



# Sediment Quality Guidelines for the Regional Discharges Project

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# Sediment Quality Guidelines for the Regional Discharges Project

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# 1 Executive Summary

## 1.1 ARC Requirements

The Auckland Regional Council requires "targets" for the Settling Zone (SZ) and the Outer Zone (OZ) of Auckland's estuaries. It could be argued that the SZs, which accumulate the bulk of stormwater-derived contaminants, should have less-protective targets because these areas are already contaminated (some sites already exceed Sediment Quality Guidelines) and have more robust animals. ARC could therefore allow some degradation of the SZ (e.g., to allow for "mixing" and balance the high costs or difficulties of retrofitting stormwater treatment). Outer Zones were envisaged to require greater protection, because these areas are larger and have more diverse habitats, have less robust animals, and concentrations presently do not exceed Sediment Quality Guidelines (SQG).

## 1.2 Recommended Targets

The new ANZECC guidelines (2000) would seem to be the most appropriate guidelines to form the basis for target values. The guideline values are termed "trigger" values, because if exceeded, they are a prompt for further investigations. Their basis is a risk-based decision tree that progresses through a hierarchy of measurements of increasing complexity to reach a decision as to whether the sediment concentrations are likely to be toxic or not, the final arbitration being toxicity tests. The current ISQG-Low and the accompanying decision tree are designed to ensure that there is a low probability of false positives.

This means that the ANZECC ISQG-Low values be used as the Target Values for the Settling Zone. For sediments to be classified as "toxic", toxicity to laboratory test animals needs to be demonstrated. If a toxic response is encountered, it is highly likely that the sediments will have an ecological effect. However, if a non-toxic response is encountered, there is no surety that ecological effects will not occur. Thus the ANZECC guidelines demonstrate a measure of protection but allow for the possibility of some ecological degradation, which is consistent with ARC management goals for the Settling Zone and with the ANZECC philosophy of trigger values for "slightly-moderately degraded ecosystems".

We have some concerns if ANZECC Guidelines were to be used as protective guidelines for Settling Zones in Auckland estuaries, because:

- recommended numerical values for Zn, Cu have been adopted from limited unpublished data,
- no-effects data has been excluded in their derivation,
- recommended numerical values for some organochlorines seem too low,
- they do not include PAH phototoxic effects, and
- they do not include fish health effects.

For the Outer Zones, where Environmental Targets seek to minimize ecological effects, much more stringent criteria are required. Therefore the ANZECC approach, which is based on the laboratory toxicity of whole sediments, is not adequately protective. In this report we examine the possibility of having trigger values that are based on concentrations in the mud fraction rather than in the whole sediment. For organics, however, because trigger values are calculated from the organic carbon content, they are applicable directly to both Settling and Outer Zones. The lower organic content in sandy sediments effectively lowers the trigger value for organic contaminants for the OZ. Conversely, the higher organic content in muddy sediment increases the trigger value.

We believe it would be highly profitable to use toxicity testing to develop unique SQG for the Settling Zones. This is in line with the ANZECC philosophy. The ubiquity of the type and ratios of urban-derived contaminants within a relatively small region simplifies the contamination issues and lend themselves to such an approach.

### 1.3 Present Situation in Auckland Estuaries

How do the concentrations of contaminants currently present in Auckland estuarine sediments compare with the various sediment quality guidelines described above?

Probability plots of Auckland Zn, Pb and Cu data show that ISQG-Low are exceeded for Pb (30% of the data), Zn (20%) and Cu (8%). These studies have shown that for metals basically:

- sediments in any sheltered muddy settling area (SZ) whose contributing catchment is strongly urbanized will exceed ER-L and in extreme cases, the ISQG-Low,
- SZ with partially or recently urbanised catchment areas will have sediment concentrations sediments that do not exceed the ER-L or ISQG-Low at the present time, and
- sediments in exposed areas (sandy sediments) (e.g, OZ) will not exceed the ER-L or ISQG-Low except near the SZ/OZ boundary.

For OZ sandy sediments, sites near the SZ of older urban areas often exceed the SQG values in the mud fraction. Sites away from the SZ/OZ boundary are unlikely to exceed SQG.

ISQG-low Guidelines for organic contaminants are exceeded:

- In most places for dieldrin, because the ISQG-low value is excessively low (probably close to background levels).
- In some places where there has been a history of industrial pollution or spills (e.g. middle reaches of the Tamaki Estuary, Mangere Inlet, Henderson Creek).
- In muddy settling zones of estuaries receiving stormwater from old, fully urbanised catchments (e.g. Motions Creek).
- 70% of the sites have PAH levels that could be potentially phototoxic.
- Approximately 50% of the sites could have PAH levels at which adverse effects on bottom-feeding fish might begin to occur.

There are a large number of sites that have one or more exceedance of ISQG-low. Under the ANZECC protocols, this means that many sites within the Settling Zone will require further

assessment. There are also a large number of sites that could exceed PAH concentrations associated with phototoxicity and fish health. Further research is needed on the possible phototoxicity of PAH to estuarine benthic animals and possible impact of PAH on fish health.

The high exceedance of trigger values for dieldrin and to a lesser extent, DDT and chlordane needs to be reassessed. There is a need to debate the use of ER-L for ISQG-Low for Dieldrin, chlordane, DDT, and to consider instead the use of TEL values.

## 1.4 Future Levels in Auckland Estuaries

The concentrations of the major contaminants Cu, Zn and PAH are predicted to increase in the estuarine sediments in the future.

Concentrations measured at the present time does not tell you what the concentration may be at some time in the future. For effective stormwater management, predictions will need to be made on the rate of increase in contaminants, in order to:

- anticipate if, and when, Environmental Targets are exceeded,
- to indicate the seriousness of the exceedance,
- help prioritise management response, and
- indicate the magnitude of source control or treatment needed to prevent exceedance of Environmental Targets

The contaminants can be prioritized in terms of their likelihood to exceed the ISQG-Low at present or in the future for Settling Zones (see Table below). We cannot make comparable assessments for the Outer Zones with the present database. There is a new model with which one can make broader predictions (Green et al. 2001), including concentrations in the OZ, but this is yet to be tested.

Likelihood of exceeding ANZECC (2000) ISQG-low values **usually**, **often**, **occasionally**, **seldom**, **never** in sheltered muddy estuaries with a significant proportion of urban land use.

	Zn	Cu	Pb	PAH	Organo-chlorines
Exceeds ISQG-low in present day					**
Exceeds ISQG-low in future					Insufficient data
Exceeds ISQG-high in future					Very unlikely

\*\* mostly dieldrin and DDT because of low values for ISQG-Low.

## 1.5 Bioavailability Procedures

The following methods have been specified to assess bioavailability of contaminants (ANZECC 2000).

**Acid soluble.** The ANZECC proposal to measure acid soluble rather than total needs careful consideration of the method used to measure acid soluble, the relationship between total and acid soluble levels, and the implications for pass/fail trigger values. The approach would favour

the proposition that Settling Zones have a lower level of protection and that some degradation is allowable, and reduce the costs and demands of remedial action.

**Acid Volatile Sulphide (AVS).** Present levels that have been measured in bioturbated surface sediments would lead to the AVS model predicting potential toxicity. However, there may be sites with higher AVS concentrations, as we have encountered a few times. It would not be sufficient to measure AVS at a monitoring site for one season only.

**Pore water.** We need lots more data and experience for heavy metals contamination. We doubt whether this approach is worth pursuing for the relatively low levels of contamination associated with ISQG-Low values, given the uncertainties outlined above. The efficacy of measuring pore water concentrations of heavy metals would need to be addressed through a research programme. This needs to be debated. There is no point in pursuing this approach with organic contaminants PAH and organochlorines.

**Equilibrium Partitioning.** There is no point in undertaking equilibrium partitioning predictions of pore water concentrations when assessing exceedance of SQG.

**Toxicity testing.** We believe that the toxicity tests are robust, and that they are a suitable assessment of bioavailability in the context of partial degradation of settling zones. We also recommend that phototoxicity assessment is included in the toxicity testing.

## 1.6 Monitoring

Monitoring needs to include organic carbon, AVS, particle size as well as the contaminants. For the Settling Zone we recommend the ARC Long Term Baseline (LTB) method (ARC 1998). For settling areas, which may not meet the criteria for Settling Zones (see Williamson and Green 2001), a similar number of samples should be collected (and composited) from over a wider area. This is to overcome the possibility of strong concentration gradients. Because of the difficulty of sampling in these muddy environments, high tide sampling may be preferable, but the method needs to be tested.

For Outer Zones, we propose a similar procedure to the LTB method, except that a wider area (50m x 100m) is sampled.

## 1.7 Recommended decision process<sup>1</sup>

### 1.7.1 Settling Zone

Step 1A Measure levels of contamination, organic carbon, AVS and particle size.

Step 1B Do USC model predictions of future levels of contamination.

Step 2 If  $[X]_{\text{present}} > \text{SQG}$  then proceed with the revamped ANZECC Protocol.

Step 3 If  $[X]_{\text{future}} < \text{SQG}$ , no problem

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<sup>1</sup>  $[X]_{\text{present}}$  = present day contaminant concentrations,  $[X]_{\text{future}}$  = future contaminant concentrations,  $[\text{metals}]_{\text{mud}}$  = heavy metal concentration in the mud fraction,  $[\text{toxic organics}]_{\text{OM}}$  = toxic organic concentration normalised to organic matter content.

Step 4 If  $[X]_{\text{future}} > \text{SQG}$  then

(i) Assign confidence factor based on relation of predicted concentration and its confidence limits to the SQG,

(ii) Assess whether treatment, structure plan, source control bring  $[X]_{\text{future}} < \text{SQG}$

(iii) Combine with Step 2A and prioritise and design remedial action.

## 1.7.2 Outer Zone

Step 1 Monitor

Step 2A If  $[\text{metals}]_{\text{mud}} > \text{SQG}$  or  $[\text{toxic organics}]_{\text{OM}} > \text{SQG}$  then reconsider source control for contributing catchments or SZ.

There is a need to develop the new prediction procedures (Green et al. 2001) into a useful tool which can generate knowledge and understanding of contaminant trends in the OZ, so more considered management decisions can be made.

## 2 Brief

The overall aim of this project is to:

- provide an overview of likely Environmental Targets, based on existing sediment quality data,
- make preliminary guesstimates of sediment quality guidelines (SQG) that would be likely Environmental Targets, in order to help complete Case Studies, and
- to identify information needs required to calculate robust Environmental Targets.

Specific tasks are:

- Describe the meaning and theories behind the definition of bioavailable toxicants in the ANZECC guidelines (ANZECC 2000).
- Define the expected Target Values using the ANZECC Guidelines for bioavailable contaminants (using Acid Volatile Sulphide (AVS), Equilibrium Partitioning (EqP), Interstitial Water Concentrations ([IW]) and other models).
- Provide expected values for Settling and Outer Zones.
- Briefly describe the purpose, capacity and limitations of the Time Series Modeling approach for predicting concentrations of contaminants in estuarine sediment into the future.
- Describe a formalized methodology for linking monitoring results with Time Series Model predictions in order to make management decisions.
- Outline what further information is needed to calculate robust sediment Environmental Targets (e.g., Local Network Operators's may need to measure AVS levels, or carry out toxicity testing).
- Provide a clear flowchart of the process used to define the Environmental Targets, so any information gaps can be plugged.

### 2.1 Glossary

- Acid Soluble Metals. Heavy metals dissolved from sediments by extracting with with 1 M HCl for 1 hour.
- Acid Volatile Sulphide (AVS). The AVS concentration in sediments is the sulphide associated with FeS, CdS, ZnS, PbS, NiS, CoS. In uncontaminated sediments, AVS is dominantly FeS.
- Equilibrium Partitioning (EqP). Pore water concentrations are predicted from concentration of toxic organics and organic matter in the total sediment. The toxic organic is "partitioned" between water and sediment using the equilibrium partitioning constant.

- ER-L. Effects Range Low (Long et al. 1995). Concentration at which 90% of toxicity studies show an effect. Developed by the National Oceanic and Atmospheric Administration (NOAA) from an extensive North American database of sediment chemistry and toxicity studies (Long et al. 1995).
- ER-M. Effects Range Medium. Concentration at which 50% of toxicity studies show an effect. See ERL.
- ISQG CCME. Interim Sediment Quality Guideline for Canada (Canadian Council of Ministers for the Environment (CCME) 1999).
- ISQG-Low. Interim Sediment Quality Guideline-Low (ANZECC 2000).
- LNO. Local Network Operators of stormwater and wastewater disposal systems.
- OC. Organic carbon
- Outer Zone. Is the area beyond the Settling Zone that is still impacted by stormwater runoff, but to a lesser extent. It is often “downstream” from several settling zones. It may receive runoff directly from stormwater discharges when these discharge directly to exposed shorelines, such as the open coast (e.g., East Coast Bays, Beaches).
- PEL. See TEL.
- Phototoxicity. Some PAHs are more toxic in the presence of ultraviolet (UV) light than in tests conducted under standard laboratory light. This increased sensitivity is termed phototoxicity. When PAH, sunlight, and organism are present simultaneously, photo-enhanced toxicity can occur if the organism is transparent/translucent to sunlight.
- Settling area. The area over which the most (nominally 75%) of catchment-derived contaminants (usually stormwater-derived) settle and accumulate. The settling area may be well defined in size and location (in which case it is similar to the Settling Zone) or it may be poorly defined in size and location. The fraction 75% derives from the ARC’s settling pond theory.
- Settling Zone. (SZ). A specific area where catchment-derived contaminants settle and accumulate. It is defined in size and location. Originally envisaged to trap 75%, the SZ concept had to be modified to take into account less efficient settling encountered in Auckland intertidal estuaries. Settling zones can only be defined for sheltered estuaries. Some urban streams discharge directly to high-energy areas, such as the open coast, so there are no settling zones for these discharges, or only very small settling areas.
- Note that the Settling Area is determined by physical processes, while the Settling Zone is arbitrarily defined to meet management requirements.
- SEM. Simultaneously Extracted Metal. Heavy metals extracted in 1 M HCl for 1 hour.
- SQG. Sediment Quality Guideline.
- TEL. Threshold Effects Level for Florida Department of Environmental Protection (MacDonald 1996). The Florida and earlier Canadian SQG (Smith et al. 1996a,b) define the Threshold Effects Level (TEL) below which adverse effects are predicted to rarely occur, and the Probable Effects Level (PEL) above which adverse effects are predicted to occur frequently. SQGs were based on a compilation by the National Oceanic and

Atmospheric Administration (NOAA) from an extensive North American database of sediment chemistry and toxicity studies (Long et al. 1995). These were subsequently modified for application in Florida (McDonald et al. 1996), and in Canada (Smith et al. 1996a,b; CCME 1999b).

- USC. Urban Stormwater Contaminant model.
- Environmental Targets.

## 2.2 The ARC's requirements

The ARC requires "targets" for the Settling Zone (SZ) and the Outer Zone (OZ) of Auckland's estuaries. It could be argued that the SZs, which accumulate the bulk of stormwater-derived contaminants, should have less-protective targets because these areas are already contaminated (some sites already exceed SQG) and have more robust animals. ARC could therefore allow some degradation of the SZ (e.g., to allow for "mixing" and balance the high costs or difficulties of retrofitting stormwater treatment). Outer Zones were envisaged to require greater protection, because these areas are larger and have more diverse habitats, have less robust animals, and concentrations presently do not exceed SQG. The ARC Discussion Document suggested Effects Range Median (ER-M) SQG values for the SZ and Effects Range-Low (ER-L) for the OZ.

Additional requirements were that the target values have:

- A low probability of "false negatives", so that there is a low probability of toxicity to estuarine animals when targets are not exceeded. This requirement precludes the use of ER-M values (where 50% of toxicity studies demonstrate toxicity to test animals).
- A low probability of "false positives", so that there is a low probability of applying unnecessary and expensive stormwater treatment procedures in the contributing catchment.

## 2.3 What are the options?

There are a number of available options for SQG values as described in the ANZECC Guidelines (ANZECC 2000). Of these, the ANZECC guidelines themselves would seem to be the most appropriate guidelines to form the basis for SQG values because:

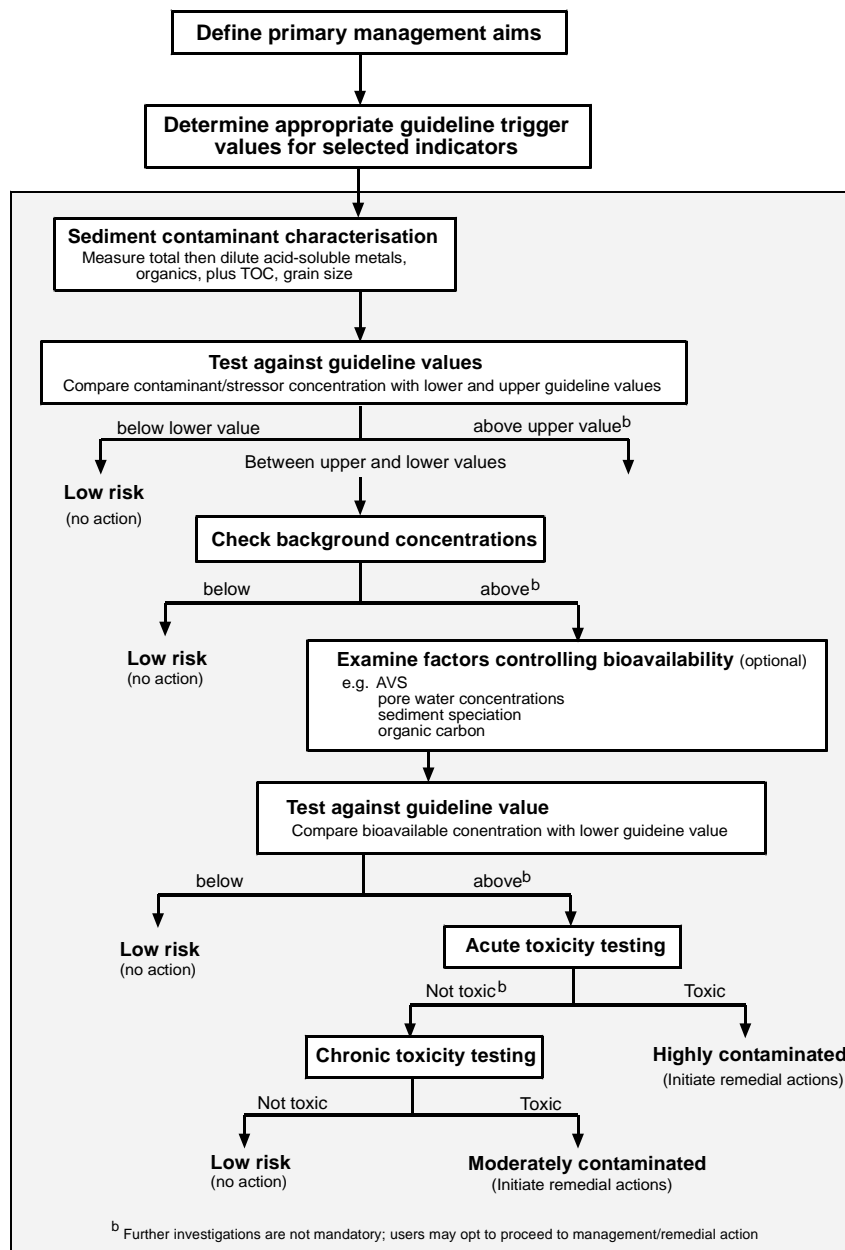
- they form a comprehensive and authoritative resource document,
- they have been prepared for use in NZ,
- are likely to be widely used in NZ, and
- they have incorporated SQG already widely used in NZ.

