

Quantifying Stormwater Contaminants in Water and Sediment in the Okeover Stream, Christchurch



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EXECUTIVE SUMMARY

Okeover Stream, a tributary of the Avon River, runs through a heavily-urbanised catchment on the University of Canterbury campus. As such, it receives substantial amounts of surface water runoff through stormwater inputs. Stormwater inputs are believed to jeopardise the successful recolonisation of aquatic fauna in the restored sections of the Okeover. Inorganic contaminants such as metals, as well as hydrocarbons and faecal matter, enter the stream in significant concentrations during storm events. A survey of the water and sediment chemistry at five points along a stream transect during baseflow conditions was conducted and compared to the water chemistry at the most visibly degraded transect sampling point (T5) during a storm event.

Total copper (Cu) levels in water were found to be above the 80% threshold for the protection of aquatic species at all five transect points during baseflow conditions. Dissolved copper levels were above the 80% threshold at four of the five sampling points. Total and dissolved zinc (Zn) levels exceeded the 80% threshold at transect point five (T5), but were comparatively low at the remaining four points at baseflow. Total lead (Pb) was found at levels above the 90% threshold at transect point five, but total and dissolved lead levels were below the 99% threshold in every other baseflow sample. Nickel (Ni) levels at baseflow were below the 99% threshold at every transect point. Both total and dissolved cadmium (Cd) levels were below detection levels at baseflow, except for total cadmium at transect point two, where it was in excess of the 95% threshold. Nitrate levels were above the 95% threshold at every transect point at baseflow. The organic BTEX (benzene complex) and PAH (hydrocarbons) were below detection levels at every transect point during baseflow.

Levels of copper and zinc (dissolved and total) peaked well above the 80% threshold during the storm event sampling at T5. Similarly, total lead peaked above the 80% threshold, but dissolved lead was found above the 99% threshold, but far below the 95% level. Dissolved and total nickel levels during the storm event were below the 99% protection threshold. Dissolved cadmium was below detection levels during the storm event, but total cadmium peaked above the 95%

threshold as did nitrate. PAH levels were below detection during the storm as were BTEX concentrations, except for low levels of toluene detected.

Arsenic and nickel levels in sediment were below the low ANZECC interim sediment quality guidelines at every point sampled along the stream transect. Zinc and copper in sediment were present at toxic concentrations (i.e. above the guidelines) throughout the stream transect. Copper levels were above the high guideline level at transect point two (T2) and above the low guideline at transect point four (T4). Zinc levels were above the high guideline level at transect points two and five, and above the low guideline level at transect points three and four.

Overall, results from the storm event showed a high correlation with those of an earlier study: concentrations of copper (Cu), zinc (Zn) and lead (Pb) were measured at concerning levels in the stormwater and sediments in Okeover stream. Furthermore, dissolved proportions of the total concentrations of each of these metals were high, indicating that they are relatively bioavailable. The contextual legislation is not ideal for regulating or mitigating stormwater discharges into Okeover since it is more aligned with the greater Canterbury region. A holistic and integrated approach towards effective stormwater management is required for the Okeover catchment through a variety of synergistic solutions. Such solutions could include ecological treatment technologies coupled with community awareness and best management practices enforced by the appropriate regulatory authorities.

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1. Introduction

1.1. Background

The traditional, utilitarian perception of urban waterways as purely functional drainage systems has been questioned only relatively recently at a local government level in New Zealand (Nolan 2005). In the past 150 years since the colonisation by European settlers, Christchurch waterways have been significantly modified. Wetlands have been drained and watercourses ‘channelised’ or straightened in order to improve the drainage efficiency during heavy rainfall (i.e. stormflow) events. Waterways were also modified in order to provide land for agricultural, residential and commercial use, and to remove the risk to human health that wetlands posed. This approach to surface water management lacked foresight and resulted in many of the ecological attributes of the waterways being severely compromised. In particular, silty sediment deposits, paucity of suitable habitat and inputs from stormwater have led to a decline in the ecological integrity of these waterways (Blakely *et al.* 2006).

A broader waterways values system has been recognised by the Christchurch City Council (CCC) in its 2003 Waterways, Wetlands and Drainage Guide. This guide sets out the Council’s long-term (40 year) plan of action, by which waterways should be designed or retrofitted with regard to the ‘six values’ set out therein. These values are listed as ecology, landscape, recreation, heritage, culture and drainage (CCC 2003). The Okeover Stream is a first-order tributary of the Avon River. Its headwaters flow mainly through a heavily-urbanised catchment on the University of Canterbury campus (Fig. 1).

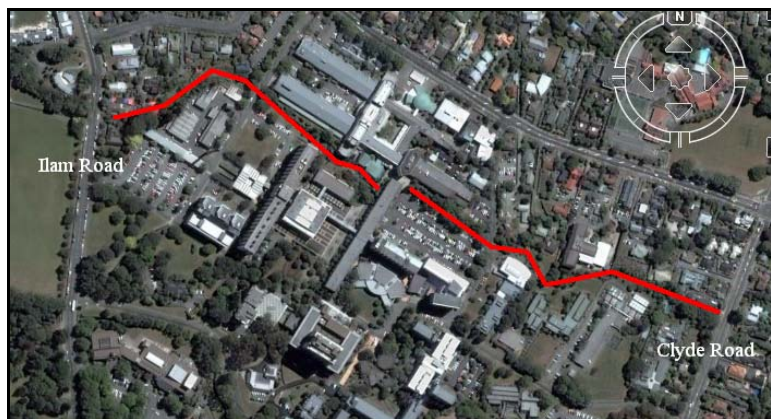


Fig. 1: Plan view of the University of Canterbury grounds with open channel parts of Okeover Stream highlighted (Source: Google Earth)

Some of its lower stretches have been the focus of ‘restoration’ efforts by the Christchurch City Council and the University of Canterbury since 1996. However, recent work has indicated that successful recolonisation by aquatic fauna in Okeover is jeopardised, in part, by inputs of stormwater arriving on campus (Blakely *et al.* 2003, Blakely *et al.* 2006). A project aimed at quantifying stormwater contributions into the Okeover from impervious surfaces was initiated in 2006 (Farrant 2006). This work highlighted that high concentrations of zinc, lead and copper enter the ephemeral reaches during stormflows.

Technically, sections of Okeover stream have been *rehabilitated* rather than *restored* since the reconstruction work has reversed some degraded parts to a near original state; they were renewed or repaired but not recovered to an original pristine state. The rehabilitation work undertaken to-date on Okeover Stream on the University of Canterbury campus has enhanced the six Christchurch City Council waterways values. Work has included riparian planting, restoring meanders, pools and riffles, removing box drains and implementing sediment drop boxes to trap foreign plant matter, especially from exotic (i.e. non-native) species. However, even though the rehabilitation has been the result of careful planning and extensive earthworks, there is great scope for further improvement.

Water quality surveys in New Zealand’s major urban centres have shown degradation in the quality of urban waterways and ecosystems (Suren *et al.* 2000, Boothroyd *et al.* 2003, EVA 2004). Common effects of urbanisation on waterways include increased flooding and pollution, lower dry-weather flows, changes to the stream substrate and riparian vegetation, and channel widening (Elliott *et al.* 2004). Rehabilitation of urban waterways in New Zealand is an acknowledged priority for urban residents (Boothroyd & Drury 2006). As Okeover Stream is representative of a typical urban stream in Christchurch, its rehabilitation is offered as an example of urban waterway rehabilitation in the CCC Waterways Guide. Therefore, it has the potential to act as a template for more extensive urban waterways rehabilitation in Christchurch and possibly at a national level.

Although rehabilitation efforts have improved the general appearance and health of the stream thus far, the high levels of zinc (Zn), copper (Cu) and lead (Pb) entering the stream as stormwater runoff at the ephemeral reaches (Farrant 2006), are thought to be compromising the ecology of the downstream sections (Blakely *et*

al. 2003). Zinc and copper have been found in concentrations toxic to biota in both dissolved and total states in the Okeover stream (Farrant 2006).

As well as contributions of contaminants from stormwater, stagnant in-stream water has negative implications for the ecological health of Okeover Stream. The stagnant water at Ilam Road (upstream of where air-conditioning discharges from Facilities Management and the Commerce Department enter Okeover) is anaerobic due to the Biochemical Oxygen Demand (BOD) from decomposing plant matter and sediments. This can lower the dissolved oxygen (DO) of the downstream sections when flushed through in a storm event. The problem is thought to be exacerbated when the air-conditioning water is not being discharged (Pers. Comm. Dr Kate Hewson, Facilities Management, UC), as there is no dilution effect. Temperature and DO are inter-linked, and because water is standing in the culvert beneath the road, it becomes warmer than the water flowing downstream. Additionally, as water temperature increases, there is a corresponding exponential decrease in dissolved oxygen levels. Thermal contamination by air-conditioning discharge may also be a concern; this water, although relatively pristine in terms of its chemistry, is thought to be approximately 2°C above spring-contributed water in the Okeover (Pers. Comm. Dr Jon Harding, School of Biological Sciences, UC). A temperature difference of this magnitude has the potential to substantially and detrimentally affect recolonisation by some in stream biota (Blakely *et al.* 2003).

1.2. Goals

In order to develop best management strategies (perhaps including ecological treatment technologies) for stormwater, it is essential to know the contaminant characteristics and their respective loadings. For this reason, our summer research focussed on quantifying stormwater contributions at critical points along a transect in Okeover Stream by measuring water chemistry and conducting stream gauging during both baseflow and storm conditions.

