterable) (mg l^{-1}).

ly 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 values were greater than the guideline at all times.

A reduction in total copper levels within the mid-salinity waters of Macquarie Harbour by 4 orders of

magnitude is required to achieve levels that are beneath the guideline value at least 90% of the time.

However, total Cu 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

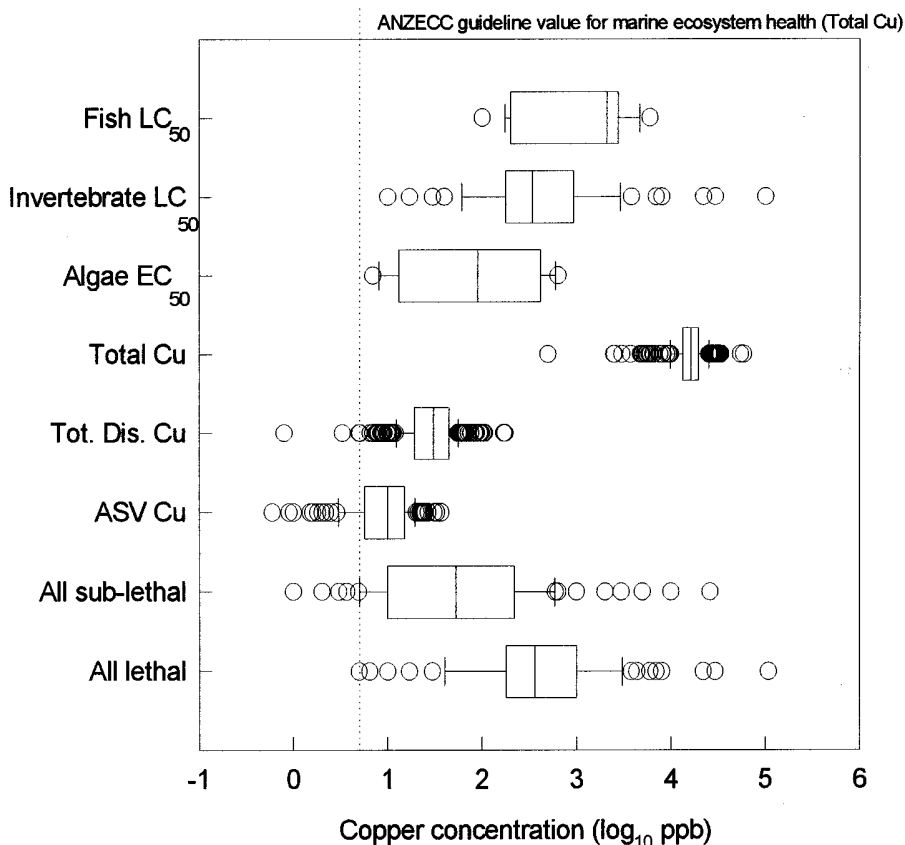


Figure 3. Box plots of measured copper concentrations at mid-salinity depths of selected Macquarie Harbour sampling stations (see text) and sub-sets of raw ecotoxicity data (lethal and sub-lethal) from the literature in relation to the ANZECC guideline copper concentration for marine ecosystem health (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.

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, detritivores 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.

Biological data

It is generally assumed that the concentrations for each of the biological end-points used in the data sorting will decrease in the order $LC_{50} > LD_{50} > EC_{50} \geq LOEC > NOEC$. 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 LC_{50} , LD_{50}).

In Figure 3 the measured copper concentrations in Macquarie Harbour waters are compared with sub-sets from the literature data (Ahsanullah et al., 1995; Hodson et al., 1979) indicating the biological effect of copper. Both acute and chronic, 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. Given the high copper loads in the Harbour at present it is unlikely that any sensitive taxa persist in that environment unless local populations of relatively fecund species have undergone gradual selective adaptation to the copper levels to which they have been exposed since mining began.

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 are providing a reasonable basis for ecosystem scale assessment.

The boxplots representing all lethal and sub-lethal data show a substantial overlap (Figure 3). 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 (LC_{50} and LD_{50} values) and sub-lethality data (EC_{50} , LOEC and NOEC values) are shown in Figures 4a and b respectively. The parameters of these distributions were chosen to give the best 'goodness-of-fit' to the raw data. The most sensitive comprehensive subset, algal EC_{50} 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 end-point are given in Table 1. Also given are the parameters derived from the fitted distributions. These are the $HC_{5\%}$ and the lower limits of the 50% and 95% uncertainty, or confidence, ranges about this critical value.

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 end-points. 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 values.