We have some concerns about the unqualified use of the guidelines for target values, which we discuss below.

### 2.3.1 Will the Guidelines generate false positives? (target value exceeded but not toxic)

The guideline values are termed "trigger" values, because if exceeded, they are a prompt for further investigations. Their basis is a risk-based decision tree that progresses through a hierarchy of measurements of increasing complexity to reach a decision as to whether the sediment concentrations are likely to be toxic or not (Figure 1). In this sense they are designed to minimize the likelihood of false positives.

**Figure 1.** The decision tree used in the ANZECC guidelines to determine whether or not sediments are toxic (reproduced from ANZECC 2000)



The ANZECC trigger values are derived by a "co-occurrence" approach (outlined in Appendix 1) relating increasing toxicity to increasing level of chemical contamination of the sediment. A potential shortcoming of using this approach to derive SQG is the possibility of a specific

chemical being falsely identified as being at a toxic level simply because its concentration is strongly correlated with the concentration of some other chemical that is actually exerting the toxicity. This may mean that false positives are implicit in the application of SQG. There is no way to check this until cause/effect relationships have been established. In the meantime, we accept that the co-occurrence approach is a valid way to derive sediment quality guidelines.

### 2.3.2 Will the Guidelines generate false negatives? (target not exceeded but toxic)

The ANZECC trigger values, the "ISQG-Low" (Interim Sediment Quality Guideline-Low), are based on the ER-L SQG guideline from Long et al. (1995). This is claimed to be commensurate with the principle of protection. However, there are some inconsistencies and uncertainties in the application of the guidelines and decision tree, and there are also some other toxic mechanisms not incorporated into the guideline trigger values. These raise the possibility of false negatives. The uncertainties associated with the ANZECC guidelines are summarized below:

- Numerical values for Copper, Lead and Zinc.** The values for Cu, Pb and Zn in the ANZECC Guidelines are higher than the ER-L (Table 1). For Pb, the reason for this is because the values have been rounded up, but no reason is given for the higher Cu and Zn values. The text accompanying the guidelines assert a high level of confidence in ER-L values for Zn and Cu, and therefore there seems no justification to alter them.

**Table 1.** SQG values (mg/kg) from Long et al. (1995) and ANZECC (2000).

Metal	ER-L	ISQG-Low
Copper	34	65
Lead	46.7	50
Zinc	150	200

The ISQG-Low values for Cu and Zn are the same as the Hong Kong interim sediment quality values for dredge spoil disposal "ISQV" (Chapman et al. 1999). The higher values for Cu and Zn in the Hong Kong data are based on local unpublished studies, which did not find toxic effects below these concentrations, and this appears to be the reason for their use in place of ER-Ls in the ANZECC guidelines. The implications for Auckland from these changes are discussed in Chapter 3.

- No effects data.** The Guidelines are derived from a database that is made up from a compilation of toxicity/sediment chemistry data for which toxic effects were recorded (the so-called "effects" database). They do not include "no effects" data (i.e. sediments which did not cause a toxic response in the tests) in their derivation. The ANZECC Guidelines consider that it is sensible to exclude no-effects data to minimize the possibility of false positives occurring. The Florida Department of Environmental Protection Guidelines (MacDonald 1996) and the derivative Canadian Guidelines (Canadian Council of Ministers for the Environment, CCME 1999) include no-effects data in their derivation. However, it is really difficult to advocate either approach. For example, the TEL (MacDonald et al 1996) for Cu is very low (18.7 mg/kg), compared with the ER-L (34 mg/kg) and the ISQG-Low (50 mg/kg), and many Auckland estuarine sediments exceed 18.7 mg Cu/kg. In contrast, an opposite effect is observed for organochlorine pesticides. For example, the ISQG-Low for dieldrin is 0.02 µg/kg (cf. a TEL of 0.72 µg/kg).

- Organic content.** The ANZECC (2000) trigger values for toxic organics specifies that toxic organic concentrations are normalized to the level of organic carbon. This means that in sediments with low organic content such as sandy sediments, the ISQG-Low become lower, while in more muddy sediments they become higher. None of the original guidelines used to derive the ANZECC guidelines use this approach – i.e., Long et al (1995) effects data (ERL and ERM). Other major guideline protocols, e.g., Canadian Interim Sediment Quality Guidelines (CCME 1999), the Florida Department of Environmental Protection (Mac Donald 1996) do not use this approach either. “It was not possible to express the guidelines in terms of the factors that may influence bioavailability because relevant data of sediment grain size, total organic carbon or AVS were often not provided” (MacDonald et al 1996).
- Phototoxicity.** Some PAHs are more toxic in the presence of ultraviolet (UV) light than in tests conducted under standard laboratory light. This increased sensitivity is termed phototoxicity. PAH molecules absorb UV light, generating excited, higher energy, states. It is thought that some excess energy is transferred to oxygen molecules, generating “singlet oxygen” which is very reactive. It can denature biomolecules, and can remain in tissues long enough to cause biological damage. When PAH, sunlight, and organism are present simultaneously, photo-enhanced toxicity can occur. If an organism accumulates PAH, but is not exposed to the sun, toxicity may not occur. However, if that organism emerges into the sunlight, phototoxicity may occur (provided the organism has sufficient transparency to allow light to penetrate into membranes where PAH can accumulate). Phototoxicity can also occur when previously exposed animals (with an accumulated body burden of PAH) are exposed to sunlight in a clean (PAH-free) environment. The degree of phototoxicity is dependent on the PAH concentration in the animal (dose), and the duration and intensity of the UV light exposure. The USEPA (1993b) estimated that the toxicity of fluoranthene in water increases by a factor of about 10 times in the presence of UV light (estimated final chronic value of 0.26 µg/L with UV cf 2.96 µg/L without). Animals potentially affected by phototoxicity are only those species that are exposed to the sun during the day. The importance of phototoxicity for benthic fauna in NZ estuaries is uncertain, and is the subject of current research at NIWA.
- Toxicity to fish.** Extensive studies in North America have established strong relationships between the concentrations of some chemical contaminants in sediments and the health (in particular, liver lesions) of benthic fish (e.g. Myers et al. 1994). Sediment quality thresholds for PAHs and the onset of liver lesions in one species of fish, English sole (*Pleuronectes vetulus*), have been developed (Horness et al. 1998). These thresholds were found to be lower than other SQGs for PAHs, and ranged from 230–2800 ng/g (ppb) total PAH for various measures of lesion prevalence. One measure, FCA (foci of cellular alteration), had a calculated threshold of 54 ng/g total PAH, with no lower confidence limit, suggesting that this effect may be proportional to PAH levels over the entire contaminant concentration range (rather than having a definite threshold concentration at which effects become significant). The thresholds were evaluated from field-collected data, where sediments contain multiple contaminants (not just PAHs). It is therefore possible that co-varying contaminants that are known or suspected to be carcinogenic to fish (e.g. PCBs) also contribute to the effect observed (a problem analogous to that for the ANZECC guideline derivation). Although this approach is in its infancy, it is worth noting because it represents an environmental health effect measure that is different from the commonly assessed benthic invertebrate toxicity tests or benthic community

assays. It also indicates that adverse ecological effects can occur at levels lower than those found in laboratory toxicity tests, and reinforces the point that guidelines relate only to the effect measures used in their derivation, and not necessarily to ecologically significant effects (as highlighted in papers by e.g. O'Connor & Paul 2000; Hyland et al. 1999).

## 2.4 Possible Target Values

**Settling Zone.** We examine the proposition that the Environmental Targets be based on the ANZECC guidelines. This means that the ANZECC ISQG-Low values be used as the SQG for the Settling Zone. The current ISQG-Low and the accompanying decision tree (Figure 1) are designed to ensure that there is a low probability of false positives. For a sediment to be classified as "toxic", toxicity to laboratory test animals needs to be demonstrated. If a toxic response is encountered, it is highly likely that the sediments will have an ecological effect. However, if a non-toxic response is encountered, there is no surety that ecological effects will not occur. Thus the ANZECC guidelines demonstrate a measure of protection but allow for the possibility of some ecological degradation, which is consistent with management goals for the Settling Zone and with the philosophy of trigger values for "slightly-moderately degraded ecosystems".

**Outer Zone.** For the Outer Zone, where Environmental Targets seek to prevent ecological effects, much more stringent criteria are required. This is particularly borne out by a preliminary study on the relationship between pollution and benthic community. There is evidence that there are effects on benthic communities in OZ at contaminant concentrations less than the ISQG-Low. The ANZECC approach, which is based on the laboratory toxicity of whole sediments, is therefore not adequately protective. In this following we examine the possibility of having trigger values for heavy metals that are based on concentrations in the mud fraction rather than in the whole sediment. This proposal is based on the following reasoning:

- The fine fraction is the most ecologically relevant component of sediments, since it is more likely that benthic animals will ingest or be in intimate contact with fine rather than coarse materials.
- Sandy areas are likely to contain more pollution-sensitive organisms than muddy areas.
- The mud fraction of the OZ sediments is roughly equivalent to the 'total' sediment in muddy areas of the OZ. So in sheltered areas (see Green et al. 2001), the ISQG-low of the mud fraction approximately equates to the ISQG-Low for the total sediment. This does mean, however, that the proposed Guideline is not stringent for muddy areas in the OZ. We do not perceive this to be a problem, because most of these areas are relatively small in the most OZs, and animals are regarded as robust.
- In most OZ situations, because of dilution and dispersions, concentrations in the mud fraction is presently lower than ISQG-Low, so we do not see widespread exceedance of this Guideline.
- If toxicity to benthic organisms in the OZ is due to ingestion of mud particles, then such a trigger value is sensible.

- Sandy sediments have a lower capacity to bind heavy metals and organic contaminants, because of smaller specific surface areas, and lower concentrations of adsorbing phases iron oxide (FeOOH), acid volatile sulphides (AVS), and organic matter.
- Sandy sediments contain few stable burrows (at least in the Auckland region) and there is less irrigative flushing of sediments. While permeability is relatively high in sandy sediments, movement of interstitial water is slow. Sediments with very low mud content are probably reasonably well flushed, though, so interstitial water concentrations of contaminants will probably be low. Sandy sediments with a significant proportion of mud may not be so well flushed dissolved contaminants may accumulate in interstitial water to effect levels.

There are definite advantages in using the mud fraction where there are large changes in sediment texture, as occurs in the OZ. This greatly simplifies monitoring (Williamson & Green 2001).

This guideline is probably not sensible for sandy sediments with low mud content (<5%) because of uncertainty in the inference of adverse effects from the mud fraction to the whole sediment when the mud fraction is very small. This point will require further scientific investigation.

We believe that using the ISQG-low in the mud fraction as the SQG for the OZ could be appropriately protective for these ecologically sensitive areas, and such a precautionary approach should be taken until the many uncertainties about the ecological effects of low levels of contaminants in such environments are resolved.

Application of this SQG would require separation and measurement of metals in the mud fraction. For organics, however, because trigger values are calculated from the organic carbon content, they are applicable directly to both Settling and Outer Zones. The lower organic content in sandy sediments effectively lowers the trigger value for organic contaminants for the OZ. Conversely, the higher organic content in muddy sediment increases the trigger value.

As with metals, this means that the proposed Guideline is not stringent for muddy areas in the OZ. We do not perceive this to be a problem, because most of these areas are relatively small in the most OZs, and animals are regarded as robust.

## 3 Application of targets to Auckland estuaries

### 3.1 Comparison of target values with the current levels of contaminants in Auckland estuaries

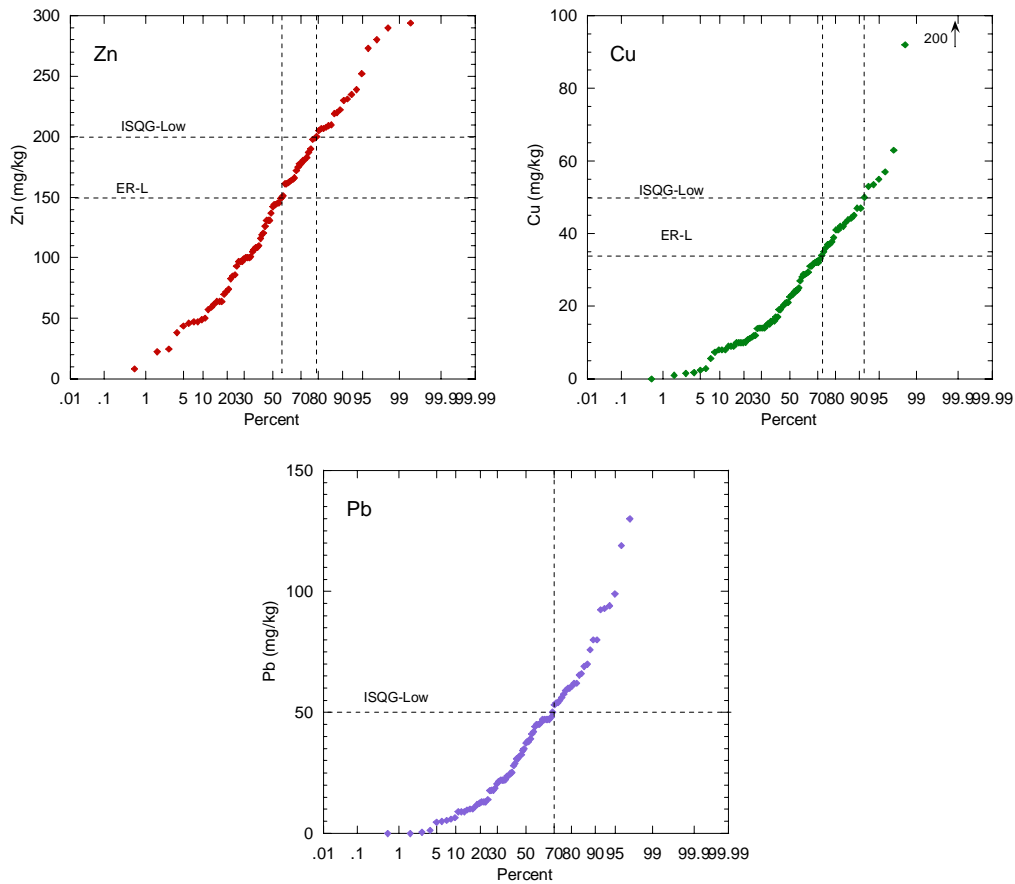
#### 3.1.1 Contaminant database for Auckland estuaries

How do the concentrations of contaminants currently present in Auckland estuarine sediments compare with the various sediment quality guidelines described above? We have tackled this question by assembling a dataset of contaminants in estuarine sediments from around the Auckland region as the basis for comparison. The dataset is tabulated in Appendix 2.

#### 3.1.2 Comparison of metals data

Probability plots of Auckland Zn, Pb and Cu data (Figure 2) show that ISQG-Low are exceeded for Pb (30% of the data), Zn (20%) and Cu (8%). Also shown in Figure 2 are ER-L values, because we have some misgivings about the current ISQG-Low values for Cu and Zn (See 2.2.2). Sites that exceed SQG are listed in Table 2. The most contaminated sites include Mangere Inlet, where contamination is probably mostly industrial origin, and estuaries that have been urbanized for the longest time, such as Whau, Motions and Meola. Most of the sites listed in Table 2 would be classified as Settling Zones.

**Figure 2.** Probability plots of total metal concentrations.



These studies have shown that basically:

- sediments in any sheltered muddy settling area whose contributing catchment is strongly urbanized will exceed ER-L and in extreme cases, the ISQG-Low,
- estuaries with partially or recently urbanised catchment areas will have sediment concentrations sediments that do not exceed the ER-L or ISQG-Low at the present time, and
- sediments in exposed areas (sandy sediments) will not exceed the ER-L or ISQG-Low in total sediment samples.

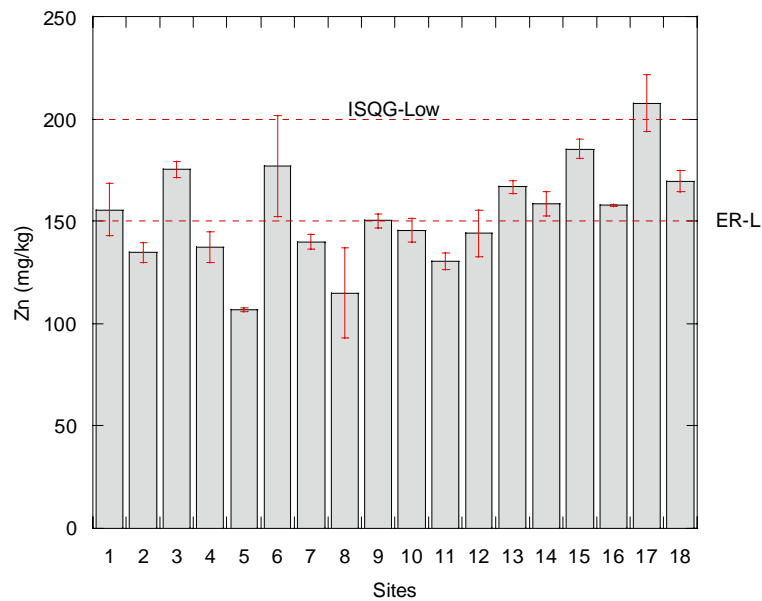
**Table 2.** Auckland sites where Zn, Cu or Pb exceed **ISQG-Low** and **ER-L**.