The primary goals of this research were to investigate the chemistry and hydrology during baseflow conditions along a five-point transect on a section of Okeover between Clyde and Ilam Roads. Data from baseflow conditions were then compared to storm event conditions at transect point five (just downstream of the Ilam Road culvert) and to the storm events captured earlier in 2006 (Farrant 2006). Inorganic contaminants (i.e. metals) and hydrocarbons in water and sediment were

quantified during baseflow conditions, and water chemistry was again measured during a storm event. Results were compared to current reference standards.

1.3. Legislative Framework

1.3.1. The Resource Management Act 1991 (RMA)

The RMA is New Zealand's foremost piece of environmental legislation. Its purpose is to promote the sustainable management of natural and physical resources (s 5). The RMA brought together and updated many older acts in an effort to acknowledge the importance of integrated environmental management. That is, ecosystems do not exist in isolation, but are inter-connected.

However, at the time the RMA was drafted, discharges of concern were considered largely confined to point-source (Nolan 2005). This has implications in relation to stormwater, which is non-point source. Discharges to water and land are prohibited under s 15 of the RMA, in recognition of the potential harm consequent to ecosystems. However, the RMA allows for discharges if permitted by the relevant Natural Resources Regional Plan. Here, the discharges are classified depending on the volume of the discharge; smaller discharge volumes to land can be permitted activities and so do not require resource consents. However, the cumulative effect of contaminants from many small-scale discharges to land can be great. Contaminants such as those derived from runoff of impervious surfaces are flushed into stormwater systems during precipitation events, and then into urban waterways. Although high intensity discharges to land and water are strictly controlled, there is a failure to recognise that diffuse pollution in a catchment with significant impervious areas is serious and originates in many cases from terrestrial surfaces (i.e. not *directly* discharged to water).

1.3.2. Natural Resources Regional Plans (NRRP)

Part of Environment Canterbury's (ECan's) role under the RMA is to control discharges of contaminants into water and discharges of water into water (s 30). Each regional council in New Zealand is required under the RMA to produce a Natural Resources Regional Plan (NRRP). Chapter 4 of ECan's Proposed NRRP deals with the ecological health of freshwater bodies in Canterbury.

It is interesting to note that the NRRP refers to stormwater discharge as point-source instead of diffuse. This is understandable in light of discharge pipes and other hydraulic structures that concentrate stormwater flow and carry it to waterways such as Okeover Stream. The NRRP states that non-point source discharges of contaminants:

‘aris[e] from widespread or dispersed sources that enter water bodies via runoff across land or by shallow sub-surface drainage’.

Applying this definition, it would follow that stormwater that enters a water body without passing through a pipe, but instead running across land, is non-point source. The pre-eminent legal text on environmental issues also describes stormwater as non-point source (Nolan 2005). From an engineering point of view, it is generally accepted that stormwater is non-point source (Davis 2001). Stormwater in rural areas is not so pressing a problem as it is in urban areas due to the comparative dearth of impervious surfaces. Perhaps then, the classification of stormwater as point-source is due to the regional, as opposed to solely civic focus, of the NRRP.

Rule WQL 5 of the NRRP is concerned with stormwater discharges to land and defines them as either controlled or permitted activities in accordance with the RMA. Rule WQL 6 defines the discharge of stormwater into a river, lake or artificial watercourse as a permitted activity if the stormwater management area, or network by which the stormwater management area is serviced, has a population of 200 people or fewer. Okeover does not meet this requirement, so stormwater discharge into the stream is a controlled activity and thus requires resource consent under Rule WQL 7. This rule further requires that an integrated catchment management plan is implemented and that discharges meet the conditions of Schedule WQL 1 (further below), including total suspended solids (TSS) and flow levels prescribed therein.

However, it is difficult to see how diffuse discharge might be considered a controlled activity. In the absence of one major party causing the bulk of the contamination, how is resource consent to be enforced? In some instances this is possible. For example, where a significant impervious area such as a car park is contributing contaminants to stormwater, the owner of the land is responsible for

the stormwater running off it. Notwithstanding this, the summed area of smaller impervious surfaces owned by the residents of an urban environment may contribute far more seriously to total stormwater on a catchment-wide basis.

In light of stormwater being regarded as *point-source* in the NRRP, the rationale behind Rule WQL 7 makes more sense. The rule assumes that the party responsible for the contaminants in stormwater is easily traceable, which is not the case in most circumstances. As mentioned earlier, diffuse discharge contamination was not always considered important. It could therefore be argued that the current legislative framework needs revision in light of the seriousness of diffuse-source pollution such as stormwater. Attempts to apply a technical legal framework such as the RMA to an end for which it was not designed might be difficult otherwise.

Under Schedule WQL 1 of the NRRP, an urban waterway such as Okeover must satisfy the following conditions:

- a) The concentration of dissolved oxygen in water shall:
 - (i) exceed 80 percent of saturation concentration at any time; and
 - (ii) exceed 90 percent of saturation concentration during daylight hours, and at all times during May to September inclusive.
 - b) The natural water temperature shall not:
 - (i) be changed by more than three degrees Celsius; or
 - (ii) exceed 20 degrees Celsius as a daily maximum temperature; or
 - (iii) exceed 11 degrees Celsius as a daily maximum temperature during May to September inclusive;
 - c) The natural pH of the water shall not vary by more than 0.5 pH [units] at any time of the day from the ambient diurnal variation on a continuous basis, and shall be within the range 6 to 9.
-
- n) The concentration of any toxicant listed in Table WQL 19 in Part 2 of this Schedule, measured as the *total* fraction, shall not exceed the concentration specified for the 90 percent level of protection for that toxicant. This is the 90% trigger value from the ANZECC Freshwater Quality Guidelines.

The nature of stormwater discharge has implications for the management of stormwater discharges into Okeover Stream: stormwater is sporadic in occurrence and variable in intensity, so required treatment system capacities are difficult to define. Stormwater originates from a multitude of sources, often in quantities that are negligible when considered individually, but which have significant cumulative effects. Furthermore, catchment boundaries are often undefined and difficult to delineate with certainty. Stormwater discharges are therefore hard to predict and mitigate, especially when the absence of any one person or body responsible for high contaminant concentrations is considered. The Resource Management Act 1991 states that no person may discharge any contaminant into water. Every person has a duty to avoid, remedy or mitigate any adverse effect on the environment that may result from their activities (s 15). However, how does one enforce the general water chemistry regulations of the NRRP when the deterrent effect recognised by making accountable those persons, who have breached the regulations, is not possible in many instances?

To redress this lack of community culpability, it is submitted that a levy be imposed or proportion of taxes set aside to investigate best management practices that will reduce stormwater toxicity. Such practices would be best discussed in cooperation with as many government bodies as are relevant, notably the catchment managers and transport authorities. Options could include investigation of the efficiency and frequency of road cleaning; the use of plastic spouting and pipes instead of metal (notably copper); the subsidy of more ecologically benign detergents; and perhaps the diversion of stormwater away from key waterways to allow 'biodiversity hot spots' to develop that will provide populations of taxa for recolonisation of other streams (Pers. Comm. Dr Angus McIntosh, School of Biological Sciences, UC).

1.4. Australian and New Zealand Environment and Conservation Council Guidelines (2000)

The Australian and New Zealand Environment and Conservation Council (ANZECC) updated their 1992 water quality guidelines in 2000. These guidelines, the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (2000), prescribe levels of contaminants, or trigger levels, above which intervention is recommended. The guide aims:

“[t]o provide an authoritative guide for setting water quality objectives required to sustain current, or likely future, environmental values for natural and semi-natural water resources in Australia and New Zealand.”

Although there are gaps in the guide indicating that there are insufficient data to give reliable trigger levels for particular contaminants, the guide is the best available source of reference in many circumstances and is specific to New Zealand and Australia. The guide has not been incorporated into the New Zealand law (i.e. it is not a National Environmental Standard under s 43 of the Resource Management Act 1991 (RMA)) and so is not binding on or enforceable by territorial or regional authorities. However, although not obligatory, it is a reference standard by which government, industry, consultants and community groups can estimate the health of an aquatic ecosystem and potential effects of their activities. Environment Canterbury (ECan) has specifically adopted the ANZECC 90% protection levels in the proposed NRRP as the maximum for some toxicants in urban streams (Schedule WQL 1). For the purpose of our research on Okeover Stream, the water quality guidelines produced by ANZECC were used as the appropriate, contextual technical reference document.

Contaminant concentrations in the water were assessed with reference to the ANZECC trigger values (Appendix E) for freshwater (ANZECC 2000). These guidelines give four protection levels that can be applied to contaminant levels in an ecosystem. The levels provide an estimation of the percentage of species living in the aquatic habitat that are expected to survive the corresponding contaminant levels. The percentage protection levels ANZECC prescribes for each contaminant are: 99%, 95%, 90% and 80% (Table 1). As the guidelines are discretionary as opposed to obligatory, the catchment management authority is free to choose which trigger level to apply, or whether to refer to the ANZECC guidelines at all in assessing stream health. Ecosystem condition levels provide a useful general guide in exercising this discretion: Condition 1 ecosystems are of high conservation or ecological value; Condition 2 ecosystems are slightly to moderately disturbed; and Condition 3 ecosystems are highly disturbed. Okeover Stream is a Condition 3 ecosystem and therefore has management aims to protect the extant biota and improve the ecology and habitats of the stream (ANZECC 2000).

a. Transect point five (T5)

In addition to baseflow data, water samples were taken during a storm event at transect point five (T5). This point was chosen as a storm data collection site as it is the most visibly degraded part of the stream on university grounds, and drains the upper catchment through a major (500 mm diameter) culvert under Ilam Road. However, it is important to note that there are numerous (> 33) inlet pipes of varying size carrying stormwater to the Okeover in this reach, and so results of the stormwater sampling do not necessarily give the worst case scenario for the contamination of the downstream sections.