Thus, for comparison of likely toxic effect, dissolved copper will give the upper limit to possibly toxic

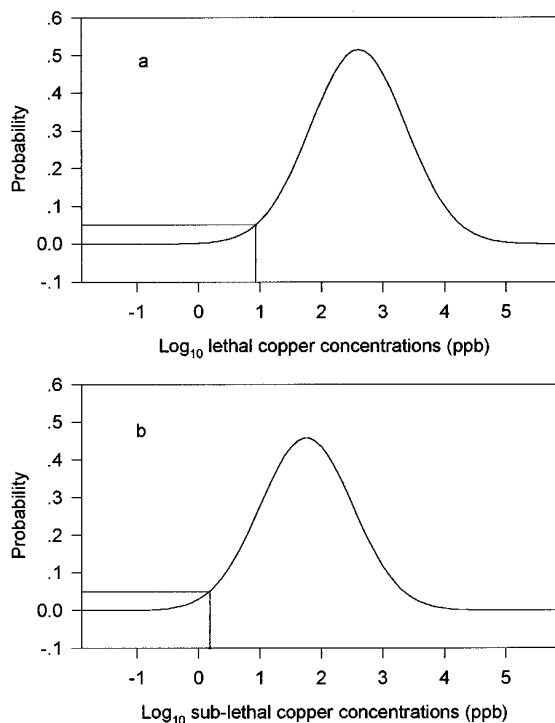


Figure 4. Probability distribution functions of copper toxicity data for (a) lethal and (b) sub-lethal end-points taken from the literature. Extreme (high) values were excluded to allow statistically adequate fit of the distributions. The intercepts indicate the copper concentrations below which only 5% of species are predicted to show a response.

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 fresh water catchments. From this, it is reasonable to refer to the ASV copper distribution for a more realistic appraisal of ecological risk. This assessment will still be conservative as the copper measured by ASV 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 (Battley, pers comm). These components of the measured copper are not considered to be biologically available. The cumulative probability distributions of ASV and dissolved copper in Macquarie Harbour mid-salinity water samples are shown in Figure 5.

In Table 2 are shown the probabilities that the measured concentrations of copper in Macquarie Harbour waters currently exceed the values that would protect 95% of species from lethal or sub-lethal effects. The

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

Taxonomic group	Criteria	Raw data		Fitted distribution		
		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

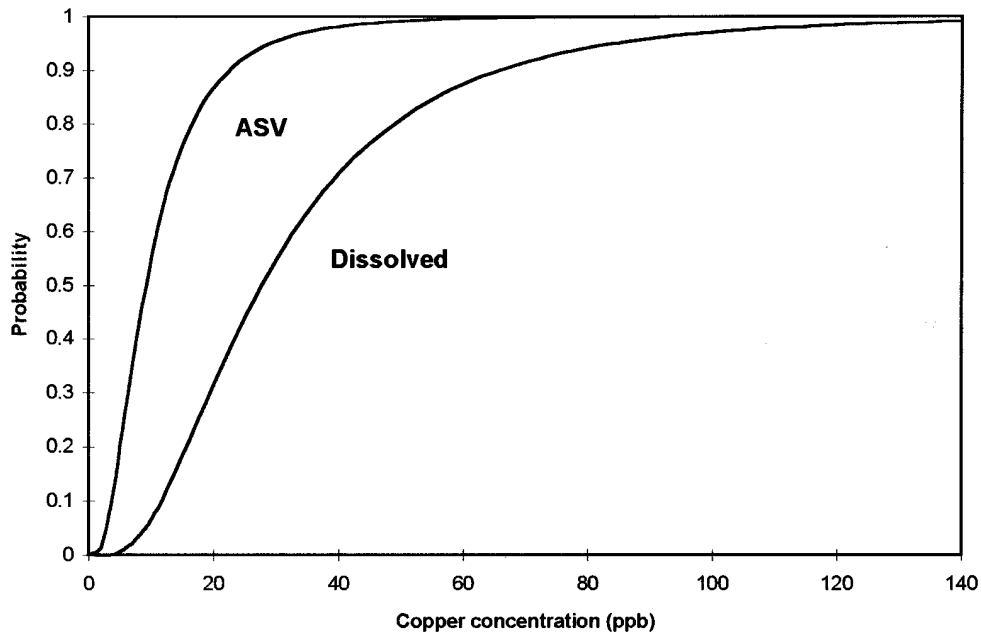


Figure 5. Cumulative probability distributions of ASV-labile and total dissolved copper in mid-salinity waters of Macquarie Harbour. The curves indicate the probability of measuring a concentration less than any specified value, based on monitoring data.

high outliers were excluded from the raw data across all species.