Site	Zn ISQG-Low	Cu ISQG-Low	Pb ISQG-Low
Whau, Wairau	Red	Red	Red
Whau, Upper	Red	Yellow	Red
Whau, Lower	Yellow	Yellow	Red
Waterview	Yellow	Yellow	Red
Henderson, Taratata	Yellow	Yellow	White
Henderson, Huruheru	Yellow	Yellow	Red
Motions	Red	Yellow	Red
Meola	Red	Yellow	Red
Barry's Point, Shoal Bay	Yellow	White	Red
Panmure, Tamaki Estuary	White	White	Red
Upper Tamaki	Yellow	White	Red
Pakuranga, Upper	Red	White	Red
Pakuranga, Lower	Red	Yellow	Red
Garbador Place, U. Tamaki	Yellow	White	White
Otahuhu Creek	Yellow	White	Red
Mangere Inlet (many sites)	Red	Red	Red
Upper Pukaki	Red	Yellow	Red

To assess the application to the OZ, we need to consider the levels of metals in the mud fraction of sandy sediments. Exceedance of the ISQG-low or ER-L in the mud fraction of muddy sediments largely mirrors Figure 2 above, where totals exceed SQG anyway. For sandy sediments, there is only limited data, which are summarised in Table 3. It can be seen that sites near the SZ of older urban areas often exceed the SQG values in the mud fraction. These include Motions, Meola, Coxes, and Hobson Bay, where sediments are decidedly muddy (they consist mostly of sand but are cohesive, soft, and 'gloopy').

Sites away from the SZ/OZ boundary are less likely to exceed SQG. The study by Green et al (2001) measured Zn in the mud and total sediment fraction at 18 sites located on the mud/sand flat that stretches from Motions Creek to the outer reaches of Te Tohunga Reef. Most of this area is intertidal sand flat, with gloopy sediments (but consisting mainly of sand-sized particles) near the head of this Bay and the SZ/OZ boundary. Zinc concentrations in the mud fraction of sandy sediments over Motions Bay are shown in Figure 3. Concentrations in the mud fraction were found to be fairly constant and oscillated around the ER-L.

**Figure 3.** Zn concentrations in the mud fraction (< 63 µm) over the intertidal sand flats of Motions Bay.



**Table 3.** Concentrations of Zn, Pb and Cu in the mud fraction of sandy sediments. Acid soluble (2M HCl overnight) metal concentrations. Sites exceeding **ISQG-Low** and **ER-L**.

Site	Date	Study	Zn	Cu	Pb
Te Tokorau, Meola Reef	1998	ARC LTB	146.0	25.8	63.5
Hobson Bay, Upper	1998	ARC LTB	118.0	22.6	69.2
Cheltenham Beach	1998	ARC LTB	87.4	11.0	39.3
Long Bay off Awaruku Stream	1998	ARC LTB	62.4	9.0	11.8
Meola Bay Upper	1997	ARC Sand sediments	275.0	24.0	74.0
Motions Bay Upper	1997	ARC Sand sediments	209.0	26.0	89.0
Motions Bay Outer	2001	Green et al. 2001	175	n.a	n.a
Coxes Bay Upper	1997	ARC Sand sediments	351.0	42.0	132.0
Hobson Bay, Middle	1997	ARC Sand sediments	117.0	14.0	65.0
St Marys Bay	1997	ARC Sand sediments	95.0	35.0	45.0
Herald Is	1997	ARC Sand sediments	84.0	14.0	34.0
Long Bay off Vaughans Stream	1999	ARC LTB	80	9	0
Browns Bay	1999	ARC LTB	131	10	1

We can use this data to get a “feeling” for the degree of protection offered by the proposed Guideline for the OZ. Let’s assume that ecological impacts currently occur in the OZs in the Auckland Region in line with current evidence (Anderson et al, in prep.). If so, then they are highly likely to occur in Motions Bay because it is one of the more contaminated estuarine areas in the Auckland region. Concentrations are almost always less than ISQG-Low, so this SQG would be not very protective. About 50% of the samples are below the ER-L, so even this SQG may also be insufficiently protective. However, the method of analysis was 2 M HCl extraction overnight, so using stronger oxidative acid digests for the analysis would “improve” the protection. If the more protective TEL is used as a SQG (the TEL for Zn is 125 mg/kg), most sites on the Motions Creek sandflat exceed this value.

### 3.1.3 Comparison with organic contaminants levels

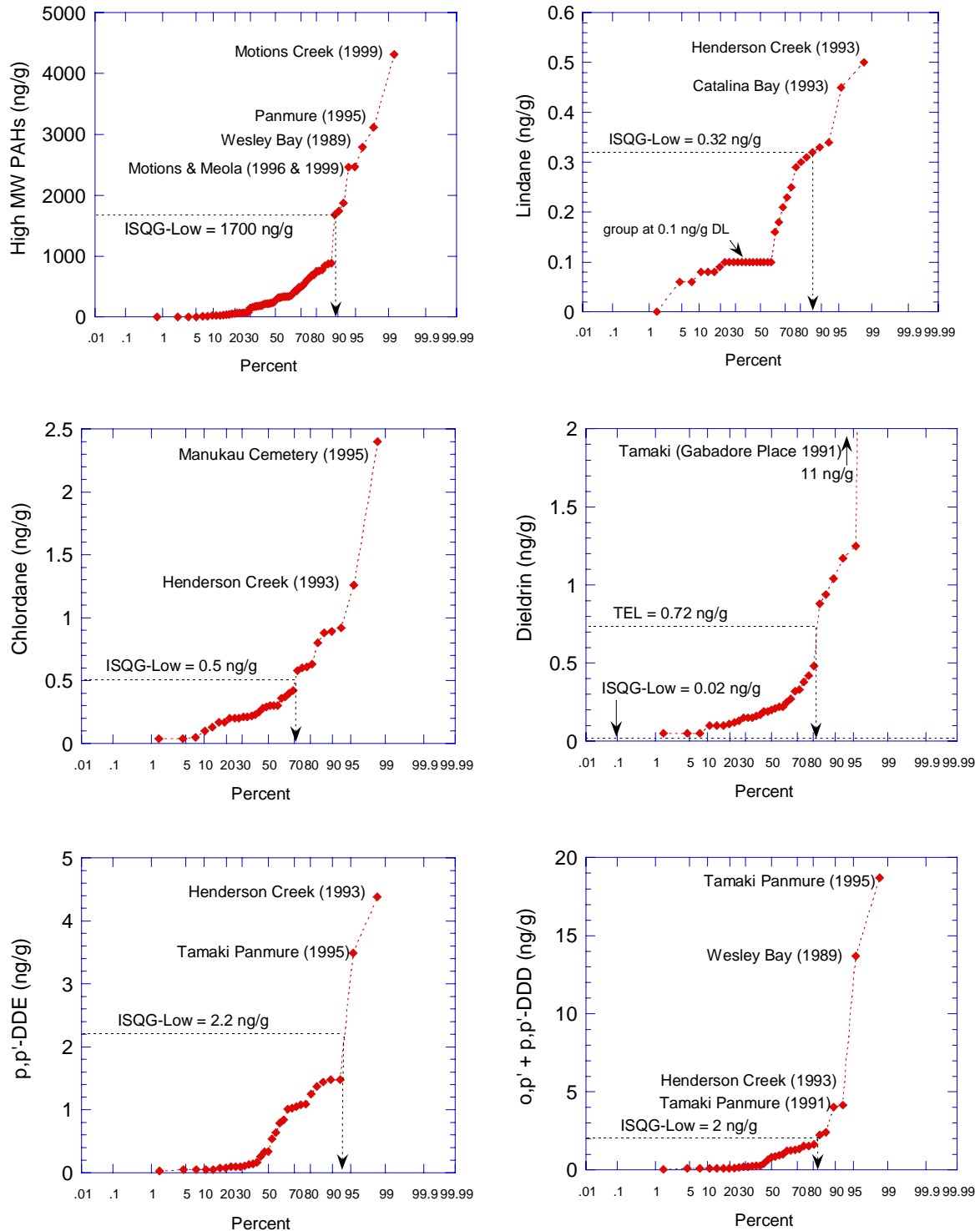
**ANZECC trigger values (ISQG-Low).** Concentration/frequency plots are shown in Figure 4 along with ANZECC (2000) trigger values (ISQG-low values) assuming an organic content of 1%. These plots reveal that ANZECC trigger values can be exceeded at some sites. Greatest proportions of exceedances occur for dieldrin (essentially all the sites because of the very low ISQG-low value), and total DDT (which also has a relatively low ISQG-low value).

For the other contaminants, exceedances ranged between approximately 30% (chlordane) and 3% (total PCBs). There appear to be a relatively small number of sites at which unusually high contaminant levels are found. These sites vary between contaminants, but samples from the mid-Tamaki estuary (Panmure and Gbadore Place) appear as high values on all the contaminant plots (except for chlordane<sup>2</sup>) in Figure 4.

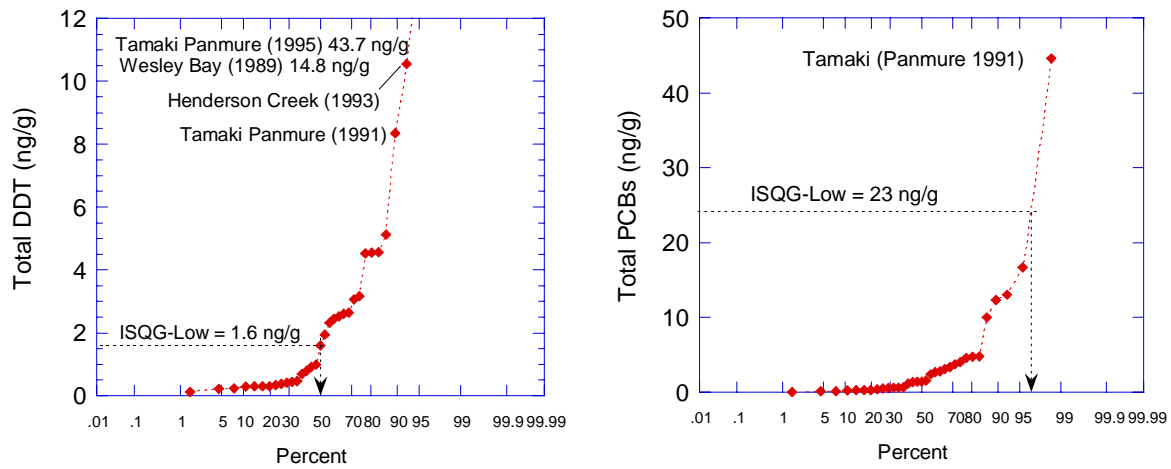
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<sup>2</sup> High concentrations of chlordane were mainly associated with the Manukau Harbour where high levels were associated with historical industrial discharges.

**Figure 4.** Probability plots of organic contaminants in Auckland estuarine and marine sediments. Plots show the percentage of samples that have concentrations below the red (data) line. Also plotted are the ISQG-low trigger values from ANZECC (2000), and for dieldrin, the threshold effects level (TEL; MacDonald et al. 1996). Note that the ISQG-low values assume 1% organic carbon in the sediment.



**Figure 4 (cont).** Probability plots of organic contaminants in Auckland estuarine and marine sediments. Note that the ISQG-low values assume 1% organic carbon in the sediment.



These plots have assumed a sediment organic carbon (OC) level of 1% – there was insufficient OC data for Auckland sediments to perform the normalisations required by the ANZECC procedures. However, OC levels in NZ sediments cover a relatively wide range. The Ministry for the Environment study of organochlorines in NZ estuaries (MFE 1998) recorded a range of 0.11–1.87% (mean = 0.6%, n=24). Very muddy environments have higher OC levels (e.g. eight Auckland muddy sites had OC of 1.6–5.4%; Nipper et al. 1998) and sandy sediments low values (e.g. 0.22–0.73% for sandy Manukau Harbour site; Holland et al. 1993). The potential effect that differences in sediment texture (sand to mud) and associated organic carbon content (0.2–several %) can have on trigger values for organic contaminants is illustrated in Table 4.

**Table 4.** Effect of sediment type and organic carbon content on the range of ANZECC ISQG-Low trigger values (in g/kg) for organic contaminants

Chemical contaminant	ISQG at OC of 1% (as used in Fig. 4)	ISQG at OC of 0.2% very sandy	ISQG at OC of 5% very muddy
High molecular weight PAHs	1700	340	8500
dieldrin	0.02	0.004	0.1
lindane	0.32	0.064	1.6
Total DDT	1.6	0.32	8
Chlordane	0.5	0.1	2.5
Total PCB	23	4.6	115

The effect of variation in OC levels on application of the ANZECC guidelines to Auckland estuaries is that guidelines for sandy sediments will be lower than those plotted in Figure 4 (and listed in the ANZECC (2000) guideline document, Table 3.5.1) and guidelines for muddy sites may be higher. Sandy sites with OC levels of (say) 0.2% will have guidelines of only 1/5<sup>th</sup> of those listed, while muds (typically 2–3%, but could be up to several %) will have guideline values of ca. 2–3 times higher than those listed (and plotted in Figure 4). Under the ANZECC regime, sandy sites are therefore more sensitive to the effects of organic contaminants than muddy sites.

The Auckland sites that exceed ANZECC trigger values (ISQG-low) are almost all muddy. The anomalously high value of DDTs in the relatively sandy Wesley Bay sediment (Holland et al. 1993) is the only exception found in the sites surveyed here. If the ISQG-low values were doubled (to account for a muddy sediment with 2%, rather than 1%, OC), there would be very few ISQG-low exceedances. Only DDT and dieldrin would have more than one or two sites above ISQG-low, and the dieldrin result is a consequence of the extremely low ISQG-low value. If the Canadian ISQG guideline value for dieldrin were used in place of the ANZECC ISQG-low, there would be few exceedances if a correction for OC content were made. The low reliability of the p,p'-DDE and total DDT guideline values also needs to be remembered when assessing the relevance of ISQG-low exceedance for these organochlorines.

We reiterate that we expect that this relationship of trigger values with organic carbon content will offer sufficient protection to Outer Zones.

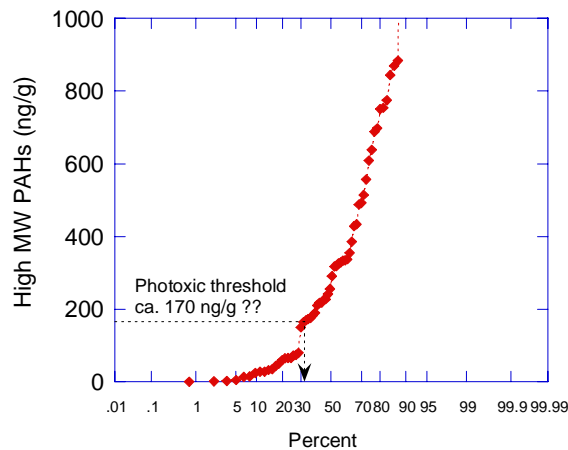
In summary, ISQG-low guidelines are exceeded in some Auckland estuarine sediments. Guidelines for organic contaminants are exceeded:

- In most places for dieldrin, because the ISQG-low value is excessively low (probably close to background levels).
- In some places where there has been a history of industrial pollution or spills (e.g. middle reaches of the Tamaki Estuary, Mangere Inlet, Henderson Creek).
- In muddy settling zones of estuaries receiving stormwater from old, fully urbanised catchments (e.g. Motions Creek).

**Phototoxicity.** There is currently insufficient information to assess the likely phototoxicity of Auckland sediments. However, phototoxicity will increase the toxicity of sediments under certain circumstances, although by how much, and under what conditions, are uncertain. If the increase in toxicity is similar to the approximately 10-fold increase observed for fluoranthene in water exposures (USEPA 1993b), then an ISQG-low value of approximately 170 ng/g high molecular weight PAH could result. The effect this would have on the potential toxicity of Auckland estuary sediments is depicted in Figure 5, which shows that 70% of the sites could have PAH levels that would be potentially phototoxic.

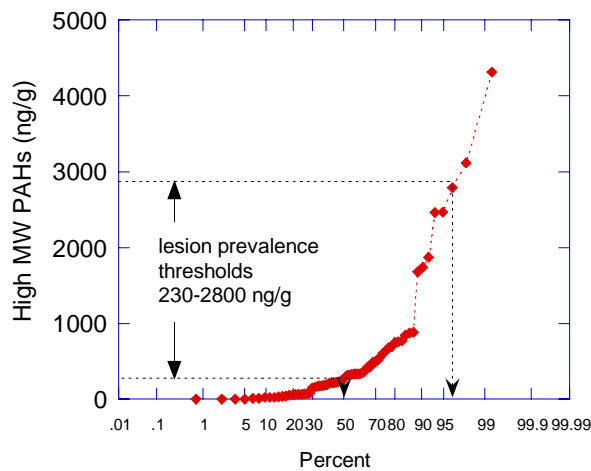
This assessment is clearly highly speculative, but it does highlight the large effect that increasing guideline sensitivity could have.

**Figure 5.** Comparison of high molecular weight PAH concentrations in Auckland estuary sediments with a hypothetical phototoxic threshold level. Approximately 70% of the sites could be phototoxic!



**Fish Health.** Figure 6 compares the distribution of PAH concentrations in Auckland sediments with potential thresholds for the onset of liver lesions in benthic fish (Horness et al. 1998). Approximately 50% of the sites could have PAH levels at which adverse effects on bottom-feeding fish might begin to occur (assuming that NZ species respond in a similar way to English sole in North American estuaries).

**Figure 6.** Comparison of PAH concentrations in Auckland estuaries with levels at which increases in the prevalence of various liver lesions were detected in English sole in the USA (Horness et al. 1998).