The water at T5 is stagnant and murky and no plant or animal life is observed, apart from some plants along the right bank (looking upstream), which are submerged and flattened by the high flow characteristic of storm events (Figs. 3, 4 & 5). At this point, Okeover receives a lot of stormwater runoff from Ilam Road as well as from its upper reaches where research was focussed in 2006 (Farrant 2006). The transect point is characterised by a wide box drain channel, fed by a 500 mm diameter culvert under Ilam road and also by runoff from Ilam Road through auxiliary drainage pipes. The width of the channel at T5 is approximately 1.56 m and the maximum water depth at baseflow is 12.5 cm.



Fig. 3: Transect point five (T5) at baseflow



Fig.4: Looking downstream from T5



Fig. 5: Looking upstream from T5

b. Transect point four (T4)

Transect point four (T4) (Figs. 6 & 7) is just downstream of the air-conditioning discharge from the Facilities Management building (Fig. 8).



Fig. 6: Transect point four (T4) at baseflow



Fig. 7: Looking upstream at T4

The almost imperceptible flow of the stagnant water upstream of T4 at baseflow conditions ensures there is little mixing of the fast flowing air-conditioning water. In fact, there appears to be a slight back-flow of the air-conditioning water upstream due to the flat slope here. The air-conditioning water contributes greatly to the total stream flow and is thought to be relatively pristine, apart from its slightly elevated temperature after circulation through the cooling system. Air-conditioning discharge, which augments the low baseflow conditions, is thought to have negligible or beneficial effects on Okeover Stream (Suren 1993; Suren and Walsh 1996; Suren and Duncan 1997; Suren, Duncan *et al.* 1998; EOS 2005). The width of the stream at this point is approximately 0.6 m and the maximum water depth is 17.5 cm.



Fig. 8: Air-conditioning discharge from Facilities Management

c. Transect point three (T3)

Transect point three (T3) (Figs. 9 & 10) is directly outside the Civil Engineering Department's Structures Laboratory and was chosen as a sampling point due to the presence of several stormwater input pipes approximately 20 m upstream, on the opposite side of Engineering Road. The stream at this point is approximately 2.4 m wide and has a maximum depth of 20.5 cm at baseflow.



Fig. 9: Transect point three (T3) at baseflow



Fig. 10: Looking upstream at T3

d. Transect point two (T2)

Transect point two (T2) (Figs. 11 & 12) is a deeper sediment drop zone outside the Maori Department. There appears to be more life in this part of the stream. The width of the stream at this point is approximately 4.7 m and the maximum water depth is 57.5 cm. During baseflow, the discharge was measured at $0.030 \text{ m}^3 \text{ s}^{-1}$.



Fig. 11: Transect point two (T2) at baseflow



Fig. 12: Looking upstream at T2

e. Transect point one (T1)

Transect point one (T1) (Figs. 13 & 14) is a relatively fast-flowing region of Okeover. It is the point farthest downstream that can be reached before access to the stream bank is obstructed by vegetation before Clyde Road. The stream at this point is approximately 2.5 m wide and has a maximum depth of 15 cm at baseflow. The discharge of Okeover Stream at this point during baseflow is $0.063 \text{ m}^3 \text{ s}^{-1}$.



Fig. 13: Transect point one (T1) at baseflow



Fig. 14: Looking upstream at T1

2.2. Baseflow Sampling

Baseflow, also referred to as 'dry weather flow,' is the portion of total stream flow that is contributed by groundwater instead of surface runoff (Allaby 2006). During times of drought, baseflow can represent nearly all of total stream flow. An

ephemeral stream, such as the upper part of the Okeover, has no baseflow component, and will therefore only flow during and shortly after a precipitation event. Baseflow in the lower regions of Okeover is comprised of air-conditioning discharges from the University of Canterbury and from remaining springs below the stream.

In order to ensure that sampling along the stream transect was conducted when the stream was at baseflow, at least 24 hours was allowed after a precipitation event for the stream to return to dry-weather conditions.

2.2.1. Water Samples

One set of water samples was taken at each transect point (T1 - T5) for analysis by an IANZ accredited Laboratory (Hill Laboratories). Samples were taken in appropriate polyethylene and glass bottles provided by Hill Laboratories specific for each parameter (Table 2):

Table 2: Sampling bottles for water samples and relevant preservatives

Parameter	Bottle
Benzene, Toluene, Ethylbenzene, Xylene (BTEX)	40 mL ascorbic acid preserved glass
Polycyclic Aromatic Hydrocarbons (PAH)	500 mL unpreserved glass
Total Suspended Sediment (TSS)	1 L unpreserved polyethylene
Dissolved/Soluble Metals (field filtered)	100 mL unpreserved polyethylene
Total Recoverable Metals	100 mL nitric acid preserved polyethylene

The sampling bottles without preservatives were rinsed three times with the stream water, and the discarded water disposed of downstream of the sampling point. The bottles were then filled with water directly from the stream and sealed under water to exclude air to the extent possible. Total Suspended Sediment (TSS) bottles were only filled to three-quarters of their total capacity. This was to prevent data being compromised if water were lost when the bottles were opened at the laboratory. The bottles containing preservatives were filled from a clean polyethylene bottle rinsed with stream water, and air was again excluded as far as possible.

Water samples collected for the analysis of dissolved/soluble metals were filtered at the laboratory instead of in the field due to time constraints during sampling, and for continuity with the previous study (Farrant 2006).

2.2.2. Sediment Samples

Composite sediment samples were taken from the bed of the stream at the five points along the transect with a plastic trowel that had been rinsed with de-ionised water. At each point, sediment was taken at intervals along the stream cross-section and deposited into a labelled polyethylene container before transport to Hill Laboratories. Separate samples for organic analysis were taken and sealed in plastic bags in order to determine the organic component of the sediments along the transect. These were stored in the environmental laboratory's refrigerator at a constant temperature of $\approx 4\text{ }^{\circ}\text{C}$ until analysis.

a. Organic Matter

As Total Organic Carbon (TOC) is thought to reduce the bioavailability of metals in oxic sediments (Landner & Reuther 2004), the organic fraction of sediment can provide an indication of how harmful metals are likely to be to an aquatic ecosystem. Thus, the greater the fraction of organic matter in the sediment of Okeover, the less toxic it is likely to be to aquatic fauna. Additionally, inorganic sediment is more likely to be derived from urbanisation, and thus have contaminants associated with an urban environment adsorbed to it (Blakely et al. 2003, EOS 2005).

Volatile solids are measured by weight loss upon ignition. Although weight loss on ignition does not just represent organic matter, the fraction of volatile solids in a sample gives an approximation of the organic matter component. To find volatile solids, the sediment samples of known weight were dried in a $105\text{ }^{\circ}\text{C}$ oven for 24 hours. Before this, crucibles containing the samples had been washed and dried in the furnace for two hours, cooled in a desiccator and then weighed. Once the samples were removed from the oven, they were left to cool in a desiccator for one hour, and then weighed to find moisture content. Samples were then placed in the muffle furnace at $550\text{ }^{\circ}\text{C}$ for five hours, cooled and reweighed. This process was repeated until no further weight loss was observed and represent the organic fraction in the sample. The formula for measuring organic solids is given below:

$$\text{Volatile Solids} = \frac{M(\text{dry}) - M(\text{ashed})}{M(\text{dry}) - M(\text{crucible})} \times 100 \quad [\text{Eqn 1}]$$

(% of sediment sample)

$M(\text{dry})$ = mass of dry sample after 105 ° oven C (mg)

$M(\text{ashed})$ = mass of sample after 550 °C furnace (mg)

$M(\text{crucible})$ = Mass of crucible (mg)

2.3. Stormwater Sampling

In order to gain the best appreciation of stormwater contaminants entering Okeover Stream, sampling was conducted only during sufficiently heavy storm events. This ensured that the roads and other impervious surfaces were flushed down of the contaminants that accumulated on them in the dry period before the rainfall event. This dry period needed to be at least 24 hours in order to allow contaminants to build up on impervious surfaces again.

During the storm event, water samples were taken at ten to fifteen minute intervals, with *in-situ* measurements and flow gauging conducted in-between sampling when practicable. Sampling was conducted by the same method for baseflow conditions described earlier.

Storm events were forecast and monitored using the rain radar on the New Zealand MetService website. Rainfall data were collected from the online weather station hosted by the School of Geography at the University of Canterbury.

2.4. Preservation Methods

At temperatures above 4 °C, biological agents in the samples can affect chemical changes that could alter the accuracy of actual results. In order to avoid this, all samples (sediment and water) were stored at 4 °C in the environmental laboratory's refrigerator until transport (within 24 hours) to Hill Laboratories in an iced chilly bin.

To determine the total component of a metal in solution, all metals in the water samples must be kept in dissolved form. To ensure this, sample bottles with known quantities of acid preservatives were used (Table 2).

2.5. Quality Assurance/Quality Control (QA/QC)

In compliance with ANZECC guidelines, at least 10 % of the storm event samples were duplicated for Quality Assurance/Quality Control purposes. Baseflow samples were not duplicated. A chain of custody form was completed for each batch of samples sent to Hill Laboratories. Facsimiles of these forms were returned from Hill Laboratories on receipt of the samples. An example of a completed chain of custody form is included in Appendix A. Once results were returned from the accredited laboratory, anion-cation balances were calculated (within 5% differences) for each set of water quality results in order to ensure accuracy of analytical measurements. An example of such a balance is provided in Appendix B.