From the sub-lethal values, 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. To protect 95% of the algal species 90% of the time a reduction in ASV 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 1. The raw data are also shown in Figure 3. 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 end-points derived for combined taxa lethal data or any sub-lethal parameters.

Table 2. Current probabilities of exceeding the critical values to protect 95% of species.

Water quality	Lethal Effects		Sub-lethal effects	
	ASV	Diss. Cu	ASV	Diss. Cu
5% value from raw data for all species	0.19	0.760.90	~1.0	
5% value (at 50% confidence level) from fitted distribution for all species	0.12	0.66	0.98	~1.0
5% value for Algae from raw data			0.24	0.82

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

The following decisions and other 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 biota.
- 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 (Figure 2) 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 mobile 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 (e.g. 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. Emans et al. (1993) also found that the Aldenberg & Slob (1993) model based on single-species data, tended to overestimate toxic effect when compared with relevant field multi-species studies.
- 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 additive or 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 Mt 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 fresh waters. The impact on euryhaline, migratory or fresh water 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.

Conclusions

When compared with the ANZECC (1992) water quality guidelines, copper loads in Macquarie Harbour are too high by at least four orders of magnitude. 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 end-points. Based on these more realistic evaluations the prevailing total dissolved copper water concentrations have a probability of close to 100% of exceeding the sub-lethal critical limit and of 66% of exceeding the critical limit for lethality.

To achieve water concentrations that have an adequately low probability (i.e. 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 is required. 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.

The risk assessment is reasonably conservative for a variety of reasons. Predominant amongst these are that a relatively low risk of hazard (5%) was chosen as the critical assessment level; that sub-lethal end-points were considered; and that bioavailable copper was over estimated.

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 could influence the overall toxicity of harbour waters. 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.

Acknowledgments

The authors would like to express their gratitude to Drs Ahsanullah, Stauber and Koehnken for providing access to their data. Mr C. Rehberg helped in data input and sorting. Both he and Mr J. Perera provided some of the figures used in this report.

References

- Ahsanullah, M., T. M. Florence & J. L. Stauber, 1995. Ecotoxicology of copper to marine and brackish water organisms. Report to the Mt Lyell Remediation Research and Development Program (Project 9). CSIRO Inv. Rep. CET/IR402.
- Aldenberg, T. & W. Slob, 1993. Confidence limits for hazardous concentrations based on logistically distributed NOEC toxicity data. *Ecotoxicol. Envir. Safety* 25, 48–63.
- ANZECC, 1992. 'Australian Water Quality Guidelines for Fresh and Marine Waters'. Australian and New Zealand Environment and Conservation Council secretariat. Government Printing Office, Canberra.
- Emans, H. J. B., E. J. van de Plassche, J. H. Canton, P. C. Okkerman & P. M. Sparenburg, 1993. Validation of some extrapolation methods used for effect assessment. *Envir. Toxicol. Chem.* 12: 2139–2154.
- Hendricks, A. J., 1995. Modeling response of species to micro-contaminants: Comparative ecotoxicology by (sub)lethal body burdens as a function of species size and partition ratio of chemicals. *Ecotoxicol. Envir. Safety* 32: 103–130.

- Hodson, P. V., U. Borgmann & H. Shear, 1979. Toxicity of copper to aquatic biota. Ch 11. In Nriagu, J. O. (ed.), 'Copper in the Environment' Pt 2. Health Effects. J. Wiley & Sons, New York.
- Hunt, D. T. E., 1987. Trace metal speciation and toxicity to aquatic organisms: A review. TR 247, Water Research Centre: Environment, Marlow, U.K., 51 pp.
- Kooijman, S. A. L. M., 1987. A safety factor for LC_{50} values allowing for differences in sensitivity between species. *Wat. Res.* 21: 269–276.
- OECD, 1992. Report of the workshop on the extrapolation of laboratory aquatic toxicity data to the real environment. OECD Environmental Monographs No. 59. Organisation for Economic Co-operation and Development. Paris. OCDE/GD (92)169.
- Steel, R. G. D. & J. H. Torrie, 1981. 'Principles and procedures of statistics. A biometrical approach' (2nd ed.). Magraw-Hill International.
- Wagner, C. & H. Lokke, 1991. Estimation of ecotoxicological protection levels from NOEC toxicity data. *Wat. Res.* 25: 1237–1242.
- Statsoft Inc., 1994. STATISTICA for Windows. Release 5. Tulsa, Oklahoma, USA.
- Stephan, C. E., D. I. Mount, D. J. Hanson, J. H. Gentile, G. A. Chapman & W. A. Brungs, 1985. Guidelines for deriving numeric National Water Quality Criteria for the protection of aquatic organisms and their uses, PB85-227049. US EPA, Duluth, Minnesota, USA.