There has been some work on fish health and organic chemical contamination in Auckland estuaries (e.g. Diggles et al. 2000). This work showed that yellowbelly flounder (*Rhombosolea leporina*) from a relatively contaminated area around Onehunga Wharf in the Manukau Harbour had significantly higher prevalence of pre-neoplastic liver lesions than fish from other less chemically contaminated sites. While no conclusions on cause-effect relationship between fish health and chemical contaminants can be made from this work, it is consistent with the known adverse effects of chemicals such as PAHs and PCBs that have been found in overseas studies.

### 3.1.4 Implications for the Environmental Targets programme

There are a large number of sites that have one or more exceedance of ISQG-low. Under the ANZECC protocols, this means that many sites within the Settling Zone will require further assessment (Figure 1). The high exceedance of trigger values for dieldrin and to a lesser extent, DDT and chlordane needs to be reassessed. There is a need to debate the use of ER-L for ISQG-Low for Dieldrin, chlordane, DDT, and to consider instead the use of TEL or ISQG-CCME values. In Chapter 4, we examine the likely outcome of this assessment.

There are also a large number of sites that could exceed PAH concentrations associated with phototoxicity and fish health. Further research is needed on the possible phototoxicity of PAH to estuarine benthic animals and possible impact of PAH on fish health.

The implications for monitoring and exceedance in the Outer Zone are far less clear. For metals, more protective SQGs may need to be adopted e.g., total concentrations and not acid soluble. For organics, we assume that the linkage of trigger values to organic content will be protective. This needs to be checked.

## 3.2 Future Levels in Auckland Estuaries

### 3.2.1 Why do we need to consider future levels?

The concentrations of the major contaminants Cu, Zn and PAH are predicted to increase in the estuarine sediments in the future. This is because these contaminants will continue to be discharged from urban areas. Pb discharges will gradually decline. These are the major potentially toxic contaminants in stormwater. While there are many other toxic substances in runoff, they occur at much lower concentrations and their impact is unknown.

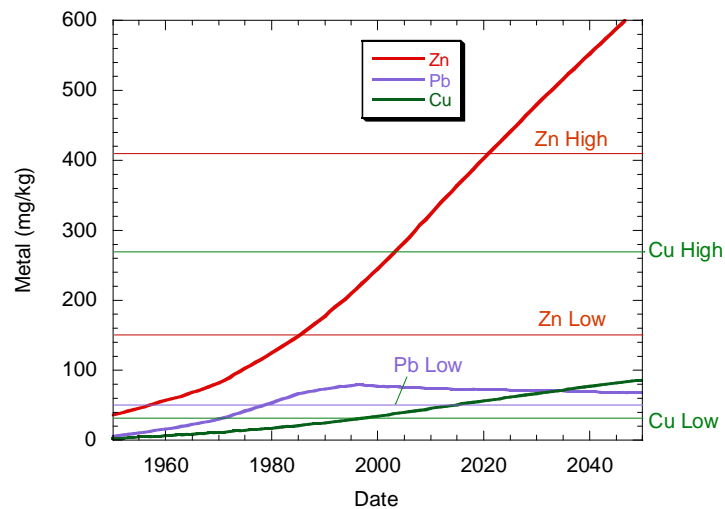
Estuaries tend to trap stormwater-derived contaminants because of the processes operating in the estuary. High proportions of the major contaminants in stormwater are adsorbed onto particulate matter, and reach the estuary in that form. Here fine particles may be flocculated and larger particles settle. Dissolved contaminants are diluted substantially when discharged to estuaries, and are not expected to exert toxic effects in the water column. They will also tend to adsorb onto particulate matter, especially under turbid conditions, and also be settled. Therefore, the fate of a large proportion of contaminants after entering the estuary is settling.

Once settled, particulate-associated contaminants can be resuspended by waves or large floods, dispersed by tidal currents to quiescent areas and mixed into the sediments by bioturbation. Their ultimate fate depends on the hydrodynamic energy of the estuary.

The rate of increase depends on the size of the input (urban area and type) and the nature of the estuary (degree of shelter, intertidal excursion).

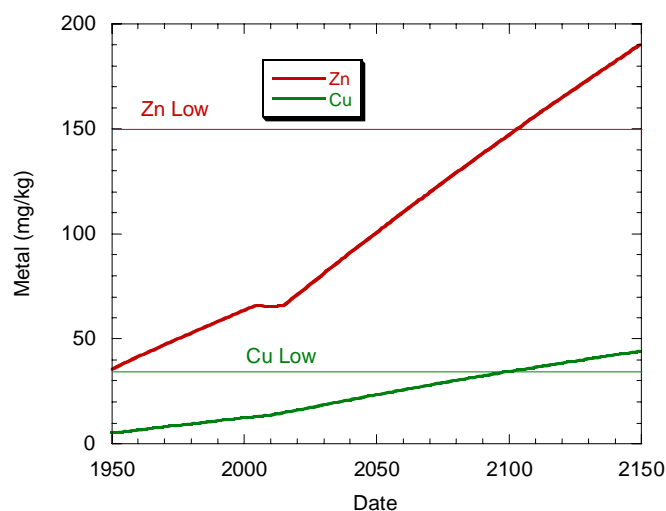
For Pakuranga Estuary, an estuary that has been progressively urbanized since 1960, and where there are no urban stormwater quality controls, the concentrations of Cu, Pb and Zn already exceed the ISQG-Low. Large increases in concentrations are predicted for Zn, which exceed the ISQG-High by 2020 (Figure 7). Smaller increases are predicted for Cu and PAH and Pb is predicted to decrease.

**Figure 7.** Predicted concentrations in Pakuranga Estuary. The horizontal lines indicate the ER-L and ER-M values (after Williamson et al. 1999b)



Concentration increases are predicted to be much less when stormwater is treated and where only a portion of the catchment is urbanized. For example, predicted concentrations for Zn and Cu in the Waiarohia estuary (Figure 8) are much less over a longer time scale. This catchment will have about 30% land area urbanized and the rest in rural living (1 ha blocks).

**Figure 8.** Predicted concentrations in Waiarohia Estuary (adapted from Diffuse Sources 2001). The horizontal lines indicate the ER-L and ER-M values.



For the other contaminants predictions are less precise. PAH concentrations are probably increasing in urbanised estuaries, and tentative predictions can be made, but this has not been validated. We suspect that the concentrations of other organics will remain static or decrease slowly, but we no information to confirm this. This needs further investigation.

At the present time, predictions can only be made for the Settling Zone, as illustrated by the examples above. Improved models have been developed (Green et al. 2001) which could be applied to the Outer Zone, but these are untested.

### 3.2.2 Implications for monitoring and management

Concentrations measured at the present time does not tell you what the concentration may be at some time in the future. For effective stormwater management, predictions will need to be made on the rate of increase in contaminants, in order to:

- anticipate if and when Environmental Targets are exceeded,
- to indicate the seriousness of the exceedance,
- help prioritise management response, and
- indicate the magnitude of source control or treatment needed to prevent exceedance of Environmental Targets.

Prioritisation should not be based solely on current or monitored levels. Estuaries with more rapid increase in contamination may justify a higher priority than those with lower rates of increase in contamination (all other factors being equal).

The major advantage of modelling contaminant build up is the ability to assess the level of source control or treatment needed to achieve a satisfactory rate of increase. It also anticipates the environmental outcomes, and allows managers to check whether implemented measures are justified.

These suggestions are not new or untried. In the past, the ARC has acknowledged the need to take this gradual build-up in concentrations into account with their approach to greenfields development, where limits are placed on the maximum allowable proportion of the catchment area that can be urbanized (the "14%" rule).

The ARC has used also used the predictive approach before in policy planning. (see Auckland Regional Council. 1994). A summary of this approach was described in Williamson & Hatton (1998).

### 3.3 Where will targets be exceeded at present and in the future?

The contaminants can be prioritized in terms of their likelihood to exceed the ISOQ-Low at present or in the future (Table 5) for Settling Zones. We cannot make comparable assessments for the Outer Zones with the present database.

**Table 5.** Likelihood of exceeding ANZECC (2000) ISQG-low values usually, often, occasionally, seldom, never in sheltered muddy estuaries with a significant proportion of urban land use.

	Zn	Cu	Pb	PAH	Organo-chlorines
Exceeds ISQG-low in present day					**
Exceeds ISQG-low in future					Insufficient data
Exceeds ISQG-high in future					Very unlikely

\*\* mostly dieldrin and DDT because of low values for ISQG-Low.

## 4 What happens when SQG triggers are exceeded?

For the Settling Zone, if total concentrations exceed the ISQG-Low, then the next step in the decision tree (Figure 1) is to consider whether concentrations exceed background concentrations. In our experience, background concentrations are low for Cu, Pb, Zn and organic pollutants c.f SQG in the Auckland Region, and this step is not necessary for these contaminants. [Note however, this step is important for As, Cr and Hg – P. Kennedy, Kingett Mitchell, pers. comm.]. The next step is to consider contaminant bioavailability.

“ If both the lower guideline trigger value and the background or reference site concentrations are exceeded, the next level evaluation will be to consider whether there are any factors which might lower the potential bioavailability of contaminants ” (ANZECC 2000).

The Guidelines suggest four possible approaches: acid soluble metals, the AVS model for metal toxicity, equilibrium partitioning model for organic contaminants, and interstitial water (pore water) concentrations.

### 4.1 Acid Soluble Metals

The following excerpt from ANZECC (2000) describes a possible approach for obtaining better estimates of bioavailable metal levels:

“ For metals, the speciation considerations might be:

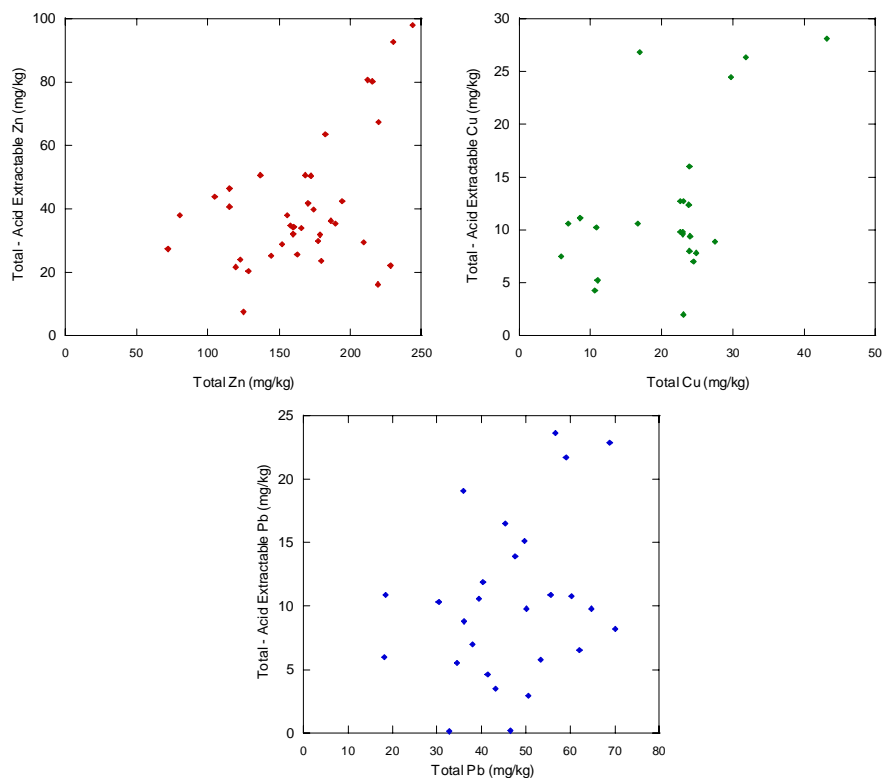
a) *Sediment speciation* — dilute-acid-extractable metals concentrations below lower guideline value. It is recommended that this should involve treatment of the sample with 1 M hydrochloric acid for 1 hour. Since a considerable fraction of the total metal concentration in sediments maybe present in detrital mineralised phases that are not bioavailable, a better estimate of the bioavailable fraction is desirable. Although the capacity of chemical extractions to selectively remove only this fraction is limited, a dilute-acid-extraction will not remove the mineralised fractions and will therefore provide more appropriate metal concentration data for use in new effects databases. Note that the field data used to derive the guidelines are likely to be based on total concentrations. Therefore a judgement against these measurements using discussion in speciation cannot be fully justified. Rather, such considerations should be applied in new guideline values developed from an NWQMS database” . [Taken from ANZECC (2000) section 3.5.5.2].

The suggestion would require careful checking. While there is no doubt that acid soluble metal is probably a better measure of the bioavailable portion than total metal concentration (usually strong oxidizing acid digests), the fact remains that the Effects Ranges were mainly based on total metal analysis. To accept the thesis that if ambient total concentrations exceed ISQG-Low then recourse should be made to acid soluble metals implies that the ER-L are too conservative (i.e., wrong). It also suggests that the ANZECC guidelines is deviating from its protective stance and is more concerned with avoiding false positive conclusions.

At high levels of contamination, acid soluble and totals are similar, but this may not hold at lower concentrations near the ISQG-Low. We do not have any Auckland data comparing Simultaneously Extractable Metal (SEM) – the procedure suggested in the ANZECC Guidelines) – with total metal. There is some unpublished data that has compared strong acid oxidizing extractions (heated, concentrated aqua regia) with acid soluble extractions (2M HCl overnight) (Figure 9). Clearly there are major differences between total and acid extractable at some sites. At most sites examined in Fig. 9, assuming that much of the scatter is experimental error, the difference is about 35 mg/kg for Zn, 10 mg/kg for Cu and 10 mg/kg for Pb. Thus the proposition to use acid extractable metals is quite significant. For example, it will shift many sites to having concentrations less than trigger values (Figure 3). The SEM procedure is far less rigorous (1 M HCl for 1 hour) compared with 2M HCl overnight, so the differences will be far greater.

The acid-soluble metal approach is consistent with allowing some degradation to occur in the Settling Zone. However, before this approach is ratified and adopted, the acid soluble method needs to be confirmed, and acid soluble– and total– concentrations and the magnitude of the effect evaluated.

**Figure 9.** Comparison of the difference between total and acid soluble, plotted against total concentrations.



## 4.2 The AVS model

The Acid Volatile Sulphide (AVS) model recognizes that a number of heavy metals form insoluble precipitates with sulphides in sediments, rendering the heavy metals non-bioavailable. When the concentration of heavy metals exceeds the concentration of sulphides (the "sulphide buffering capacity"), then heavy metals are released into the interstitial water where they are able to exert toxicity. The model has been well tested in North America.

The heavy metals react with FeS to form ZnS, CuS etc. This occurs because Zn, Cd, Cu and Pb are more insoluble than FeS. The AVS concentration is the sulphide associated with FeS, CdS, ZnS, PbS, NiS, CoS. In uncontaminated sediments, AVS is dominantly FeS.

Estuarine sediments contain relatively high concentrations of sulphide from anaerobic metabolism of organic matter. The rate of breakdown exceeds the ability of oxygen and other oxidants (e.g., nitrate), and the ability of microbes to use solid state MnO<sub>2</sub> and FeOOH. They therefore utilize SO<sub>4</sub><sup>2-</sup> and in the process produce sulphides.

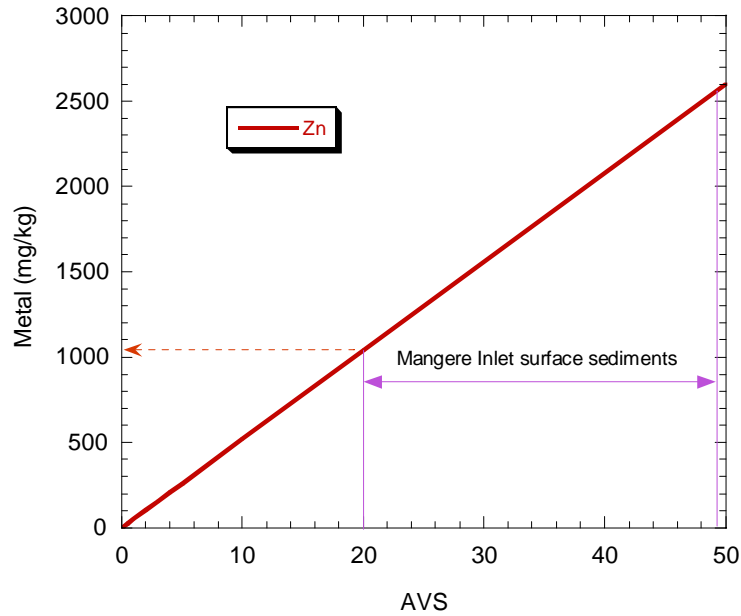
The application of the AVS approach is somewhat suspect when applied to relatively low heavy metal concentrations in the Auckland situation. The model was originally developed and tested in situations with relatively high metal concentrations and AVS concentrations. In these situations, when [SEM]>[AVS], there is a large excess of metals available to swamp the complexing/adsorption capacity of other sediment solid phases such as organic matter and FeOOH, and provide high concentrations of heavy metals in the pore water. This will happen to a much lesser extent at concentrations around ISQG-Low.

### 4.2.1 What are the AVS Concentrations in Auckland Sediments?

Many overseas studies have found high AVS concentrations and have shown that sediments were not acutely toxic when the heavy metal concentrations were lower than the AVS concentrations. High AVS concentrations can also be found in Auckland surface sediments (e.g., Mangere Inlet 20-50 µmole/g - Williamson et al. 1995). Concentrations of this magnitude are usually more typical of deeper surface sediments in Auckland (e.g., 0-10 cm) (Nipper et al. 1998, Morrisey et al. 1999). Concentrations of heavy metals necessary to exceed such AVS concentrations are very high (Figure 10), and much higher than presently observed in Auckland. An example is given in Figure 10 for surface sediments containing AVS concentration of 20 mmoles/kg. The AVS model would predict that Zn concentration would need to exceed 1000 mg/kg before the 'sulphide buffering capacity' is exceeded and Zn is predicted to become potentially toxic. Note that at this Zn concentration, the concentrations, Cu will be 170 mg/kg and Pb will be 300 mg/kg assuming Zn:Cu:Pb ratios observed in Pakuranga sediments.