2.6. Stream Discharge

Stream velocity was measured during both baseflow and stormflow conditions. Velocity was measured with a Global Water FP 101 Flow Probe at each transect point during baseflow conditions and during stormflow conditions at T5, where the stormwater sampling was focussed. Concurrently, the stream width and depth in sections were measured to obtain a cross-section of the stream.

The depths and widths corresponding to the measured velocities along the cross-section were used to convert velocity to flow (or discharge) in $\text{m}^3 \text{s}^{-1}$ with the following formula:

$$Q = A \cdot v \quad [\text{Eqn. 2}]$$

Q = discharge ($\text{m}^3 \text{s}^{-1}$)

A = area (m^2)

V = velocity (m s^{-1})

Area of the stream cross-section, A, was estimated by summing the areas between measurement points along the cross-section with the formula for the area of a trapezium.

$$A = \frac{h(a+b)}{2} \quad \text{[Eqn. 3]}$$

In this formula, a and b are the lengths of the sides of the strip in question, while h is the width of the strip (Fig. 15):

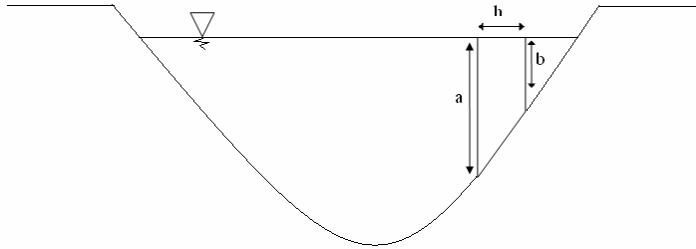


Fig. 15: Diagram showing the division of a stream cross-section into area strips so the trapezium formula can be used to calculate the total area of the cross section.

Examples of the cross-sections of transect five during the storm event and at baseflow are included in Appendices C and D, respectively. By calculating discharge of the various sections along Okeover during baseflow and storm flow conditions, actual contaminant loadings at peak and lowest concentrations could be calculated by multiplying by the respective concentrations. The formula for calculating contaminant loadings is given in equation 4 below.

$$QC = \text{Loading (g s}^{-1}\text{)} \quad \text{[Eqn. 4]}$$

$$Q = \text{discharge (m}^3 \text{s}^{-1}\text{)}$$

$$C = \text{mean concentration (g m}^{-3}\text{)}$$

2.7. In-situ Measurements

The following water quality parameters were taken with calibrated field instruments in each sampling event:

Table 3: Field instruments used to measure *in-situ* water chemistry parameters

Parameter	Units	Instrument
pH	- log [H ⁺]	YSI 60 pH System
Dissolved oxygen	g m ⁻³	YSI Environmental 550A
Conductivity	(μS cm ⁻¹)	Thermo Electron Corp Orion 130A
Turbidity	(NTU)	Hach 2100P Turbidimeter
Oxidation-Reduction Potential	(mV)	YSI Environmental pH 100

The average of at least three turbidity measurements was taken in order to find the mean turbidity at each sampling event. The pH, dissolved oxygen, and conductivity probes each had an ancillary device for measuring temperature. The temperature readings from these three instruments were averaged to find the mean temperature for each sampling. All instruments were calibrated and checked to 5% accuracy before each sampling event. Instruments were also checked after sampling to verify that they had held their calibration in the field in accordance with our Quality Assurance Quality Control (QAQC) sampling regime.

3. RESULTS

3.1. Baseflow

3.1.1. In-situ Parameters

ANZECC has compiled a set of trigger values for physical and chemical stressors in slightly disturbed (i.e. Condition 2) ecosystems (Table 4). Although Okeover Stream is a highly disturbed, Condition 3 waterway, these values may still provide a useful benchmark.

Table 4: ANZECC Trigger Values for Lowland Rivers

	DO (% Saturation)	pH	Turbidity NTU
Lower Limit	98	7.2	-
Upper Limit	105	7.8	5.6

a. pH

The pH at baseflow was below the lower ANZECC limit of 7.2 (Table 4) at every sampling point along the transect (Table 5). A low pH encourages metals to exist in their dissolved, and thus more bioavailable, form. However, considering that Okeover is a Condition 3 stream, a circum-neutral pH level, although slightly acidic, is still acceptable. The lowest pH value was 6.44 at T5, but pH values at the other sampling points were more circumneutral of between 6.65 and 6.77.

b. Dissolved Oxygen and Temperature

Dissolved oxygen (DO) at baseflow was generally within acceptable limits for a slightly disturbed stream (Table 4). However, DO at T5 was 2.16 g m⁻³ or 21.2 % saturation; this is far below the lower limit of 98% and would probably deter any aquatic species from living here. In a transect study conducted on Okeover in 2003, only one out of seven sampling points had DO levels lower than the DO at T5 in our study (Blakely *et al.* 2003). In the earlier study, DO was 1.27 ± 0.23 g m⁻³ at site O1, but was higher (8.60 g m⁻³ - 9.50 g m⁻³) at the six other points, which generally agrees with the DO at the remaining four transect points in the present study. At T4, there is a sharp increase in DO levels (9.41 g m⁻³), attributable to the fast flowing air-conditioning discharge just upstream. DO levels drop at T3 and T2 to below the lower ANZECC limit, possibly because of the slower-flowing water in these sections. DO levels rise again at T1 due to turbulence from higher flow rates furthest downstream. Temperature at baseflow was fairly consistent along the transect, ranging from 14.1 °C to 14.8 °C (Table 5). These values generally agree with temperature at baseflow in Okeover found in 2003 (Blakely *et al.* 2003).

Table 5: In-situ water chemistry results in Okeover stream (December 2006)

Baseflow	pH	Dissolved Oxygen	Dissolved Oxygen	Temperature	Conductivity	Specific Conductance (calculated)	Mean Turbidity	Oxidation - Reduction Potential (ORP)
Transect Point		g m ⁻³	% Saturation	°C	µS cm ⁻¹	µS cm ⁻¹	NTU	mV
T1	6.77	10.04	98.24	14.4	137.50	172.82	1.25	135
T2	6.69	9.41	92.98	14.8	139.50	112.06	0.63	137
T3	6.67	9.37	92.04	14.6	141.70	177.25	0.35	173
T4	6.65	10.68	104.09	14.1	132.50	167.74	0.22	207
T5	6.44	2.16	21.26	14.7	160.70	200.53	5.26	134
Storm Event:	pH	Dissolved Oxygen	Dissolved Oxygen	Temperature	Conductivity	Specific Conductance (calculated)	Mean Turbidity	Oxidation - Reduction Potential (ORP)
T5 at:		g m ⁻³	% Saturation	°C	µS cm ⁻¹	µS cm ⁻¹	NTU	mV
14:26	6.53	5.13	50.20	14.5	155.5	194.97	42.9	134
15:29	6.65	8.63	88.60	16.8	52.5	45.38	110.0	111
16:00	6.66	9.49	96.64	15.6	25.6	27.95	26.3	135

c. Conductivity/Specific Conductance

Conductivity is the measure of a liquid’s ability to conduct an electrical current. This current is transported through a liquid by free ions, the total levels of which determine the net conductivity of the solution. Conductivity is often used as a surrogate measurement for in-stream contaminants. In order to compare conductivity measurements taken at different temperature values, measurements were converted to specific conductance which is used to standardise conductivity at varying temperatures to 25 °C with the following formula:

$$SC = \frac{Conductivity}{1 + TC(T - 25)} \quad \text{[Eqn. 5]}$$

Where SC = Specific Conductance (25 °C) ($\mu\text{S cm}^{-1}$)
 TC = a constant = 0.0191 (i.e. = 2 %)
 T = Temperature (°C)

Specific conductances during baseflow were relatively high. The highest specific conductance was at T5 ($200.53 \mu\text{S cm}^{-1}$), which indicates that the water here is more polluted in terms of free ions than at other parts of Okeover. The water at T2 had the lowest specific conductance ($112.06 \mu\text{S cm}^{-1}$). The remaining three transect points had similar specific conductances, ranging from $167.74 \mu\text{S cm}^{-1}$ to $177.25 \mu\text{S cm}^{-1}$. Conductivity (as opposed to the standardised specific conductance) was found at higher levels in a previous study on Okeover (Blakely *et al.* 2003).

d. Turbidity

Turbidity is the cloudiness or haziness of water caused by suspended sediments. High turbidity can seriously affect the ability of aquatic organisms to survive. In addition, many metals adhere to suspended solids and so high suspended solids concentrations can indirectly lead to high metal concentrations. Turbidity was measured in Nephelometric Turbidity Units (NTU), which is a test of how light is bent through a column of the sample water.

Turbidity was below the ANZECC limit of 5.6 NTU at all points along the baseflow sampling transect (Table 5). Turbidity was negligible at T2, T3 and T4, but was

comparatively high at T1 (1.25 NTU). Turbidity was highest at T5 at 5.26 NTU, close to the ANZECC limit of 5.6 NTU (Table 4).

3.1.2. Baseflow Discharge

Discharge during baseflow conditions varied along the transect (Table 6). Velocity and depth measurements along the stream cross-sections, which were used to calculate discharge, are included in Appendix D. Discharge at T5 was extremely low, almost imperceptible. The velocity of the water was below the flow meter’s detection level of 0.01 m s^{-1} . Velocity was therefore taken to be half that limit (0.005 m s^{-1}), in accordance with the standard practice for flow gauging with the available instrumentation. Discharge was found to be $0.04 \text{ m}^3 \text{ min}^{-1}$ at baseflow upon calculation from the stream cross-section. Baseflow at T4 was significantly higher at $0.84 \text{ m}^3 \text{ min}^{-1}$. The width of the stream channel increased at T3, and so discharge at baseflow was lower here at $0.28 \text{ m}^3 \text{ min}^{-1}$. Downstream, discharge increased significantly at T2 ($1.81 \text{ m}^3 \text{ min}^{-1}$) and again at T1 ($3.77 \text{ m}^3 \text{ min}^{-1}$).