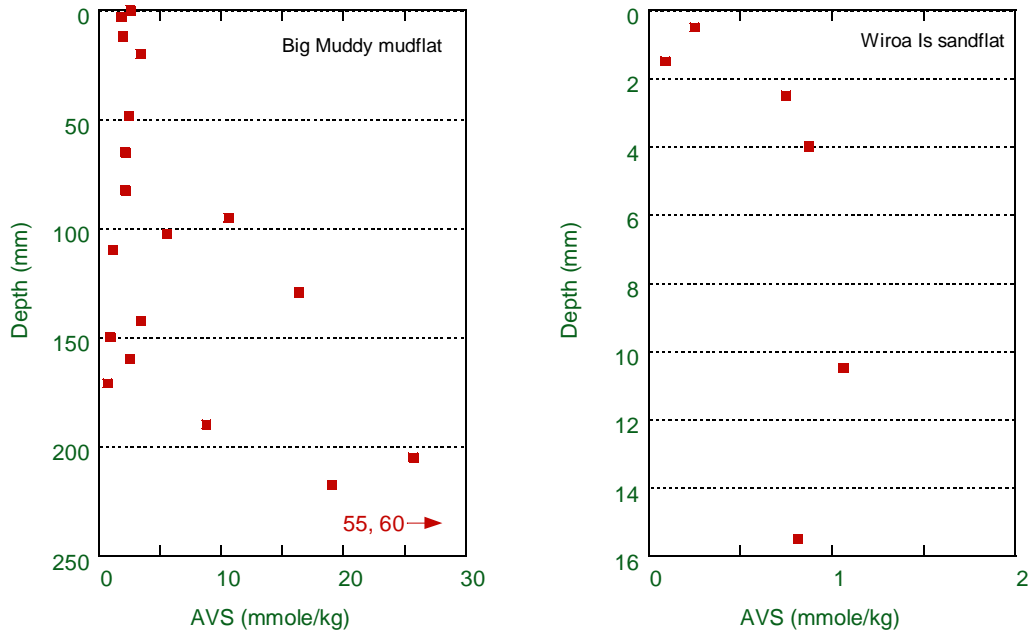
With these AVS concentrations, the AVS model would predict that metals are not toxic in Auckland sediments. However, most studies in Auckland have found substantially lower concentrations in intertidal sediments. This is because of strong bioturbation, where burrowing and burrow irrigation brings oxygen into the sediments, which in turn oxidizes AVS.

**Figure 10.** Potentially toxic Zn concentrations in sediments. The lower observed AVS concentration (mmol/kg) in Mangere Inlet (Williamson et al. 1995) is indicated with the predicted potentially toxic Zn concentration.



Shallow cores taken from Pukaki Creek, Big Muddy Creek, Mangere Inlet foreshore, Pakuranga Creek, Puherere, Hellyers (Williamson et al. 1994, Williamson et al. 1999a, Morrissey et al 1999, Bull & Williamson 2001) have looked at the spatial variation in AVS and showed the large influence of burrows. Figure 11 and Table 6 shows the variation of AVS concentrations with depth in a shallow core from Big Muddy Creek and Mangere foreshore. AVS concentrations of 2-4 mmole/kg are common in these muddy sediments at 0-2 cm. Even lower concentrations AVS concentrations were found in sandy sediments near Wiroa Is near Pukaki Creek (Williamson et al. 1994), and there is a strong inverse relationship between AVS and particle size (D. Bull, NIWA, pers. comm.).

**Figure 11.** AVS concentration profile in shallow core from Big Muddy Creek mudflat and Wiroa Is (Pukaki Ck) sand flat. Note the much smaller AVS concentration range (X-scale) for the Wiroa Is data.



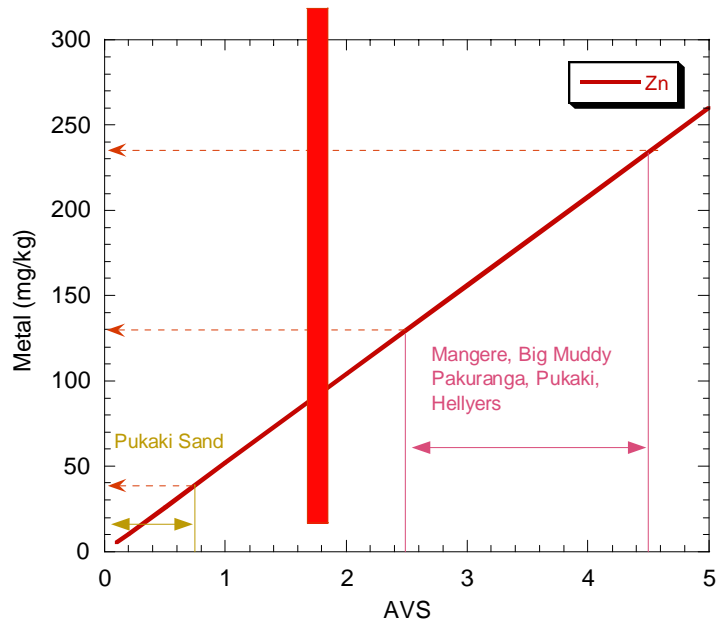
The reasons for large temporal difference between AVS concentrations found by Williamson et al (1995) and other studies hasn't been investigated, but may be due to seasonal variations in bioturbation, rates of formation of AVS, and/or organic matter supply (OM is the "fuel" that creates AVS).

**Table 6.** Variation in AVS concentrations (mmol kg<sup>-1</sup>) for different depth intervals in a shallow Mangere Inlet core.

Depth	0-1 cm	0-2 cm	0-5 cm	0-10 cm	0-15 cm
Mean AVS	3.4	3.8	4.3	8	11.8
Range	2.5-4.5	2.5-5.7	2.5-5.7	1.8-35.3	1.8-35.3

Concentrations of heavy metals necessary to exceed these AVS concentrations are relatively low (Figure 12). The potentially toxic Zn concentrations have been indicated on Figure 12 for some commonly encountered AVS concentrations in surface (0–2 cm) sediments. This occurs where acid extractable [Zn+Cu+Pb] = [AVS]. Unfortunately, we do not have data for SEM Zn (acid extractable in 1 M HCl for 1 hour) for the Auckland marine environment.

**Figure 12.** Potentially toxic Zn concentrations in sediments predicted from AVS concentrations (mmol/kg). The red bar shows the range of Zn measured in Auckland muddy sediments after overnight 2M HCl extraction.



#### 4.2.2 Implications of AVS model for Auckland

The concentrations of AVS in surface sediments are more usually low, and are similar to the sum of the concentrations of Cu, Pb and Zn commonly observed in Auckland. Therefore, the AVS model does not usually predict lower toxicity in Auckland sediments. The situation is even more extreme for sandy sediments, because these can have AVS concentrations less than 1 mmole/kg.

When considering deeper surface sediments there is probably sufficient AVS to precipitate all the heavy metals Cd, Cu, Ni, Pb, Zn as insoluble sulphides and render them largely unavailable to sediment-dwelling organisms. High concentrations of AVS have been observed in surface sediment as well from time to time.

The AVS data summarized above suggests that application of the AVS model as the next step in the ANZECC Decision Tree (Figure 1) will probably lead to the conclusion that the sediments are potentially toxic (i.e.,  $[SEM] > [AVS]$ ) and further investigation is needed.

There is a problem with applying the AVS model approach in site-specific cases. Measurement of AVS on one occasion may yield high AVS concentration and the implication that the sediments are well buffered against heavy metal toxicity. However, if AVS is controlling metal toxicity and the AVS concentrations are much lower at other seasons, such a conclusion would yield a false negative conclusion. We need to know more on the temporal variation of AVS concentrations in surface sediments in Auckland.

Note that the AVS model also identifies Zn as the major contaminant. This is because it is the most soluble (least stable) of the three metal sulphides, which decrease in order of solubility  $ZnS > PbS > CuS$ ,  $Cu_2S$ . Let us consider this more carefully and assume that the only heavy

metal contaminants are Cu, Pb and Zn (this is a reasonable assumption because levels of Cd, Ni and Co are low) in urban stormwater contaminated sediments. When the  $[Zn+Cu+Pb]>[AVS]$ , Zn will be potentially toxic, but not Cu or Pb. Because Zn is always in excess of Cu and Pb concentrations in urban stormwater contaminated sediments, ZnS acts as a 'buffer' to Cu and Pb toxicity, just as FeS acts as a buffer to Zn toxicity. In other words, the AVS model predicts that Cu will not be potentially toxic in urban stormwater impacted sediments. In other words, it will only be toxic when its concentration exceeds the AVS concentration. Further, the AVS model predicts that Pb will only be toxic when  $SEM[Pb+Cu]>[AVS]$ .

To summarise the forgoing paragraph, the AVS model predicts:

- Zn is potentially toxic when  $SEM[Zn+Cu+Pb]>[AVS]$ ,
- Pb is potentially toxic when  $SEM[Pb+Cu]>[AVS]$ ,
- Cu is potentially toxic when  $SEM[Cu]>[AVS]$ , and
- because Zn is far in excess of Cu and Pb, even if  $SEM[Pb+Cu]>[AVS]$  or  $SEM[Cu]>[AVS]$ , Zn concentrations will be so far in excess of AVS and the complexing capacity of other sediment phases that it would be a major toxicant in sediments.

Cd is the only other toxic metal that is more soluble than Zn in sulphide media. If its concentration increased to ISQG-Low concentrations, there would be concerns for its potential toxicity. This is unlikely, however.

In conclusion, our appraisal of the AVS model in the Auckland situation would predict that:

- only Zn is toxic of the three metals Cu, Pb and Zn,
- AVS concentrations are low enough to suggest Zn is a concern at some sites in the present day (and will become more of a concern in the future), and
- we recommend measurement or estimation of SEM and measurement of the temporal variability of AVS in Auckland sediments.

If  $SEM > AVS$  then the Guidelines specify that the bioavailability is further assessed through measuring pore water concentrations. We do not recommend this approach until further research designs more realistic methodology. Instead we recommend proceeding directly to toxicity testing.

If  $SEM < AVS$  then we recommend that this is not immediately categorized as "non-toxic", but further consideration is given to the likely seasonal variation of AVS, and whether significantly lower AVS concentrations will occur at that site at other times.

### 4.3 Pore water metal concentrations

The few pore water concentrations have been measured in Auckland sediments and summarized in Figure 13. These are concentrations in the pore water after it had been separated from the sediment by centrifugation. Also included in Figure 13 are burrow waters and surface runoff waters (rivulets flowing over and through contaminated sediments) from Mangere inlet.

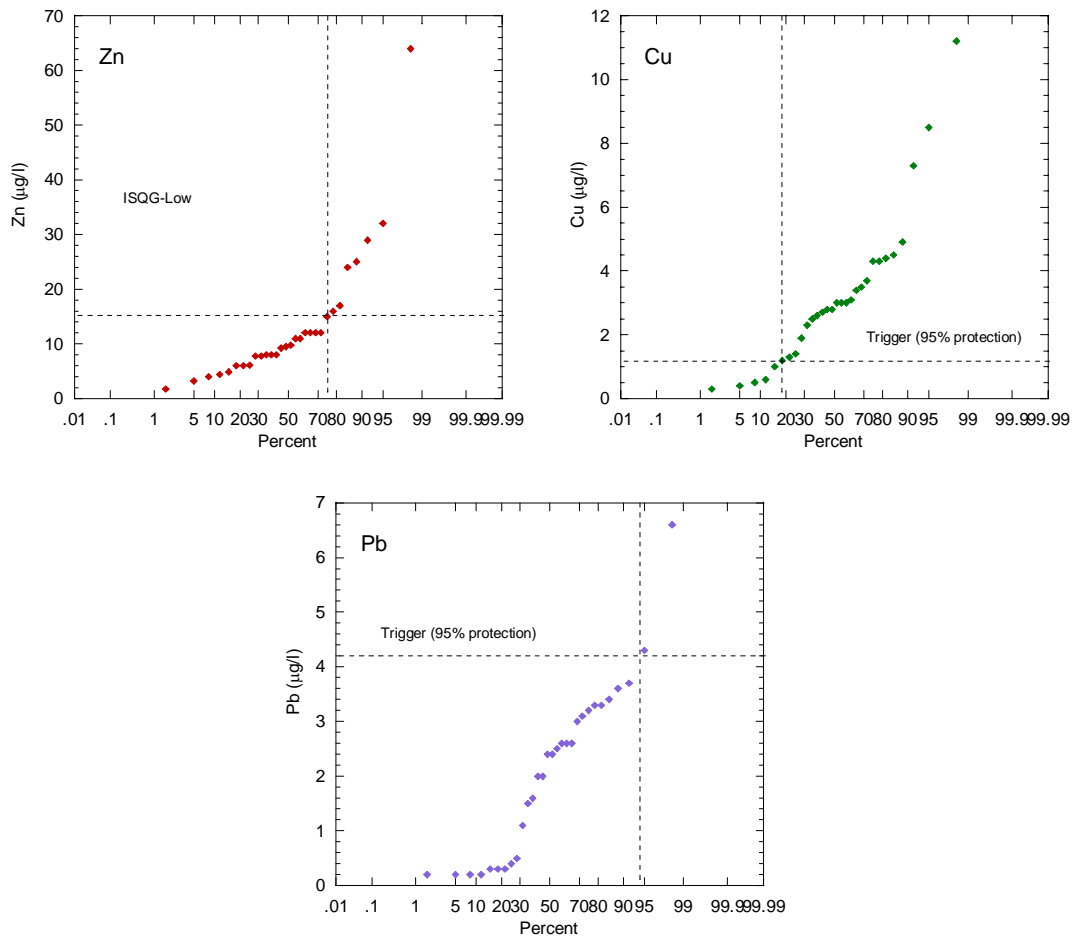
The ANZECC Water Quality Guideline (WQG) trigger value (for 95% protection) is often exceeded for Cu, occasionally for Zn, and seldom for Pb. (The 99% values for Cd and Ni were not exceeded and the data is not shown).

This preliminary assessment suggests (as with the AVS data) that the metal contamination of Auckland estuaries is potentially toxic in places and further work is needed.

There are major uncertainties in the approach of extracting pore water across the complex redox environments encountered in sediments (Williamson and Burgess *in press*; Adams et al. *in press*). Concentrations are likely to be highly variable across the profile measured. The most commonly used method, centrifugation, only measures an average concentration. This method also mixes sediments of different composition, which can both release metals (e.g., oxidation of AVS) or adsorb metals (e.g., precipitation of metal sulphides). The combined effects of all these mechanisms may have a large effect on the magnitude of pore water concentrations measured and may vary from site to site. Therefore measuring the pore water concentrations, to which individual species are exposed, is very difficult.

There are also important bioavailability issues in assessing exceedance, e.g., the "soluble" metals may be colloidal or complexed, and therefore have lower bioavailability.

**Figure 13.** Measured interstitial water concentrations (data summarised in Appendix 3).



#### 4.4 Comparison with Equilibrium Partitioning (Eq P) guidelines

Toxic threshold concentrations of some organic contaminants (for which there are water quality guideline values and USEPA EqP guidelines available) are compared with contaminant levels in typical urban sediment and a hypothetical “worst case” sediment in Table 7 and Figure 14.

Table 7 and Figure 14 show that for typical urban sediment (e.g. Pakuranga) there is a 30–1150 fold safety factor between sediment concentrations and the concentrations predicted by the EqP model to be toxic (at 1% OC). For a hypothetical worst-case sediment (highest concentrations of all contaminants in Auckland sediment database, and only 1% OC), there is a 3–76 fold safety factor. In reality, highly contaminated sediments would probably have a higher OC content than 1%, thus giving a greater safety margin than is shown here. Of those modelled, the contaminant coming closest to reaching a toxic level is the PAH fluoranthene.

**Table 7.** Comparison of EqP sediment quality guidelines for selected organic contaminants with concentrations in typical and “worst case” Auckland estuarine sediments. Comparison of shaded values for each contaminant shows that even in worst case conditions, EqP guidelines are unlikely to be reached.

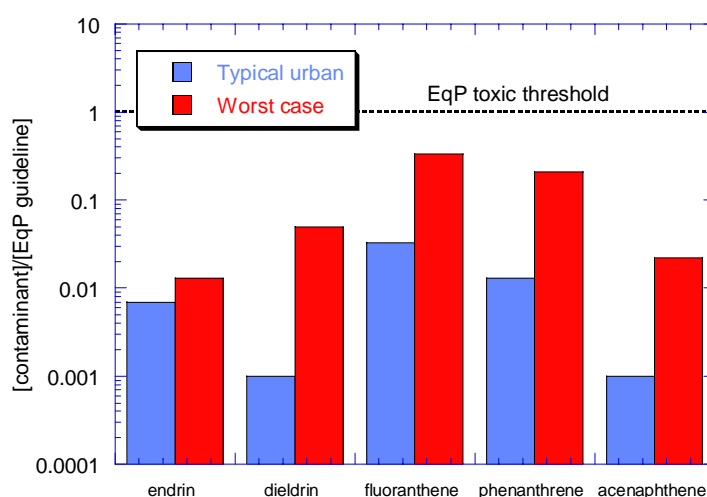
Contaminant	EqP sediment Quality Guidelines		Auckland estuarine sediments (g/g d.w.)	
	g/g OC	g/g d.w. (at 1% OC) <sup>a</sup>	Typical urban <sup>b</sup>	Worst case <sup>c</sup>
endrin	0.76	0.0076	<0.00005	<0.0001
dieldrin	20	0.2	0.0002	0.01
fluoranthene	300	3	0.1	1
phenanthrene	240	2.4	0.03	0.5
acenaphthene	230	2.3	0.002	0.05

<sup>a</sup> Guideline expressed in units of contaminant concentration per unit dry weight (d.w.) of sediment, assuming 1% organic carbon (OC) content. An OC level of 1% is probably low for a typical muddy sediment, which may be as high as several % OC. EqP-guidelines will be proportionately higher at higher OC levels (e.g. twice those listed above in a sediment with 2% OC).

<sup>b</sup> concentrations taken from Pakuranga Estuary

<sup>c</sup> concentrations are the highest from the Auckland sediment database used in this study (Appendix 2). There are higher levels in Auckland sediments, but these are usually associated with discrete, highly polluted zones e.g. port sediments

**Figure 14.** Comparison of organic contaminant concentrations in Auckland sediments with EqP-based sediment quality guidelines. Note the log scale, and that the predictions are based on sediments with 1% organic carbon.