Table 6: Baseflow at points the stream transect

Transect Point	Flow ($\text{m}^3 \text{ min}^{-1}$)
1	3.77
2	1.81
3	0.28
4	0.84
5	0.04

3.1.3. Water Chemistry

a. Copper (Cu)

Baseflow concentrations of copper were abnormally high and apparently not localised to the most obviously disturbed part of Okeover Stream at T5 (Fig. 16). Although total and dissolved copper concentrations were found to be above the 80% trigger (0.0025 g m^{-3}) at T5, levels were actually higher at T4 (0.0117 g m^{-3}). While total copper at T4 was only marginally above total copper at T5 (0.0093 g m^{-3}), dissolved copper levels were found to have more than trebled between T5 and T4. As dissolved copper is the more bioavailable form, it is the one used as a measure of ecotoxicity. The rise in dissolved copper levels is therefore of great concern. A possible source of the dissolved copper at T4 is the air-conditioning discharge, which is just upstream of this sampling point. It is conceivable that the dissolved copper originates from copper piping. This is largely unsupported conjecture, and

further investigation is required for verification and identification of the source. However, from these results, it would appear that copper is the metal of most concern for this part of Okeover Stream even during non-storm conditions.

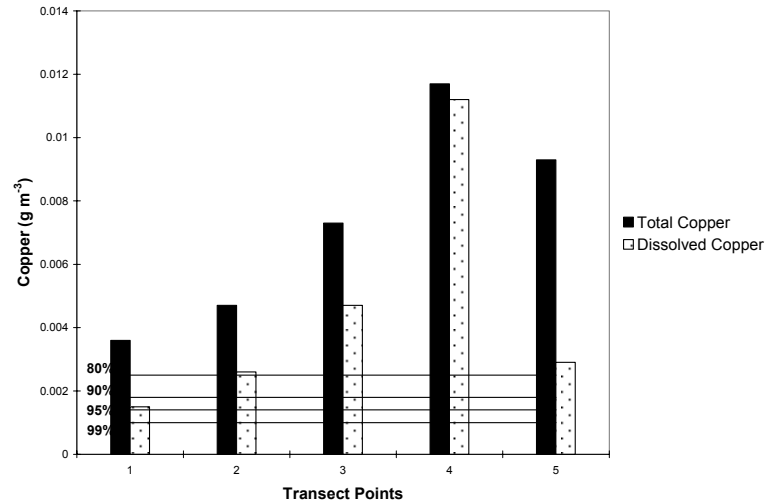


Fig. 16: Copper concentrations at baseflow compared to ANZECC trigger levels

b. Lead (Pb)

Similarly, lead (Pb) levels at baseflow posed no threat at four transect points (T1 - T4), with total and dissolved levels being below the ANZECC 99% protection threshold (0.001 g m⁻³) (Fig. 17). However, total lead at T5 was 0.0077 g m⁻³, substantially above the 90% ANZECC trigger value, although still below the 80% trigger value (0.0094 g m⁻³). Dissolved lead at T5 was below the 99% threshold, which would seem to indicate that lead bioavailability at baseflow is low.

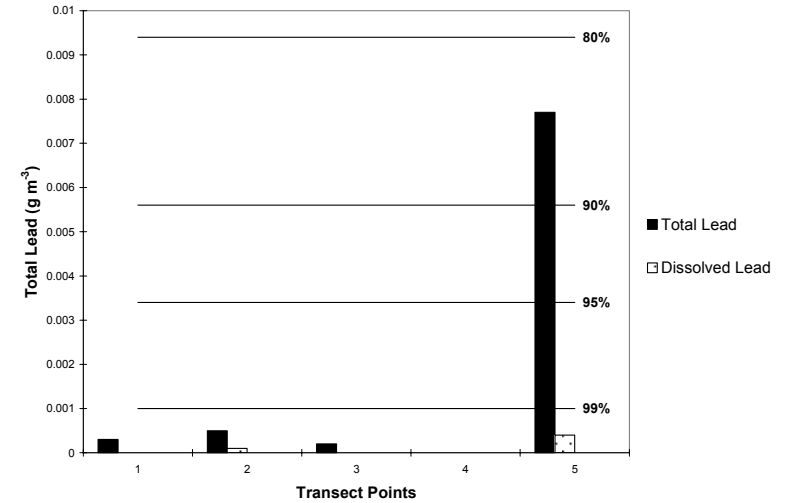


Fig. 17: Lead concentrations at baseflow compared to ANZECC trigger levels

c. Zinc (Zn)

Baseflow concentrations of total and dissolved zinc at T5 (0.124 g m⁻³ and 0.102 g m⁻³, respectively) were far in excess of the 80% threshold (Fig. 18). This suggests that bioavailable zinc is present in toxic quantities at this part of Okeover Stream. The levels of zinc at the other four transect points (T1 - T4) were comparatively low. Total and dissolved zinc concentrations at T1 - T3 were above the 95% threshold, and at T4 were just above the 99% value. There was some error in the data, with results suggesting greater concentrations of dissolved zinc than total zinc at T2 and T4. However, since concentrations were actually very low here, analytical imprecision may account for the anomaly.

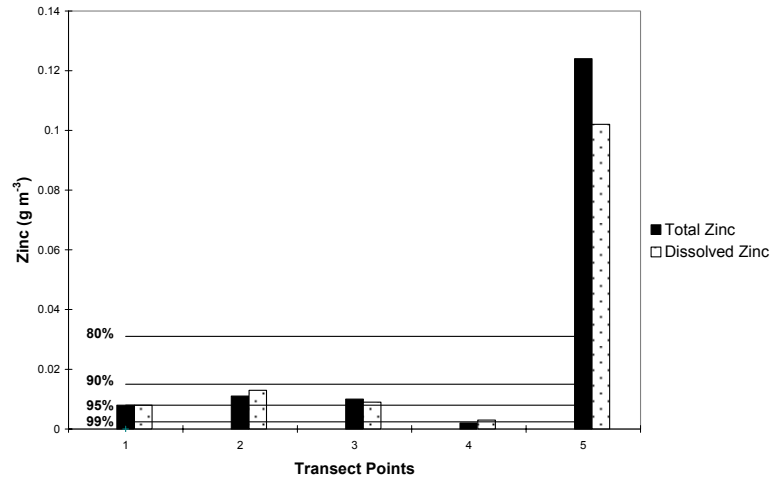


Fig. 18: Zinc concentrations at baseflow compared to ANZECC trigger levels

Table 7: Metals and hydrocarbons concentrations during baseflow conditions in Okeover, n = 3 ± S.E.

Parameter (g m ⁻³)		Transect Points				
		T1	T2	T3	T4	T5
Zinc (Zn)	total	0.008	0.011	0.01	0.002	0.124
	dissolved	0.008	0.013	0.009	0.003	0.102
Copper (Cu)	total	0.0036	0.0047	0.0073	0.0117	0.0093
	dissolved	0.0015	0.0026	0.0047	0.0112	0.0029
Lead (Pb)	total	0.0003	0.0005	0.0002	< 0.0001	0.0077
	dissolved	< DL	< DL	< DL	< DL	0.0004
Cadmium (Cd)	total	< DL	0.003	< DL	< DL	< DL
	dissolved	< DL	< DL	< DL	< DL	< DL
Nickel (Ni)	total	< DL	< DL	< DL	< DL	0.0008
	dissolved	< DL	< DL	< DL	< DL	< DL
Nitrate (NO ₃ ⁻)		2.84	3.22	2.94	2.78	1.79
BTEX	Benzene	< DL	< DL	< DL	< DL	< DL
	Toluene	< DL	< DL	< DL	< DL	< DL
	Ethylbenzene	< DL	< DL	< DL	< DL	< DL
	o-Xylene	< DL	< DL	< DL	< DL	< DL
	m & p-Xylene	< DL	< DL	< DL	< DL	< DL
PAH	Acenaphthene	< DL	< DL	< DL	< DL	< DL
	Acenaphthylene	< DL	< DL	< DL	< DL	< DL
	Anthracene	< DL	< DL	< DL	< DL	< DL
	Benzo[a]anthracene	< DL	< DL	< DL	< DL	< DL
	Benzo[a]pyrene [BAP]	< DL	< DL	< DL	< DL	< DL
	Benzo[b]fluoranthene	< DL	< DL	< DL	< DL	< DL
	Benzo[g,h,i]perylene	< DL	< DL	< DL	< DL	< DL
	Benzo[k]fluoranthene	< DL	< DL	< DL	< DL	< DL
	Chrysene	< DL	< DL	< DL	< DL	< DL
	Dibenzo[a,h]anthracene	< DL	< DL	< DL	< DL	< DL
	Fluoranthene	< DL	< DL	< DL	< DL	< DL
	Fluorene	< DL	< DL	< DL	< DL	< DL
	Indeno[1,2,3-cd]pyrene	< DL	< DL	< DL	< DL	< DL

< DL = below detection limits (tabulated in Appendices F & G)

d. Nickel (Ni)

Nickel levels were found to be acceptable at all transect points (Table 7). The highest total and dissolved nickel levels were found at T5 but were well below the point at which the ANZECC guidelines estimate 99% of species in the ecosystem are expected to survive. Total and dissolved nickel levels were 0.0008 gm^{-3} and 0.0007 g m^{-3} , respectively compared to the 99% threshold of 0.008 gm^{-3} . Nickel levels at the remaining four transect points were below detection levels and for this reason are not discussed further.

e. Cadmium (Cd)

Cadmium levels were found to be generally very low along the stream transect (Table 7). At T2, cadmium levels exceed the 90% threshold; at all other sampling points, total and dissolved cadmium concentrations remained below the 99% level. Elevated levels at T2 may be explained by the great amounts of sediment trapped at this transect point, which could result in temporary elevated cadmium concentrations in the water upon disturbance of the stream bed.

f. Nitrate (NO₃)

Nitrate is essential for the growth of aquatic plants, but elevated levels can stimulate algal growth, with the potential to cause eutrophication of the waterway (ANZECC 2000). Sufficiently high levels can be toxic to aquatic life (ECan 2004). Nitrate levels in Okeover Stream were found to be between the 95% (0.7 g m^{-3}) and 90% (3.4 g m^{-3}) ANZECC trigger values at every point along the transect (Table 7). These results are acceptable in light of the disturbed condition of the stream, and are therefore not discussed further here.

g. Aromatic Hydrocarbons

Compounds containing benzene rings are referred to as aromatic hydrocarbons (Conklin 2004). Many of these compounds are of environmental concern as toxins or carcinogens. BTEX is the common abbreviation of the group of aromatic hydrocarbons comprised of Benzene, Toluene, Ethylbenzene and Xylene. The compounds in this group have only one benzene ring. Polycyclic Aromatic Hydrocarbons (PAH) are those aromatic hydrocarbons containing two or more benzene rings and are of more environmental concern due to their greater chemical complexity and potential half-life.

Neither BTEX nor PAH appear to pose a risk at baseflow conditions since concentrations were below detection levels at every transect point along Okeover (Table 7). Therefore, they will not be discussed further.

From the results of the water quality during baseflow conditions, it appears that copper is the contaminant of greatest concern sampled throughout the transect. Zinc is also present in toxic quantities, but only at T5. High lead levels are similarly localised to T5, and do not breach the 80% ANZECC trigger value. The high concentrations of these contaminants in Okeover reveal that the stream is probably hostile to sensitive aquatic fauna even in non-storm conditions and may explain the lack of recolonisation by aquatic organisms.

3.1.4. Sediments

Sediment is important, both as a source and a sink of dissolved contaminants (ANZECC 2000). Sediment has the potential to affect the aquatic food chain through the bioavailable contaminants it may contain. ANZECC has prescribed a set of interim sediment quality guidelines (ISQG), representing what is known of the effects of contaminants in sediment on the health of an ecosystem (Table 8). These are applicable to moderately and highly disturbed aquatic ecosystems, of which Okeover Stream is the latter.

Table 8: ANZECC Interim Sediment Quality Guidelines (ISQG) (mg kg^{-1} dry wt)

	Arsenic	Nickel	Copper	Zinc
ISQG - Low	20	21	65	200
ISQG - High	70	52	270	410

In the previous stormwater project on Okeover (Farrant 2006), sediment quality was analysed along a transect starting in the ephemeral reaches and ending at a point between the sites named T5 and T4 in this study. The lowest transect point (named site number 5 in the 2006 study) was compared with data from the present sediment analysis to ascertain existing metal contaminants in sediments in Okeover.

a. Arsenic (Ar)

Arsenic levels were consistently below the low ISQG value (20 mg kg^{-1} dry wt) along the transect (Table 8), with a maximum value of 5 mg kg^{-1} dry wt at T2 and T3

(Table 9). From this, it can be deduced that arsenic is not a contaminant of concern in the sediment of the transect sampled, and is probably present at low levels in other parts of the stream also. For this reason, arsenic is not discussed further.

Table 9: Total Recoverable Metals (mg kg⁻¹ dry wt) in sediment samples:

Transect	Arsenic	Copper	Nickel	Zinc
1	3	27	8	121
2	5	336**	10	441**
3	3	14	17	297*
4	5	146*	9	364*
Site 5 from previous study	-	170*	11.8	691**
5	4	51	10	522**

* Above ANZECC ISQG-Low

** Above ANZECC ISQG-High

b. Nickel (Ni)

Similarly, nickel levels were all below the low ISQG level (21 mg kg⁻¹ dry wt), with the highest amount occurring at T3 (17 mg kg⁻¹ dry wt) (Table 9). This aligns with the results obtained from a previous study (Farrant 2006), although sediment analysis was performed on samples taken from points further upstream in the other study.

c. Copper (Cu)

Copper levels in sediment at T4 (146 mg kg⁻¹ dry wt) were double what the low ISQG recommends (65 mg kg⁻¹ dry wt) (Table 8). Copper concentrations in sediment were even higher at T2 (336 mg kg⁻¹ dry wt), far in excess of the high (270 mg kg⁻¹ dry wt) ISQC trigger level. T2 is an apparent sediment settling zone, which could explain the higher levels of copper there. Copper can accumulate in soils from the long-term application of fertilizers or fungicides (IPCS 1998) and these are likely to be washed off surfaces during storm events. Sediment is reportedly frequently removed from this section of Okeover by maintenance staff and so the high levels of copper in the sediment may not pose as significant a problem for downstream sections. However, should the sediment be allowed to

build up beyond the design constraints of the sediment-drop area, there is a risk that the highly contaminated sediment will be flushed downstream during a heavy precipitation event, thus contaminating further the downstream sections of the stream.

Copper was also found at levels exceeding the low ISQG value of 65 mg kg⁻¹ dry wt in the earlier study (17.8 mg kg⁻¹ dry wt to 170 mg kg⁻¹ dry wt) (Farrant 2006). Copper concentrations at Site 5 in the previous study, showed a substantial rise in concentration from the comparable area sampled T5 in the present study. A study in 2003 found that levels of copper in sediment in Okeover Stream were relatively low (32.3±7.2 mg kg⁻¹ dry wt) (Blakely and Harding 2005; EOS 2005). These data concur with the lower copper concentrations found at T1, T3 and T5 downstream in this study (Fig. 19), but does not concur with the high copper concentrations at T2, T4 and Site 5 from Farrant’s work conducted upstream (Farrant 2006).

Sediment sampled at T3 was taken in front of the Structures Laboratory and it is possible that this section of Okeover experienced an accidental discharge since the sediment was of a highly clay-like and plastic consistency and a grey colour. It did not resemble the sediment samples taken from any of the other transect points.

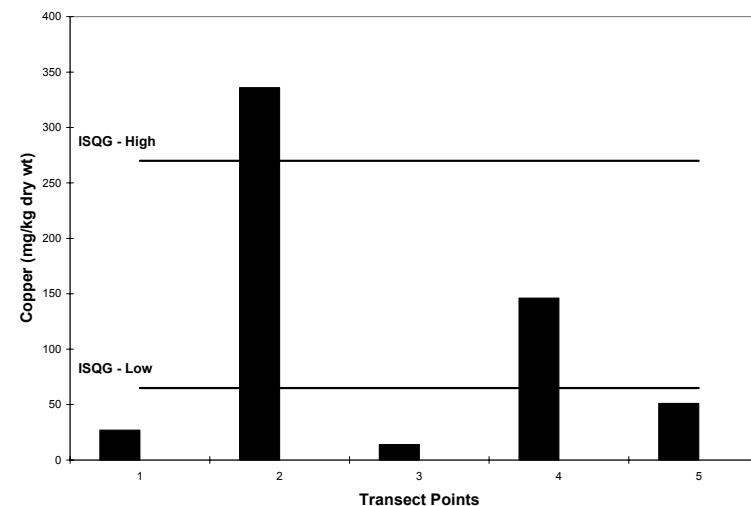


Fig. 19: Total recoverable copper in sediment (mg kg⁻¹ dry wt)

d. Zinc (Zn)

Zinc was present in sediments of Okeover Stream at levels above the low ISQG value (200 mg kg⁻¹ dry wt) (Fig. 20), except at T1. At T2 and T5, zinc levels are in excess of the high ISQG value (410 mg kg⁻¹ dry wt), while concentrations at T3 and T4 were above the recommended low ISQG value (200 mg kg⁻¹ dry wt). Zinc in the earlier study by Farrant (2006) was also found at high levels (406 mg kg⁻¹ dry wt to 955 mg kg⁻¹ dry wt), and Site 5 had comparable concentrations to T5, at 691 mg kg⁻¹ dry wt (Table 9). In the 2006 study, four transect points out of five were above the low ISQG level while Site 5 was above the highest threshold (Farrant 2006). EOS Ecology (2005) reported an average zinc value of 109.8±9.4 mg kg⁻¹ dry wt in the sediment of the Okeover stream, only half of the lower ISQG trigger value stipulated in the ANZECC guidelines.