An additional factor that would increase the margin between the contaminant concentrations and the EqP-predicted toxic thresholds is the presence of soot-carbon in the sediments. This highly aromatic form of organic carbon is known to bind aromatic contaminants, in particular PAHs, very strongly. This reduces the PAH partitioning into pore water, giving concentrations lower than might be predicted from the EqP model.

Preliminary measurements of soot-carbon content in Auckland estuary sediments indicated that up to 60% of the organic carbon present in sediments from Motions and Meola Creeks could be of this type, with highest levels in the finer sediment fractions (Mills, unpublished data). These measurements need to be checked (because they are so high), but if real could mean that PAHs in our urban estuaries are of low bioavailability, and hence will have lower toxicity than would be predicted by current guidelines.

In summary, this assessment shows that even in a worst-case scenario, toxic levels estimated by the EqP approach would not be found in Auckland estuarine sediments. It is conceivable that such levels might occur in small areas affected by gross pollution (e.g. spills, port sediments), but not for the significant areas for which we currently have data.

#### 4.5 Pore water organic concentrations

This is related to the EqP approach, but instead of predicting the pore water concentrations from sediment concentrations (the EqP approach), the pore water is actually analysed and the contaminant levels compared with water quality guidelines to assess potential toxicity.

Disadvantages with this approach are:

- Concentrations of organic contaminants in pore waters are difficult to reliably determine, especially for NZ sediments where contaminant levels are generally low. A reasonably large volume of pore water must be extracted from the sediment to allow the low levels of contaminants to be measured. The separation process can result in significant losses of the contaminants (which are readily adsorbed to laboratory apparatus used in the separation procedures), producing artificially low results.
- There are few water quality guidelines for organic contaminants to assess the potential effects of the pore water concentrations. e.g. ANZECC (2000) gives no marine water quality trigger values given for the organic contaminants commonly detected in the Auckland aquatic environment.

There are very few results from pore water assessments to use in the present project. The most recent attempts to obtain pore water concentrations of organics that we are aware of are for PAHs in pore water from two of Auckland's most contaminated estuaries, Motions and Meola Creeks, assessed in 2000 (Mills, unpublished data). The results from these determinations, and comparisons with predictions from the EqP model are summarised in Table 8.

**Table 8.** Preliminary concentrations of PAHs in sediment and pore waters from Motions and Meola Creek estuaries. Note the very low measured pore water concentrations compared with predictions made from the EqP model.

Measure	Motions Creek	Meola Creek
Total organic carbon (% , estimated)	1.0	2.0
Measured Total PAH <sup>a</sup> in sediment (ng/g)	8000	4700
Measured Total PAH in pore water (ng/L)	160	90
Predicted Total PAH in pore water (ng/L)	11500	3200
Ratio of Measured/Predicted PAH	0.0028	0.0014

a. Total of 16 PAHs for which appropriate physicochemical data were found (e.g.  $K_{ow}$  or  $K_{oc}$ )

The data listed in Table 8 indicate that pore water concentrations of PAHs are either much lower than would be predicted based on EqP, or that substantial losses of PAHs occurred

during analysis. Even if 90% of the PAHs were lost during separation of pore water from the sediment, the pore water concentrations would still be 14% (Meola) and 28% (Motions) of the predicted levels. Clearly, there is a large disparity between actual and predicted levels of PAHs in sediment pore waters.

The toxicity of these pore waters is difficult to predict. The pore water PAH concentrations are very low, but there are few water quality guidelines with which to compare them. As a basis for comparison, the old USEPA (1993) Final Chronic Value for fluoranthene (which was used in the EqP-derived SQG) was 2960 ng/L (or 260 ng/L in UV light). This compares with pore water concentrations of 15 ng/L and 9 ng/L for Motions and Meola Creeks respectively. These are well below even the more sensitive UV-exposure guideline value. It would appear, therefore, that pore water toxicity from PAHs is unlikely to occur.

## 4.6 Toxicity testing

As described above, the ANZECC ISOQ-Low is not completely protective because the final arbitrator in the decision tree is toxicity testing, and at present, there are only 3 toxicity test organisms available for sediment testing. If after following the risk-based decision tree, a toxic response is encountered, it is highly likely that the sediments will have an ecological effect. However, if a non-toxic response is encountered, there is no surety that ecological effects will not occur. Therefore the present level of ecosystem protection from sediment toxicity testing is not high.

Nonetheless, we believe that the toxicity tests are robust in themselves, and that they are a suitable assessment of bioavailability in the context of partial degradation of settling zones.

We also recommend that phototoxicity assessment is included in the toxicity testing.

## 4.7 Conclusions on Bioavailability Procedures

### 4.7.1 Acid soluble

The ANZECC proposal to measure acid soluble rather than total needs careful consideration of the method used to measure acid soluble, the relationship between total and acid soluble levels, and the implications for pass/fail trigger values. The approach would favour the proposition that Settling Zones have a lower level of protection and that some degradation is allowable, and reduce the costs and demands of remedial action.

### 4.7.2 AVS

Present levels that have been measured in bioturbated surface sediments would lead to the AVS model predicting potential toxicity. However, there may be sites with higher AVS concentrations, as we have encountered a few times. It would be necessary to measure AVS at the monitoring site in all seasons.

### 4.7.3 Pore water

We need lots more data and experience to assess the efficacy of this step for heavy metals contamination. We doubt whether this approach is worth pursuing for the relatively low levels of contamination associated with ISQG-Low values, given the uncertainties outlined above. The efficacy of measuring pore water concentrations of heavy metals would need to be addressed through a research programme. This needs to be debated. There is no point in pursuing this approach with organic contaminants PAH and organochlorines.

### 4.7.4 Equilibrium Partitioning

There is no point in undertaking equilibrium partitioning predictions of pore water concentrations when assessing exceedance of target values.

### 4.7.5 Recommendations

For the Settling Zone, if sediment contaminant levels exceed ISQG-Low, we have insufficient information to ratify all the steps in the follow-up procedures. The use of acid soluble levels needs to be further investigated and debated. AVS should be measured, but a clear understanding of seasonal effects is required. There is no point in measuring or predicting pore water concentrations. However, toxicity testing is a valid endpoint in the decision process for settling zones.

We believe it would be highly profitable to debate the possibility of developing unique Environmental Targets for the Settling Zones from toxicity testing. This is in line with the ANZECC philosophy. The ubiquity of the type and ratios of urban derived contaminants simplifies the contamination issues and lends itself to such an approach. A range of sediments from sites that presently exceed the ISQG-Low and ER-L could be tested for toxicity to amphipods and worms. The results could then be used to develop pass/fail target values.

## 5 Incorporating monitoring and future predictions into the Environmental Targets programme

### 5.1 Monitoring

Monitoring present day levels will identify exceedance and allow priorities to be set. Monitoring needs to include organic carbon, AVS, particle size as well as the contaminants.

We do not recommend monitoring to include parameters to assess fish health; this requires a research programme.

Monitoring will also provide useful information for predictive model coefficients and calibration data for model predictions.

Toxicity testing of sediments from sites that exceed ISQG-Low may lead to improved trigger values for the Settling Zone (see Section 4.6.5).

### 5.2 Monitoring methods

For the Settling Zone we recommend the ARC Long Term Baseline method (ARC 1998).

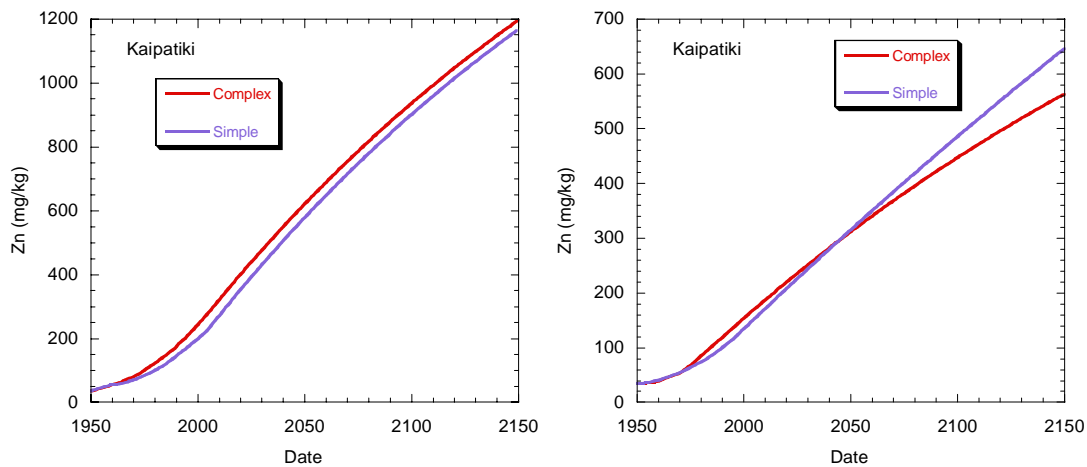
For settling areas, which may not meet the criteria for Settling Zones (see Williamson and Green 2001), a similar number of samples should be collected (and composited) from over a wider area. This is to overcome the possibility of strong concentration gradients. Because of the difficulty of sampling in these muddy environments, high tide sampling may be preferable, but the method needs to be tested.

For Outer Zones, we propose a similar procedure to the LTB method, except that a wider area (50m x 100m) is sampled.

### 5.3 Is a simple version of the USC Model useful?

Most time spent in assembling the USC model comes from interrogating information on catchment development (council records, aerial photographs) in order to assemble a detailed history of development. It would be useful to have a simple version of the USC model, than uses an approximate history of development and some default values for minor parameters. Figure 15 compares a simple prediction of metal concentrations in Pakuranga Creek and Kaipatiki Creek with the more complex model predictions, and shows that there is reasonable agreement.

**Figure 15.** Comparison of simple and complex (Williamson & Morrisey 1999) predictions.



We therefore recommend that simple predictive modelling is carried for any Settling Zone, and these predictions are included in the assessment of Environmental Targets.

However, the choice of parameters was relatively simple for these well-known cases, and this will not be the case for new areas for which we have little information or experience.

It is therefore very important that modelling predictions include error bounds, because there is a great deal of uncertainty in the parameters, and that this uncertainty needs to be included in the assessment. An example of this is shown in Figure 15. (The monitoring programme will provide useful information for predictive model coefficients and calibration data for model predictions).

The inclusion of error bounds helps prioritization. This is illustrated in Figure 16 for the situation where decisions are based on predicted concentration in the year 2100.

When the SQG > upper bound (Case A), then future concentration is not potentially toxic (and further action is unnecessary).

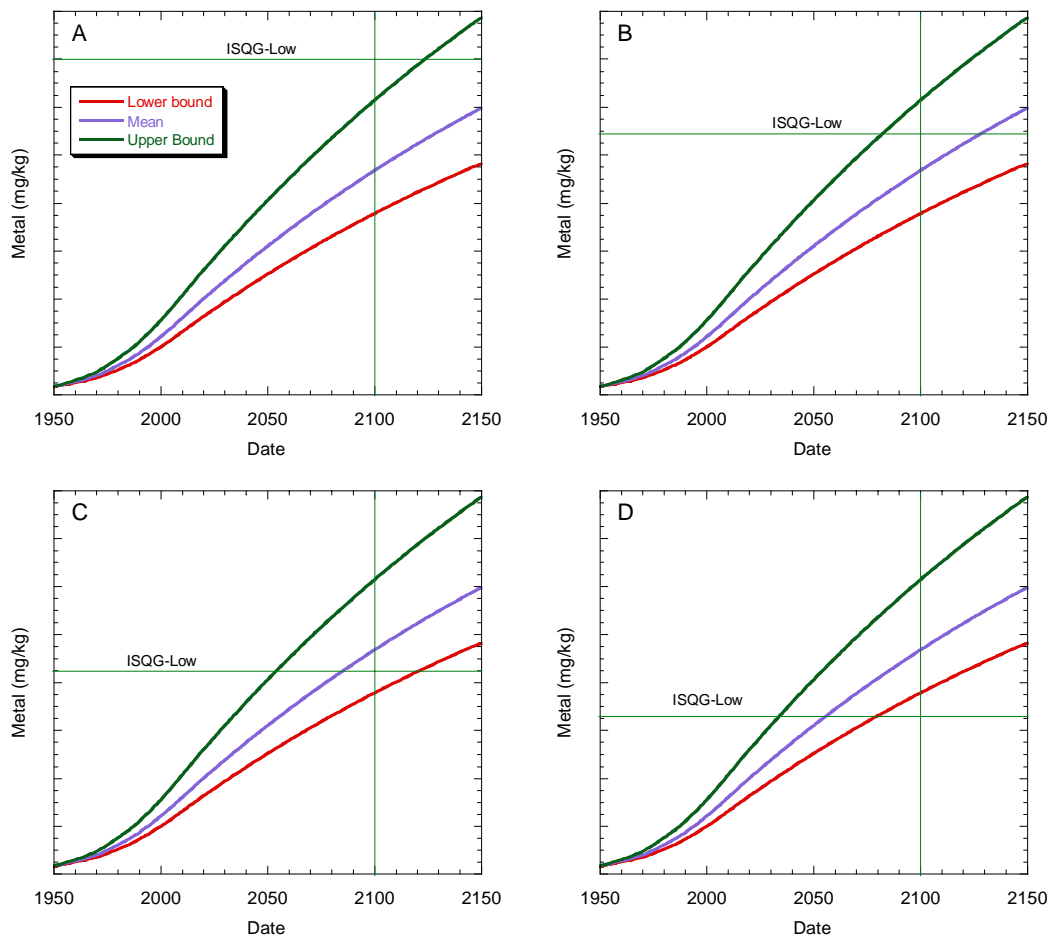
When the upper bound > SQG > mean (Case B), then future concentration might be potentially toxic, so further assessment is recommended such as refining modelling. If the condition - upper bound > SQG > mean - still holds, then further assessment is warranted. For example, simple catchment management may shift the situation to Case A, or the situation may be given low priority.

When the mean > SQG > lower bound (Case C), then the future concentration is potentially toxic, and there is a higher priority for further investigations/management intervention.

When the lower bound > SQG (Case D), then future concentration is highly likely to be toxic, and assessment for remediation has highest priority.

These model predictions can only be applied to the Settling Zone. There is a new model with which one can make broader predictions including OZ (Green et al. 2001), which is likely to be tested in late 2002.

**Figure 16.** Model predictions incorporating uncertainties (see text).



## 5.4 Recommended decision process<sup>3</sup>

### 5.4.1 Settling Zone

Step 1A: Measure levels of contamination, organic carbon, AVS and particle size.

Step 1B: Do predictions of future levels of contamination.

Step 2: If  $[X]_{\text{present}} > \text{SQG}$ , then proceed with the revamped ANZECC Protocol (see section 6.4).

Step 3: If  $[X]_{\text{future}} < \text{SQG}$ , no problem

Step 4: If  $[X]_{\text{future}} > \text{SQG}$  then

(i) Assign confidence factor based on Figure 16

<sup>3</sup>  $[X]_{\text{present}}$  = present day contaminant concentrations,  $[X]_{\text{future}}$  = future contaminant concentrations,  $[\text{metals}]_{\text{mud}}$  = heavy metal concentration in the mud fraction,  $[\text{toxic organics}]_{\text{OM}}$  = toxic organic concentration normalised to organic matter content.

(ii) Assess whether treatment, structure plan, source control bring  $[X]_{\text{future}} < \text{SQG}$

(iii) Combine with Step 2A and prioritise and design remedial action.

## 5.4.2 Outer Zone

Step 1: Monitor

Step 2A: If  $[\text{metals}]_{\text{mud}} > \text{SQG}$  or  $[\text{toxic organics}]_{\text{OM}} > \text{SQG}$  then reconsider source control for contributing catchments or SZ.

There is a need to develop the new prediction procedures (Green et al. 2001) into a useful tool which can generate knowledge and understanding of contaminant trends in the OZ, so more considered management decisions can be made.

## 6 Summary: Environmental Targets and the Settling and Outer Zone Concept

### 6.1 ARC Requirements

The ARC requires SQG for the Settling Zone (SZ) and the Outer Zone (OZ) of Auckland's estuaries. It could be argued that the SZs, which accumulate the bulk of stormwater-derived contaminants, should have less-protective targets because these areas are already contaminated (some sites already exceed SQG) and have more robust animals. ARC could therefore allow some degradation of the SZ (e.g., to allow for "mixing" and balance the high costs or difficulties of retrofitting stormwater treatment). Outer Zones were envisaged to require greater protection, because these areas are larger and have more diverse habitats, have less robust animals, and concentrations presently do not exceed SQG.

### 6.2 Recommended Targets

The new ANZECC guidelines (2000) would seem to be the most appropriate guidelines to form the basis for target values (after the suggested changes to the value of ISQG-Low in section 6.3). The guideline values are termed "trigger" values, because if exceeded, they are a prompt for further investigations. Their basis is a risk-based decision tree that progresses through a hierarchy of measurements of increasing complexity to reach a decision as to whether the sediment concentrations are likely to be toxic or not, the final arbitration being toxicity tests. The current ISQG-Low and the accompanying decision tree is designed to ensure that there is a low probability of false positives.

This means that the ANZECC ISQG-Low values be used as the Target Values for the Settling Zone. For sediments to be classified as "toxic", toxicity to laboratory test animals needs to be demonstrated. If a toxic response is encountered, it is highly likely that the sediments will have an ecological effect. However, if a non-toxic response is encountered, there is no surety that ecological effects will not occur. Thus the ANZECC guidelines demonstrate a measure of protection but allow for the possibility of some ecological degradation, which is consistent with management goals for the Settling Zone and with the ANZECC philosophy of trigger values for "slightly-moderately degraded ecosystems".

For the Outer Zone, where Environmental Targets seek to prevent ecological effects, much more stringent criteria are required. Therefore the ANZECC approach, which is based on the laboratory toxicity of whole sediments, is not adequately protective. In this report we assess the possibility of having trigger values that are based on concentrations in the mud fraction rather than in the whole sediment. For organics, however, because trigger values are calculated from the organic carbon content, they are applicable directly to both Settling and Outer Zones. The lower organic content in sandy sediments effectively lowers the trigger value for organic contaminants for the OZ. Conversely, the higher organic content in muddy sediment increases the trigger value.