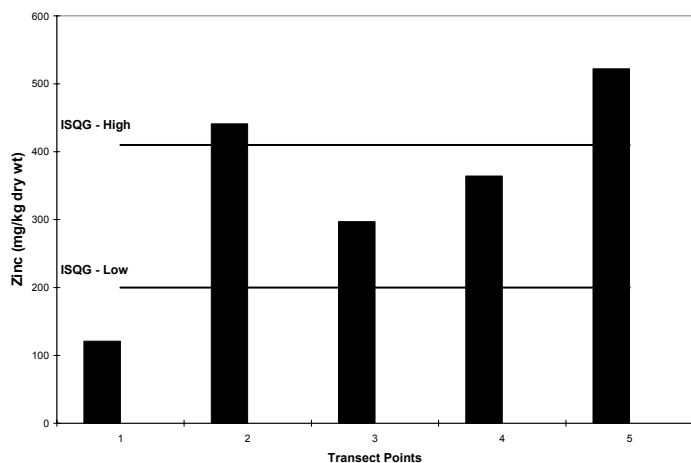


Fig. 20: Total recoverable zinc in sediment (mg kg⁻¹ dry wt)

3.1.5. Bioavailability of metal-contaminated sediments

The ANZECC Interim Sediment Quality Guidelines are the most contextual guidelines available for New Zealand sediments at present. However, there is some debate amongst sediment scientists on the appropriateness of using total dry weight metal concentrations in sediments to measure the toxicity of metal-contaminated sediments (Landner & Reuther 2004). It has been said that ‘empirical methods based on total dry weight metals concentrations in sediments should not be used to predict the toxicity from sediment-associated metals’. This is because such guidelines do not give an indication of bioavailability of the

contaminants in sediment. That is, for any given total metal concentration, the toxicity will depend on the prevailing physiochemical sediment characteristics such as oxidation-reduction potential, pH, hardness etc. (Ankley *et al.* 1996). The ANZECC ISQG values do however, provide trigger levels of contaminant concentrations at which further investigation of the state or ‘health’ of sediment is recommended.

Organic material in sediment is thought to reduce bioavailability by acting as a sink for contaminants. Therefore, to complement the ANZECC ISQG values by giving an indication of the potential bioavailability of contaminants in the stream sediment, volatile solids were calculated and used as an estimation of organic matter. The experimental procedure (as outlined in APHA 2005) was followed to give the results in Table 10:

Table 10: Percentage of volatile solids in sediment samples as an estimate of organic matter

Mass of:	Sediment sample taken from transect point:					
	T1	T2	T3	T4	T5(a)	T5(b)
Volatile Solids (%)	2.20	26.04	22.55	3.37	12.07	12.78

a. T1

Samples from T1 had a low percentage of organic matter (2.2 %) (Table 10). However, since contaminant levels were low here, increased bioavailability of the contaminants is not likely to have an adverse affect on aquatic fauna but may be a concern in terms of minimal suitable substrata available for aquatic communities.

b. T2

Sediment taken from T2 (26 %) had the highest percentage of (equivalent) organic matter (Table 10). This may be accounted for by organic litter decomposition as this area is a sediment drop zone and designed to accumulate and contain leaf litter. The high zinc and copper concentrations found at T2 (above the high ISQG values) might therefore be mitigated by reduced contaminant bioavailability through the relatively high level of organic matter. Also, sediment in this area is reportedly regularly removed to prevent the accumulated sediment from being flushed downstream in an acute storm event. It might not therefore, pose a problem for downstream sections if such maintenance is conducted regularly.

c. T3

T3 had 22 % of volatile solids (Table 10). Copper concentrations were low here, but zinc concentrations were above the ISQG - low level. Hence bioavailability of zinc could be limited by the relatively high organic component found here.

d. T4

Zinc and copper levels at T4 were relatively high (Table10), but not above the ISQG - high level. However, volatile solids were very low at this point (3.4%) and so bioavailability of the contaminants present could therefore be quite high.

e. T5

A duplicate of the T5 sample was taken for QA/QC compliance. The two percentage values of volatile solids (12.07% and 12.78%) were within the 5% of each other (Table 10). Percentage of equivalent organic matter was relatively low. However, in this instance it would be interesting to measure the oxygen level of the sediment in order to determine if organic material will give the best indication of bioavailability. If the sediment is anoxic, which is likely considering the low oxygen level in the water at this point (21.3%), sulphide from the ubiquitous sulphate-reducing bacteria in the pore-water can form some relatively insoluble compounds under circum-neutral conditions with metals such as lead, copper and zinc (Landner & Reuther 2004). High levels of these compounds (called 'acid volatile sulphides' (AVS)) are characterised by low solubility and thus low bioavailability and toxicity. Measured of oxidation-reduction potential in these sediments could indicate whether conditions were conducive to sulphide formation.

3.2. Storm Event

On Wednesday 20 December 2006, a storm event was captured in the late afternoon. Persistent yet light rain fell earlier in the mid-morning, but amounts were insufficient to disturb contaminants from impervious surfaces. Increased rainfall intensity was observed at approximately 14:30 at which time positions were taken up at the selected sampling location, T5. Sampling commenced at approximately 15:00, when an influx of water with floating plant debris exited the culvert. This may indicate that the initial influx was composed mainly of the water that had been lying stagnant in the stream in the upper regions of Okeover stream. At approximately 15:10, the rainfall intensified substantially, rising from 2.4 mm hr⁻¹ to 19.2 mm hr⁻¹.

The total rainfall over the entire storm event was 47.5 mm. To put the size of the storm event in context, for a rainfall event to be classified a storm in Christchurch, the general guide is that the volume of precipitation must exceed 25 mm. The average intensity of the entire storm was 7.80 mm hr⁻¹, but over the sampling period, the average intensity was actually higher at 10.52 mm hr⁻¹.



Fig 21: Drain on Ilam Rd that leads to Okeover via a 500 Ø culvert



Fig. 22: View of T5 from Ilam Road. The stormwater drain shown in Fig. 21 is to the left of the kerb.

3.2.1. In-situ Parameters

The pH was relatively constant (6.5 - 6.66) over the storm event, remaining slightly acidic but essentially circumneutral (Table 11). The temperature of the stream during the storm event rose to 16.8 °C at one point from 14.73 °C at baseflow. The specific conductance of the water fell to 27.9 µS cm⁻¹ from 195.0 µS cm⁻¹ during the storm event, possibly indicating initial dilution effects. The drop in conductivity with time is in line with the 'first flush' trend, a pattern followed by most of the contaminants, whereby their concentration peaked shortly after the storm began and then gradually declined thereafter. Turbidity rose dramatically to

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a mean value of 120 NTU at 15:20 from the baseflow turbidity of 5.26 NTU. Dissolved Oxygen concentration rose from 21 % saturation at baseflow to 97 % saturation at the end of the sampling period. These measurements evidence how the water quality of the stream changes dramatically over a short period. Of most concern are the elevated turbidity and temperature readings, which prevent the ecosystem from being an optimal habitat for aquatic fauna.

Table 11: *In-situ* water chemistry results in Okeover stream during storm conditions

Sampling time:	pH	Dissolved Oxygen	Dissolved Oxygen	Temperature	Conductivity	Specific Conductance (calculated)	Mean Turbidity	Oxidation - Reduction Potential (ORP)
T5 at:		g m ⁻³	% Saturation	°C	µS cm ⁻¹	µS cm ⁻¹	NTU	mV
14:26	6.53	5.13	50.20	14.5	155.5	194.97	42.9	134
15:29	6.65	8.63	88.60	16.8	52.5	45.38	110.0	111
16:00	6.66	9.49	96.64	15.6	25.6	27.95	26.3	135

3.2.2. Discharge

Flow gauging was conducted twice during the storm event and flow discharge was found to increase rapidly over the sampling event, as anticipated (Fig. 23). This increase was readily apparent during sampling; the water level was observed to rise from 17 cm to 200 mm in less than 60 minutes at T5.

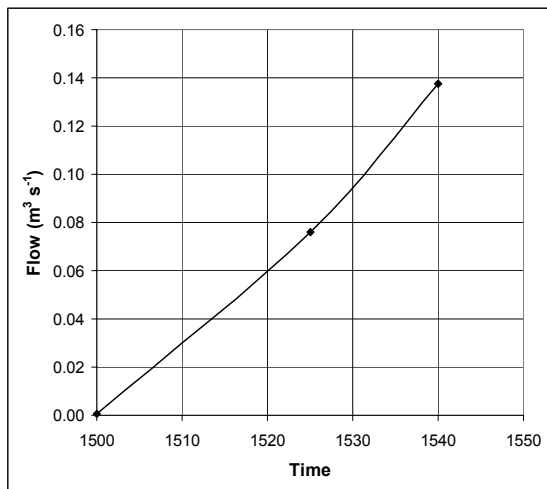


Fig. 23: Flow during Storm Event

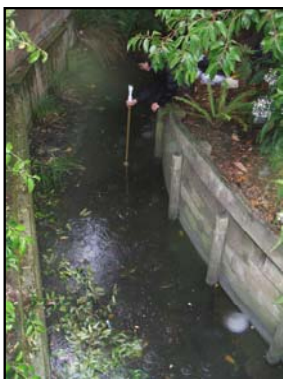


Fig. 24: Flow gauging at T5 during storm event

3.2.3. Water Chemistry

a. Copper (Cu)

Copper is widely distributed in water because it is a naturally occurring element (IPCS 1998). Uncontaminated natural freshwater streams normally have copper concentrations in the range of 1.0-20 µg litre⁻¹ (or 0.001 - 0.02 g m⁻³) (Nriagu 1979).

Total copper levels in the initial samples during the storm event were 0.0279 g m⁻³ (Table 12). These levels were far in excess of the 80% trigger level (0.0025 g m⁻³); the baseflow concentration (0.0093 g m⁻³); or the average level for uncontaminated freshwater streams (0.001 - 0.0002 g m⁻³). As sampling progressed, copper levels dropped slightly before a peak occurred at 15:20 of 0.0525 g m⁻³, representing the 'first flush' effect. Copper levels dropped from this point onward and towards the conclusion of sampling at 16:20, concentrations returned to baseflow levels.