We believe it would be highly profitable to use toxicity testing to develop unique Environmental SQG for the Settling Zones. This is in line with the ANZECC philosophy. The ubiquity of the type and ratios of urban-derived contaminants within a relatively small region simplifies the contamination issues and support such an approach.

### 6.3 Suggested changes to ISQG-Low

The following Table 9 lists ANZECC ISQG-Low and our recommended alternatives to the ISQG-Low values. Note these recommendations only refer to urban stormwater contamination within Auckland marine sediments, and are based on local knowledge and an assessment of the ANZECC SQG values and procedures in the local context. Deriving local values is entirely consistent with the ANZECC philosophy.

Values for Zn and Cu were obtained from unpublished studies on Hong Kong sediments, and so do not have the robustness of the ER-L values. We recommend that the ER-L values be retained.

For the organochlorines, we recommend adopting the Canadian Interim Sediment Quality Guidelines (CCME 1999), and the Florida Department of Environmental Protection (Mac Donald 1996) instead of the ER-L values. The former are more robust because of the inclusion of no-effects data. This is particularly true for dieldrin.

**Table 9.** Recommended changes to ANZECC (2000) ISQG-Low.

Contaminant	ANZECC	Recommended	Source
Cu	60	34	ER-L
Zn	200	150	ER-L
Chlordane	0.5	2.3	ISQG (CCME)
p, p'-DDD	2	3.2	ISQG (CCME)
p,p'-DDE	2.2	2.1	ISQG (CCME)
Total DDT	1.6	3.9	TEL
Dieldrin	0.02	0.72	ISQG (CCME)
Lindane	0.32	0.3	ISQG (CCME)
Total PCB	23	24	ISQG (CCME)

### 6.4 Suggested changes to ANZECC Decision Tree

The use of acid soluble levels for heavy metals needs to be further investigated and debated. AVS should be measured, but a clear understanding of seasonal effects is required. There is no point in measuring or predicting pore water concentrations. Toxicity testing is a valid endpoint in the decision process for settling zones, and we recommend adding the assessment of phototoxicity to the presently recommended tests (worms, amphipods ± phototoxicity, benthic algae).

## 6.5 Present Situation in Auckland Estuaries

How do the concentrations of contaminants currently present in Auckland estuarine sediments compare with the various sediment quality guidelines described above?

These studies have shown that for metals basically:

- sediments in any sheltered muddy settling area (SZ) whose contributing catchment is strongly urbanized will exceed ER-L and in extreme cases, the ISQG-Low,
- SZ with partially or recently urbanised catchment areas will have sediment concentrations sediments that do not exceed the ER-L or ISQG-Low at the present time, and
- sediments in exposed areas (sandy sediments) (e.g, OZ) will not exceed the ER-L or ISQG-Low except near the SZ/OZ boundary.

In OZ, exceedance of the ISQG-low or ER-L in the mud fraction of muddy sediments largely mirrors exceedance in the total sediment. For more sandy sediments, sites near the SZ of older urban areas often exceed the SQG values in the mud fraction. Sites away from the SZ/OZ boundary are less likely to exceed SQG

ISQG-low Guidelines for organic contaminants are exceeded:

- In most places for dieldrin, because the ISQG-low value is excessively low (probably close to background levels).
- In some places where there has been a history of industrial pollution or spills (e.g. middle reaches of the Tamaki Estuary, Mangere Inlet, Henderson Creek).
- In muddy settling zones of estuaries receiving stormwater from old, fully urbanised catchments (e.g. Motions Creek).

## 6.6 Monitoring

Monitoring needs to include organic carbon, AVS, particle size as well as the contaminants.

For the Settling Zone we recommend the ARC Long Term Baseline method (ARC 1998), which collects composite samples from a 20 x 50 m area.

For settling areas, which may not meet the criteria for Settling Zones (see Williamson and Green 2001), a similar number of samples should be collected (and composited) from over a wider area. This is to overcome the possibility of strong concentration gradients. Because of the difficulty of sampling in these muddy environments, high tide sampling may be preferable, but the method needs to be tested.

For Outer Zones, we propose a similar procedure to the LTB method, except that a wider area (50m x 100m) is sampled.

## 6.7 Recommended decision process

### 6.7.1 Settling Zone

Step 1A Measure levels of contamination, organic carbon, AVS and particle size.

Step 1B Do model predictions of future levels of contamination.

Step 2 If  $[X]_{\text{present}} > \text{SQG}$ , then proceed with the revamped ANZECC Protocol (see section 6.4).

Step 3 If  $[X]_{\text{future}} < \text{SQG}$ , no problem

Step 4 If  $[X]_{\text{future}} > \text{SQG}$  then

(i) Assign confidence factor based on relation of predicted concentration and its confidence limits to the SQG,

(ii) Assess whether treatment, structure plan, source control bring  $[X]_{\text{future}} < \text{SQG}$

(iii) Combine with Step 2A and prioritise and design remedial action.

### 6.7.2 Outer Zone

Step 1 Monitor

Step 2A If  $[\text{metals}]_{\text{mud}} > \text{SQG}$  or  $[\text{toxic organics}]_{\text{OM}} > \text{SQG}$  then reconsider source control for contributing catchments or SZ.

There is a need to develop the new prediction procedures (Green et al. 2001) into a useful tool which can generate knowledge and understanding of contaminant trends in the OZ, so more considered management decisions can be made.

## 7 References

- Adams, B., Burgess, R., Gold, G., LeBlanc, L., Liber, B., Williamson, B. *In press*. Pore water chemistry; effects of sampling, handling, storage and toxicity testing. *In "Porewater Toxicity"* Edrs., Carr, R.S., Nipper, M., Germano, J., Schreider, R. Setac Press, Pensocola, FL.
- ANZECC (2000). Australian and New Zealand Guidelines for Fresh and Marine Water Quality. National Water Quality Management Strategy. Australian and New Zealand Environment and Conservation Council. Agriculture and Resource Management Councils of Australia and New Zealand. Canberra, Australia.
- ARC (1991). Tamaki Estuary Water Quality Survey 1988–1991. ARC Environment and Planning Division Technical Publication No. 12, August 1992.
- ARC (1998). Marine sediment monitoring programme design and 1998 results. NIWA Client Report 90240.
- ARC (1999). Marine sediment monitoring programme: 1999 results. NIWA Client Report 00253.
- Auckland Regional Council. (1994). Auckland Strategic Planning Study. Ecological Impact Evaluation. Letter to Territorial Authorities in the Auckland Region). ARC (1998) LTB
- Bull, D.; Williamson, R.B. (2001). The relationship between colour and sediment chemistry. *Environ. Sci. Technol* 35(8) 1658-1662.
- CCME (1999). Canadian environmental quality guidelines. Canadian Council of Ministers of the Environment, Winnipeg.
- Chapman, P.M.; Allard, P.J.; Vigers, G.A. (1999). Development of Sediment Quality Values for Hong Kong Special Administrative Region: A Possible Model for Other Jurisdictions. *Marine Pollution Bulletin* 38(3): 161–169.
- Diffuse Sources Ltd. (2001) A detailed assessment of the impacts of stormwater loads on the Waiarohia Estuary and Upper Waitemata Harbour. For Waitakere City Council.

- Diggles, B.K.; Smith, M. et al. (2000). Final report on the parasites and pathological lesions of yellowbelly flounder *Rhomboselea leporina* and their relationship with contamination in Mankau Harbour. NIWA Client Report WLG 2000/24, prepared for Auckland Regional Council.
- Green, M.; Williamson, R.B. et al. (2001). Prediction of contaminant accumulation in estuaries. NIWA Client Report ARC01252.
- Gustafsson, O.; Haghseta, F.; et al. (1997). Quantification of the dilute sedimentary soot phase: implications for PAH speciation and bioavailability. *Environmental Science and Technology* 31: 203–209.
- Holland, P.T.; Hickey, C.W. et al. (1993). Variability of Organic Contaminants in Inter-tidal Sandflat Sediments from Manukau Harbour, New Zealand. *Archives of Environmental Contamination and Toxicology* 25: 456–463.
- Horness, B.H.; Lomax, D.P. et al. (1998). Sediment quality thresholds: Estimates from hockey stick regression of liver lesion prevalence in English Sole (*Pleuronectes vetulus*). *Environmental Toxicology and Chemistry* 17(5): 872–882.
- Hyland, J.L.; Van Dolah, R.F.; Snoots, T.R. (1999). Predicting stress in benthic communities of Southeastern U.S. estuaries in relation to chemical contamination of sediments. *Environmental Toxicology and Chemistry* 18(11): 2557–2564.
- Larcombe, M.F. (2001). Stormwater disposal to the Auckland urban coastal marine area: receiving environment objectives, criteria, and monitoring. Working document. ARC files.
- Long, E.R.; MacDonald, D.D. et al. (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management* 19: 81-97.
- MFE (1998). Organochlorines in New Zealand: Ambient concentrations of selected organochlorines in estuaries. Organochlorines Programme report by S. Scobie, S.J. Buckland, H.K. Ellis, and R.T. Salter. November 1998, Ministry for the Environment, Wellington, NZ.
- Morrisey, D.J.; Williamson, R.B.; Van Dam, L.; Lee, D.J. 2000. Stormwater contamination of urban estuaries. Testing a predictive model of the build-up of heavy metals in sediments. *Estuaries* 23, 67-79.

- Morrisey, D.J.; DeWitt, T.H.; Roper, D.S.; Williamson, R.B. 1999. Variation in the depth and morphology of burrows of the mud crab, *Helice crassa*, among different types of intertidal sediment in New Zealand. *Marine Ecology Progress Series* 182, 231-242.
- Myers, M.S.; Landahl, J.T. et al. (1994). Relationships between toxicopathic hepatic lesions and exposure to chemical contaminants in English sole (*Pleuronectes vetulus*), starry flounder (*Platichthys stellatus*), and white croaker (*Genyonemus lineatus*) from selected marine sites on the Pacific Coast, USA. *Environmental Health Perspectives* 102: 200–215.
- Nipper, M.G.; Roper, D.S. et al. (1998). Sediment toxicity and benthic communities in mildly contaminated mudflats. *Environmental Toxicology and Chemistry* 17(3): 502–510.
- O'Connor, T.P.; Paul, J.F. (2000). Misfit Between Sediment Toxicity and Chemistry. *Marine Pollution Bulletin* 40(1): 59–64.
- Smith, S.L.; MacDonald, D.D.; Keenleyside, K.A.; Gaudet, C.L. (1996). The development and implementation of Canadian Sediment Quality Guidelines. In: Munawar, M. & Dave, G. (ed.). *Development and Progress in Sediment Quality Assessment: Rationale, Challenges, Techniques & Strategies*, pp 233-249.
- Swatz, R.C.; Schults, D.W. et al. (1995). ΣPAH: A model to predict the toxicity of polynuclear aromatic hydrocarbon mixtures in field-collected sediments. *Environmental Toxicology and Chemistry* 14(11): 1977–1987.
- USEPA (1993a). Technical basis for establishing sediment quality criteria for non-ionic contaminants for the protection of benthic organisms by using equilibrium partitioning. EPA 822-R-93-011. Office of Science and Technology, Washington, DC.
- USEPA (1993b). Sediment Quality Criteria for the Protection of Benthic Organisms: Fluorathene. EPA 822-R-93-012. Office of Science and Technology, Washington, DC.
- Williamson, R.B; Green, M. (2001). Regional Identification of Settling Areas. For Auckland Regional Council.
- Williamson, R. B.; Hume, T. M.; Pridmore, R. D.; Smith, D. G.; Thrush, S.J.; Wilcock R. J.; Glasby, G.P. 1991. Factors affecting the fate of contaminants in the Manukau Harbour. For Auckland Regional Council

- Williamson, R. B.; Hume, T. M.; Mol, J. 1994: A comparison of the early diagenetic environment in intertidal sand and muds of the Manukau Harbour, New Zealand. *Environmental Geology* 24: 254-266.
- Williamson, R. B.; Mol, J.; Van Dam, L. 1995: Trace metal partitioning in bioturbated, contaminated, surficial sediments from Mangere Inlet, New Zealand. *N. Z. J marine and freshwater research* 29, 117-130.
- Williamson B.; Hatton C. (1998). Stormwater contaminants in estuaries. *Aniwaniwa, No.8*.
- Williamson, R.B.; Wilcock, R. J.; Kerr, B. E.; Pickmere, S. E. 1999a: The effect of burrowing by the crab *Helice crassa* Dana on the sediment chemistry in intertidal sediments. *Environmental Toxicology and Chemistry* 18, 2078-2086.
- Williamson, R.B.; Morrissey, D.J. 2000. Stormwater contamination of urban estuaries. Predicting the build-up of heavy metals in sediments. *Estuaries* 23, 56-66.
- Williamson, Bruce and Burgess, Rob. *In press*. Sediment and pore water chemistry. *In "Porewater Toxicity"* Edrs., Carr, R.S., Nipper, M., Germano, J., Schreider, R. Setac Press, Pensocola, FL.
- Williamson, R.B., et al. 1999b. "The build up of contaminants in urbanised estuaries". Proceedings of the Comprehensive Stormwater and Aquatic Ecosystem Management Conference, Auckland, February 1999. Vol 1, pp 59-66.

# Appendix 1: Co-occurrence Based Sediment Quality Guidelines

The most commonly used Sediment Quality Guidelines (SQGs) are based on the “co-occurrence” approach, where the concentrations of contaminants in bulk sediments are related to the incidence of a variety of adverse biological effects that are observed for these sediments in laboratory and field tests. This empirical approach provides ranges of chemical concentrations in sediments in which adverse biological effects are i) rarely observed, ii) sometimes observed, or iii) frequently observed. Large databases of chemical concentrations and associated biological effects have been compiled for US estuaries to derive and test these SQGs.

This approach has been used to formulate the Effects Range values of Long et al (1995), the Canadian SQGs (Smith et al. 1996, CCME 1999) and the recent ANZECC guidelines (ANZECC 2000).

Advantages of this approach include:

- Guidelines are based on a large number of observations covering a wide range of chemical concentrations and estuarine areas.
- The SQGs apply to a comprehensive range of chemicals commonly found in urban estuaries.
- They are most reliable for predicting when sediments will be non-toxic, which may be appropriate for the relatively low levels of contamination we have in NZ.
- They are expressed in terms of total dry weight of sediment, which is the most commonly determined units of contaminant concentrations.

Limitations include:

- They were developed for US estuaries, and may not apply directly to NZ
- They rely on a definition of toxicity, which in many cases is a single-species laboratory-based toxicity measure (e.g. 10-day amphipod survival test) rather than a multiple-species field measure (which would have greater ecological relevance)
- They are most useful in the types of sediments used in their derivation and testing (fine grained sediments) and may not work well in other types of sediments (e.g. coarser sandy sediments, sediments contaminated with particulate contaminants e.g. coal fragments)
- They provide no insight into reasons or mechanisms for toxicity, and cannot be used to determine cause-effects relationships.
- These SQGs may predict non-toxicity (relative to a given test) reliably, but, by themselves, they should never be used to conclude that a sediment will have a toxic effect on the environment, or that particular chemicals are going to have toxic effects.

Rather, they signal the need for further investigations to determine whether significant impacts are likely to occur in the environment, and which contaminants (if any) are likely to be responsible for adverse effects. This is reflected in the ANZECC (2000) decision tree approach to determining impacts of contaminated sediments (Fig. 1).

The ANZECC (2000) guidelines for metals and organic contaminants are based largely on the effects range guidelines of Long & Morgan (1995). It is interesting to note that later variations (e.g. MacDonald et al. 1996; CCME 1999) were not adopted. The later variations use chemistry/biological effects data sets containing both effects and no effects data to derive the effects ranges.

The major features of the ANZECC SQGs (ISQG-Low) are:

- The very low trigger values for endrin and dieldrin. These levels (0.02 µg/kg) are near or below commonly attainable analytical detection limits (which are usually around 0.05 µg/kg for sensitive analysis methods). Because of its historically widespread use in NZ, many estuarine areas in NZ could have dieldrin concentrations above 0.02 µg/kg.
- The total DDT trigger value is also relatively low (1.6 µg/kg), and is lower than either of the two major components of "total DDT" i.e. pp-DDE and pp-DDD, which together have trigger values of 4.2 µg/kg.
- The reliability of the guideline values is not given in the ANZECC guidelines. The original Long & Morgan (1995) description of the ER-Ls notes that these are of low reliability for pp'-DDE and total DDT.
- The guidelines are referenced to the organic carbon content of the sediment. This acknowledges the potentially important role of organic matter (carbon) in controlling the bioavailability of organic contaminants in sediments.

The implications of these ANZECC ISQG-low trigger values for Auckland estuaries are discussed in section 3.

# Appendix 2: Dataset of contaminants in estuarine sediments from around the Auckland region

A dataset of contaminants in estuarine sediments from around the Auckland region has been assembled for the comparisons with SQGs. Important characteristics of the dataset, and the approach taken to compare the data with SQGs are:

- The database does not include heavily contaminated sites associated with point-source pollution e.g. port and wharf sediments, dredge spoil, sites associated with known historical discharges. The data are intended to represent the typical range of contaminant levels present in urban and rural/urban estuaries. The sites are mostly urban.
- The investigations of sediment chemistry were varied, especially in the numbers and types (e.g. depths) of samples taken. To avoid biasing the data distributions towards locations where intensive sampling has occurred (e.g. Pakuranga estuary), average concentrations at each location were determined and used in the dataset. The disadvantage of this approach is that data for some large, well characterised areas (e.g. Pakuranga estuary) have the same “weighting” in the database as data from sites where very limited sampling has been undertaken.
- For metals, data was used uncritically, i.e., we did not reduce multiple investigations at the same (or nearly the same) site to a single set of data by deleting older datasets.
- For organics, where possible, multiple investigations at the same (or nearly the same) site were reduced to a single set of data by deleting older datasets, or those with limited suite of analytes. This enabled the most comprehensive, up-to-date, data to be used. Where there was some doubt about the exact location of the sampling site, or where analytical results were markedly different in each survey, each dataset was retained. There may, therefore, be a small amount of duplication of sites.
- For metals data was limited to that collected from 1986, but most was collected in the 1990s.
- For organics, data was limited to that collected from approximately 1989 (analysed or reported from approximately 1991 onwards). Older data can be unreliable, as analytical procedures have improved markedly in the past 10–15 years. It is also possible that conditions have changed over the past decade, and historically high concentrations of some contaminants in some areas (e.g. industrial areas) may have decreased over this time.

Organic data were summarised into the major groups of contaminants for which ANZECC SQGs are given. PAHs were summarised as the “High Molecular Weight PAH” (HMWPAH) total because there were insufficient reliable data for the “Low Molecular Weight PAH” group, and variable data to use in the “Total PAH” group. The HMWPAH group includes seven of the major combustion-sourced PAHs that make up the majority of the PAHs commonly found in Auckland estuarine sediments. Chlordane was either the sum of cis- and trans-chlordane multiplied by 2.38 (to give an estimate of total chlordane) or the total of cis- plus trans-

chlordane, cis- plus trans-nonachlor, heptachlor, and heptachlor epoxide. Total PCBs included the major congeners, commonly a sum of 24–29 compounds.

## Metals Data (Total metals, mg/kg dry weight)

Site	Year	Study	Zn	Cu	Pb
Armour Pt	1991	Hickey & Roper 1991	64.0	11.0	9.0
Barry's Point	1995	ARC ASP Survey	166	29	66
Big Muddy	1993	Roper & De Wit	59.0	9.0	10.0
Big Muddy	1986	Roper et al. 1988	70	10	13
Big Muddy	1995	Nipper et al. 1998	47	8	10
Big Muddy Creek	1998	ARC LTB	61.5	10.1	9.6
BlockHouse Bay	1991	Hickey & Roper 1991	64.0	10.0	6.0
Brighams	1992	ARC UWH	101.0	14.7	21.4
Browns Bay	1998	ARC LTB	43.9	2.3	4.6
Cheltenham Beach	1998	ARC LTB	47.15	2.78	10.96
Covil Park	1995	ARC ASP Survey	149	32	46
Coxes	1996	ARC Sandy Sediments	144.0	17.0	47.0
Cox's	1995	ARC ASP Survey	144	17	47
Duders	1995	ARC ASP Survey	93	14	28
Garbador Place	1991	ARC Tamaki	190.0	31.0	44.0
Garbador Place	1993	Roper & De Wit	178.0	36.0	48.0
Granny's Bay	1991	Hickey & Roper 1991	105.0	16.0	9.0
Harania	1995	ARC ASP Survey	207	45	61
Harania Ck (mouth)	1993	Roper & De Wit	200.0	53.0	54.0
Henderson Creek	1998	ARC LTB	177.5	44.3	32.5
Henderson Rutledge Rd,	1995	ARC ASP Survey	199	41	59
Hobson Bay, Upper	1998	ARC LTB	46	5.6	17.8
Hobson Lower	1995	ARC ASP Survey	131	15	45
Hobson Lower	1996	ARC Sandy Sediments	131.0	15.0	45.0
Huruhuru Creek Selwood Rd	1995	ARC ASP Survey	161	32	42
Kaipatiki Creek	1998	ARC LTB	96.9	16	29
Long Bay off Awaruku Stream	1998	ARC LTB	24.43	1.66	1.3
Long Bay off Vaughans Stream	1998	ARC LTB	22.45	1.43	0
Lucas	1992	ARC UWH	120.3	22.5	25.2
Lucas Creek	1998	ARC LTB	96.9	19.1	22.3
Mangere Anns Creek	1995	ARC ASP Survey	198	43	38
Mangere Anns Creek	1993	Roper & De Wit	220.0	63.0	50.0
Mangere Cemetry	1995	ARC ASP Survey	219	47	53
Mangere Cemetry	1993	Roper & De Wit	162.0	47.0	240.0
Mangere Cemetry	1995	ARC ASP Survey	175	37	256
Mangere Favona Rd	1986	Roper et al.	290	92	60
Mangere Pikes Point	1991	Hickey & Roper 1991	231.0	200.0	76.0
Mangere S4	1993	Williamson et al. 1995	210.0	55.0	80.0

Metals Data continued (Total metals, mg/kg dw)

Site	Year	Study	Zn	Cu	Pb
Mangere S5	1993	Williamson et al. 1995	205.0	57.0	60.0
Mangere, Anns Creek	1998	ARC LTB	180.5	43.8	47.1
Mangere, Cemetery	1998	ARC LTB	137	29.4	37.4
Meola	1995	ARC ASP Survey	222	14	31
Meola Creek	1998	ARC LTB	280	38.9	94
Motions	1995	ARC ASP Survey	208	14	45
Motions Creek	1998	ARC LTB	294	24.4	65.5
Oakley	1995	ARC ASP Survey	172	35	56
Onewa	1995	ARC ASP Survey	119	24	38
Otahuhu Creek	1995	ARC ASP Survey	181	33	47
Otahuhu Gt South Rd	1991	ARC Tamaki	164.0	23.0	54.0
Otahuhu Gt South Rd	1995	ARC ASP Survey	187	27	93
Otara Weir	1991	ARC Tamaki	131.0	21.0	35.0
Pahurehure Inlet, Papakura	1998	ARC LTB	64	13.8	6.5
Pakuranga Creek, Lower	1998	ARC LTB	145	20.9	30.9
Pakuranga Creek, Upper	1998	ARC LTB	183	28.8	41
Pakuranga Lower	1991	ARC Tamaki	239.0	42.0	80.0
Pakuranga Lower	1993	Roper & De Wit	209.0	34.0	55.0
Pakuranga Lower	1995	ARC ASP Survey	230	37	119
Panmure	1991	ARC Tamaki	151.0	28.0	39.0
Panmure	1995	ARC ASP Survey	126	32	69
Panmure Basin	1993	Roper & De Wit	142.0	24.0	32.0
Papakura	1986	Roper et al. 1988	100	8	22
Paremeroemo	1992	ARC UWH	108.3	20.8	18.7
Paremoremo Creek	1998	ARC LTB	96.9	23.1	24
Paturoa Bay	1991	Hickey & Roper 1991	57.0	9.0	5.0
Puherehere	1986	Roper et al. 1988	110	9	14
Puhinui Creek	1998	ARC LTB	99	10.8	12.4
Pukaki Upper	1995	ARC ASP Survey	235	42	70
Pukaki Lower	1989	Williamson et al 1994	50.0	8.0	12.0
Pukaki Middle	1986	Roper et al. 1988	85	10	13
Pukakia Waiokauri Creeks	1998	ARC LTB	74	11.9	9
Rangitopuni	1992	ARC UWH	108.7	20.3	20.5
Rarawaru	1992	ARC UWH	82.7	15.8	23.8
St Mary's Bay	1995	ARC ASP Survey	86	25	22
Tahuna Torea	1991	ARC Tamaki	38.0	0.0	0.0
Tamaki Bridge	1995	ARC ASP Survey	72	14	18
Taratata Creek	1995	ARC ASP Survey	150	41	47

Metals Data continued (Total metals, mg/kg dw)

Site	Year	Study	Zn	Cu	Pb
Te Tokorau, Meola Reef	1998	ARC LTB	100	7.3	24.9
Upper Tamaki, Otahuhu	1998	ARC LTB	145	19.8	34.2
Waitangi Falls	1993	Roper & De Wit	107.0	10.0	13.0
Wallace	1992	ARC UWH	116.0	11.5	22.1
Waterview Inlet	1998	ARC LTB	161	31.8	57.6
Weiti River Silverdale	1998	ARC LTB	49	11.8	5.4
Wesley Bay	1991	Hickey & Roper 1991	100.0	19.0	18.0
Whau Creek (Wairau)	1998	ARC LTB	207	53.5	92.3
Whau Creek Lower	1998	ARC LTB	163	28.8	62
Whau Creek Upper	1998	ARC LTB	252	37.8	99
Whau Middle Hepburn Park	1995	ARC ASP Survey	165	31	62
Whau Upper	1995	ARC ASP Survey	273	50	130
Wiroa Is	1989	Williamson et al 1994	8.0	1.0	0.5

## Organic contaminant data

OC = organic carbon (%). Other concentrations are ng/g dry weight

Estuary/Harbour	Location	Date	N	OC	High PAH	lindane	dieldrin	endrin	Total chlordane	p,p'-DDE	op+pp-DDD	Total DDT	Total PCB
Tamaki	Pakuranga Creek (total)	1996	24		290.54	<0.1	0.48	<0.1	0.92	0.64	0.86	1.95	4.82
Tamaki	Otara Weir	1991	5	1.70	333.40	0.10	0.88	<0.06	0.25	0.84	0.95	2.65	3.73
Tamaki	Tahuna-Torea	1991	5	0.70	27.74	0.08	0.22	<0.06	0.04	0.10	0.09	0.23	0.57
Tamaki	Gabador Plc	1991	5	2.70	687.20	<0.06	10.99	<0.06	0.60	1.25	2.41	4.57	13.05
Tamaki	Panmure	1991	5	2.00	637.80	<0.06	1.17	<0.06	0.40	1.37	4.02	8.35	16.71
Tamaki	Panmure	1995	1	2.16	3111.76	<0.1	0.94		0.36	3.49	18.72	43.70	44.61
Tamaki	Great Sth Rd	1995	1	2.20	1682.33	<0.1	1.25		0.58	1.48	1.53	4.55	10.02
Tamaki	Tamaki (ARC site)	1999	3		774.66								
Tamaki	Otahuhu Creek	1996	3		433.85								
Waitemata	Hellyers Creek	1996	24		384.92	<0.1	0.27	<0.1	0.61	1.09	1.35	3.07	4.59
Waitemata	Paremoremo Creek	1996	24		189.11	<0.1	0.15	<0.1	0.22	1.05	0.98	2.33	1.43
Waitemata	Catalina Bay	1993	3		316.67	0.45	0.42	0.00	0.80	0.79	1.29	2.52	4.00
Waitemata	Kendall Bay	1993	3		15.04	0.25	0.17	0.00	0.23	0.17	0.24	0.44	0.53
Waitemata	Little Shoal Bay	1993	3		169.95	0.33	0.12	0.00	0.21	0.13	0.26	0.42	2.79
Waitemata	Little Shoal Bay outer	1994	5		337.34								
Waitemata	Little Shoal Bay inner	1994	3		1740.00								
Waitemata	Pollen Island	1993	3		25.03	0.30	0.19	0.00	0.28	0.10	0.10	0.30	0.38
Waitemata	Whau River	1993	3		65.46	0.31	0.20	0.00	0.29	0.33	0.42	0.91	1.36
Waitemata	Whau Upper (ARC site)	1999	3		883.94								
Waitemata	Whau Lower (ARC site)	1999	3		513.95								
Waitemata	Whau Wairau (ARC site)	1999	3		754.08								
Waitemata	Henderson Creek	1993	3		217.48	0.50	0.32	0.00	1.26	4.38	4.16	10.55	3.13
Waitemata	Henderson Creek (ARC site)	1999	3		355.09								
Waitemata	Rangitopuni	1992	3		164.70	0.08	0.15	0.02	0.20	1.03	1.23	2.61	1.44
Waitemata	Lucas Creek	1992	3		329.50	0.00	0.11	0.00	0.17	1.44	2.25	5.13	4.77
Waitemata	Lucas Creek (ARC site)	1999	3		241.41								
Waitemata	Wallace Inlet	1992	3		182.93	0.10	0.10	0.02	0.04	0.54	0.83	1.60	2.40
Waitemata	Rarawaru Creek	1992	3		844.30	0.16	0.25	0.00	0.37	1.08	1.24	2.46	3.40
Waitemata	Brighams creek	1992	3		210.40	0.09	0.19	0.00	0.10	1.01	1.62	3.17	1.13

Organic contaminant data (cont.)

Estuary/Harbour	Location	Date	N	OC	High PAH	lindane	dieldrin	endrin	Total chlordane	p,p'-DDE	op+pp-DDD	Total DDT	Total PCB
Waitemata	Meola Creek (lower?)	1996	3		427.68								
Waitemata	Meola Creek (ARC site)	1999	3		2464.18								
Waitemata	Motions Creek (lower?)	1996	3		2460.13								
Waitemata	Motions Creek (ARC site)	1999	3		4313.47								
Waitemata	Te Tokarau Reef (ARC site)	1999	3		325.85								
Waitemata	Te Taharoa Reef (same as above?)	1993	3		318.29	0.32	0.21	0.00	0.88	0.14	0.16	0.34	0.64
Waitemata	St Marys Bay	1996	3		492.33								
Waitemata	Barry's Point	1996	3		697.12								
Waitemata	Oakley Creek	1996	3		869.27								
Waitemata	Rutledge Rd	1996	3		556.78								
Waitemata	Oakley Creek (ARC site)	1999	3		750.83								
Waitemata	Hobson Bay (ARC site)	1999	3		487.51								
Manukau	Cape Horn	1991	1						0.20				
Manukau	Mangere Inlet central	1991	1		172.50								
Manukau	Mangere Inlet nearshore	1991	1		255.70								
Manukau	Grannys Bay	1989	3	0.30	65.03	0.23	0.22	0.00	0.63	0.11	0.27	0.69	0.30
Manukau	Wesley Bay	1989	3	0.73	2793.00	0.34	0.38	0.00	0.89	0.26	13.71	14.76	1.54
Manukau	Blockhouse Bay	1989	3	0.72	34.47	0.18	0.16	0.00	0.42	0.08	0.66	0.99	0.28
Manukau	Paturoa Bay	1989	3	0.25	32.33	0.29	0.15	0.00	0.13	0.05	0.03	0.29	0.23
Manukau	Armour Point	1989	3	0.48	27.57	0.21	0.10	0.00	0.17	0.03	0.13	0.38	0.29
Manukau	Cemetery	1995	1	1.67	608.35	<0.1	1.04		2.40	1.48	1.53	4.53	12.35
Manukau	Alfred St (Cemetery?)	1996	3		1872.11								
Manukau	Mangere Cemetery (ARC site)	1999	3		227.28								
Manukau	Annes Creek (ARC site)	1999	3		225.97								
Manukau	Big Muddy Creek (ARC site)	1999	3		49.95								
Manukau	Big Muddy Creek	1995	1	5.38	218.11	<0.1	0.33		0.21	0.34	<0.2	0.47	0.16
Manukau	Pukaki Creek (ARC site)	1999	3		71.70								
Manukau	Puhinui Creek (ARC site)	1999	3		79.37								
Manukau	Pahurehure Inlet (ARC site)	1999	3		74.23								

Organic contaminant data (cont.)

Estuary/Harbour	Location	Date	N	OC	High PAH	lindane	dieldrin	endrin	Total chlordane	p,p'-DDE	op+pp-DDD	Total DDT	Total PCB
Manukau	Lewis Bay	1998	1		64.44	<0.1	<0.05		<0.3	<0.05	<0.1	<0.3	<0.6
Manukau	Awhitu	1998	1		0.20	<0.1	<0.05		<0.3	<0.05	<0.1	<0.3	<0.6
Manukau	Purukau Channel	1993	5		4.59	0.08	0.13	0.00	0.20	0.08	<0.1	0.12	2.70
Manukau	Harania	1996	3		334.85								
Okura	upper estuary	1995	1	1.60	59.96	<0.1	<0.1		<0.3	<0.1	<0.2	<0.8	0.12
Waiheke Island	Te Matuku Bay	1996	24		43.08	<0.1	<0.05	<0.1	0.05	<0.05	0.10	0.24	0.04
Hauraki Gulf	Cheltenham Beach (ARC site)	1999	3		175.49								
Hauraki Gulf	Awaruku Stm (ARC site)	1999	3		3.18								
Hauraki Gulf	Vaughn Stm (ARC site)	1999	3		2.20								
Hauraki Gulf	Weiti Stream (Orewa) (ARC site)	1999	3		150.47								
Hauraki Gulf	Browns Bay (ARC site)	1999	3		13.56								

# Appendix 3: Pore water metals data ( $\mu\text{g/L}$ , ppb)

Study	Site	Site No.	Zn	Cu	Pb	Cd	Ni	Cr	Fe	Mn
Nipper et al. 1998 10 cm frozen? cores	Aotea	1	3.2	0.3	1.1	0.27	1.7		3450	2000
	Raglan	2	9.8	4.5	2	0.39	6.6		14600	6000
	Big Muddy	3	4.4	0.4	3.2	0.12	3.3		1000	2000
	Okura	4	6.1	11.2	3.3	0.11	3		3200	2200
	Panmure	5	64	2.6	3.1	0.11	3.1		5800	2900
	Pakuranga	6	15	2.7	2.6	0.08	3.6		6200	3800
	Carbine	7	29	7.3	3.4	0.12	5.6		900	3800
	Mangere Inlet (Ann)	8	4.9	0.6	4.3	0.19	3.3		1600	1400
Morrisey, pers. comm. 15 cm frozen cores	Pakuranga	1	8	1	0.5					
	Pakuranga	2	11	1.3	0.3					
	Pakuranga	3	6	1.4	0.4					
	Pakuranga	4	12	0.5	0.2					
	Pakuranga	5	12	1.2	0.2					
	Hellyers	1	16	3	0.2					
	Hellyers	2	32	8.5	0.3					
	Hellyers	3	17	3.4	0.3					
	Hellyers	4	11	4.3	0.2					
	Hellyers	5	25	4.9	1.5					
Williamson et al (1992) Middle of Mangere	Surface (0-1 cm)	2	12	2.3	2	<0.4	8.5	0.6	<50	5200
	Surface (0-1 cm)	4	24	3.5	2.5	<0.4	4.8	0.8	<50	3840
Inlet	Surface (0-1 cm)	5	8	3.1	3	<0.4	7.2	1	3000	4350
	Sub surface	2	6	1.9	6.6	<0.4	2	5.1	420	700
	Sub surface	4	8	2.8	2.4	<0.4	0.5	1.8	800	1300
	Sub surface	5	4	2.8	2.4	<0.4	1.8	0.7	3000	1600
	Crab Burrows	2	9.5	4.4	3.7	<0.4	4.6	0.5	<50	115
	Crab Burrows	4	9.2	2.5	3.3	<0.4	3.7	0.6	<50	400
	Crab Burrows	5	7.8	3	2.6	<0.4	2.8	1.1	<50	400
	Surface runoff (rivulets draining surface and burrows	2	1.7	4.3	1.6	<0.4	2.1	3.1	<50	80
		4	12	3.7	3.6	<0.4	2.9	1.1	<50	290
		5	7.8	3	2.6	<0.4	2.8	1.1	<50	400