These trends closely mirror those for total copper observed further upstream (ephemeral) during a storm event in May 2006 (Farrant 2006). In that reported event, a brief decline in total copper levels was observed followed by a sharp peak and then another, more gradual, decline. In both the 2006 study and the study reported here, total copper levels remained above the 80% ANZECC trigger threshold for the entire sampling period, indicating that copper could pose a threat to the biota of downstream regions.

Copper toxicity for aquatic biota is critically dependent on the bioavailability of the copper in the water. Thus, total copper is rarely used as an indicator of toxicity. Bioavailability can depend on the speciation of the copper, the level of adsorption and complexation by organic matter (including sediment particles), and the pH and hardness of the water and so ecotoxicity tests should be conducted, along with water quality monitoring, to ascertain metal bioavailability.

Dissolved copper followed a similar trend to that of total copper, but the peak concentration (0.0087 g m⁻³) occurred earlier in the sampling period (Fig. 25). In essence, the first flush of dissolved copper occurred sooner than that of the total copper. These results would suggest that the dissolved copper takes a shorter time

to travel to the stream from the impervious surfaces. The same general trend is similar to that of the May 2006 study (Farrant 2006). Furthermore, in both studies, dissolved copper peaked at approximately the same concentration at approximately 0.01g m⁻³, indicating that dissolved copper concentrations are on average about this level.

Dissolved copper levels peaked above the 80% threshold and remained above this threshold for the duration of stormwater sampling (Fig. 25). An Environmental Health Criteria monograph for copper has been published by the International Programme on Chemical Safety (IPCS), a joint venture of the United Nations Environment Programme (UNEP), the International Labour Organization (ILO), and the World Health Organization (WHO). For the level of dissolved copper found in the Okeover during this storm event, the monograph advises that significant effects can be expected for diatoms and sensitive invertebrates (International Programme on Chemical Safety (1998).

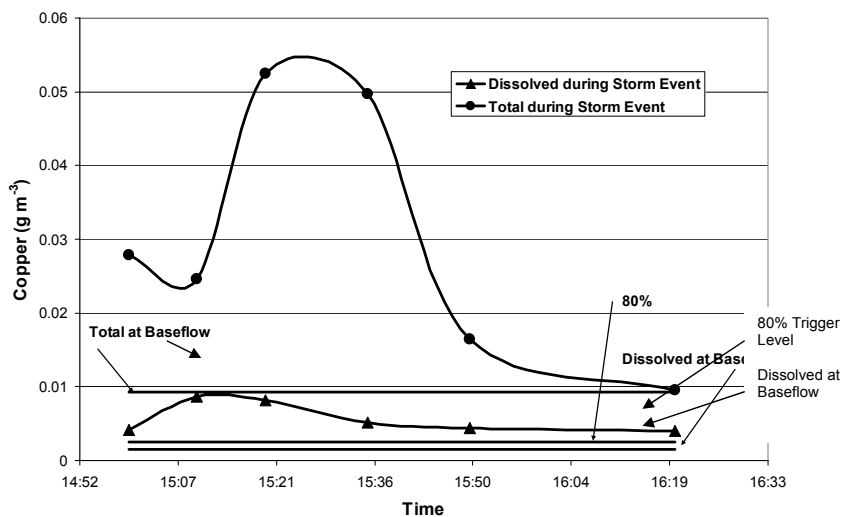


Fig. 25: Copper at T5 during storm event and at baseflow

Table 12: Concentrations of metals and hydrocarbons in water during storm event conditions in Okeover, n = 3 ± S.E.

Parameter (g m ⁻³)	Sample							
	1	2	3	4	5	QA*	6	
	Time	15:00	15:10	15:20	15:35	15:50	15:50	16:20
Zinc (Zn)	total	0.200	0.140	0.521	0.516	0.220	0.181	0.126
	dissolved	0.068	0.104	0.195	0.145	0.113	0.106	0.089
Copper (Cu)	total	0.0279	0.0246	0.0525	0.0497	0.0164	0.0144	0.0096
	dissolved	0.0041	0.0087	0.0081	0.0052	0.0044	0.0045	0.0040
Lead (Pb)	total	0.0095	0.0084	0.0653	0.0734	0.0275	0.0227	0.0105
	dissolved	0.0004	0.0005	0.0013	0.0012	0.0010	0.0009	0.0008
Cadmium (Cd)	total	0.00013	< DL*	0.00026	0.00017	0.00007	< DL	< DL
	dissolved	< DL	< DL	< DL	< DL	< DL	< DL	< DL
Nickel (Ni)	total	0.0030	0.0016	0.0046	0.0039	0.0016	0.0012	0.0008
	dissolved	< DL	0.0007	0.0006	< DL	< DL	< DL	< DL
Nitrate (NO ₃ ⁻)		1.07	1.91	0.239	0.276	0.187	0.176	0.135
BTEX	Benzene	< DL	< DL	< DL	< DL	< DL	< DL	< DL
	Toluene	< DL	< DL	0.008	0.009	0.003	0.002	0.002
	Ethylbenzene	< DL	< DL	< DL	< DL	< DL	< DL	< DL
	o-Xylene	< DL	< DL	< DL	< DL	< DL	< DL	< DL
	m & p-Xylene	< DL	< DL	< DL	< DL	< DL	< DL	< DL
PAH	Acenaphthene	< DL	< DL	< DL	< DL	< DL	< DL	< DL
	Acenaphthylene	< DL	< DL	< DL	< DL	< DL	< DL	< DL
	Anthracene	< DL	< DL	< DL	< DL	< DL	< DL	< DL
	Benzo[a]anthracene	< DL	< DL	< DL	< DL	< DL	< DL	< DL
	Benzo[a]pyrene [BAP]	< DL	< DL	< DL	< DL	< DL	< DL	< DL
	Benzo[b]fluoranthene	< DL	< DL	< DL	< DL	< DL	< DL	< DL
	Benzo[k]fluoranthene	< DL	< DL	< DL	< DL	< DL	< DL	< DL
	Chrysene	< DL	< DL	< DL	< DL	< DL	< DL	< DL
	Dibenzo[a,h]anthracene	< DL	< DL	< DL	< DL	< DL	< DL	< DL
	Fluoranthene	< DL	< DL	< DL	< DL	< DL	< DL	< DL
Fluorene	< DL	< DL	< DL	< DL	< DL	< DL	< DL	
	Indeno[1,2,3-cd]pyrene	< DL	< DL	< DL	< DL	< DL	< DL	< DL

* QA = Quality Assurance sample for comparison with sample number five
 ** < DL = below detection limits (tabulated in Appendix G)

b. Lead (Pb)

Total lead levels rose to well above the 80% ANZECC trigger level during the storm event and then gradually declined to base levels, following the same ‘first flush’ trend seen with other metals (Fig. 26). However, although the levels fall appreciably compared with the peak lead concentration at 0.0734 g m^{-3} , the base level value was still above the 90% trigger level and is therefore of concern in the Okeover stream.

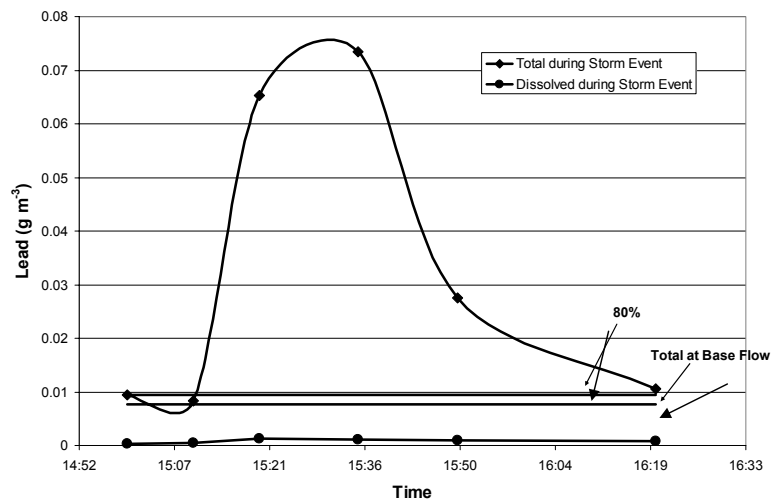


Fig. 26: Lead at T5 during storm event and at baseflow

It was noted in an earlier study, that an extremely high total lead value measured at the start of sampling may have been an anomaly (Farrant 2006). However, when compared to the levels found here, it is perhaps conceivable that the high lead value was actually not an anomaly. Further investigation would be required to verify this.

The high level of total lead is of concern considering that fuel in New Zealand is now unleaded (and most pipes in Christchurch are no longer made from lead). The lead may instead come from painted wooden structures (Davis *et al.* 2001). A common form of lead used in paint decades ago was basic lead carbonate ($\text{Pb}(\text{CO}_3)_2(\text{OH})_2$) (Barnes & Davis 1996, Davis *et al.* 2001). Lead can be released in particulate form or through dissolution. Considering that the residential area

within the upper Okeover catchment was established more than twenty years ago, it is possible that the particulate lead originated from such paint.

Dissolved lead levels seem to pose no serious threat to stream health. As with baseflow results, the level of dissolved lead in the storm event was negligible when compared to total lead concentrations. Dissolved lead levels were above the 99% threshold at two sampling points, but fell below again shortly thereafter (Fig. 26). The dissolved lead concentration peaked later than the other metals in the course of sampling. This is perhaps due to the relative heaviness of lead (atomic weight of 207 g) compared to other metals (e.g. zinc has an atomic weight of 65 g). Lead in the environment is strongly adsorbed onto sediment particles, reducing its availability to organisms (IPCS 1989) and so this may account for relatively low dissolved lead concentrations in the water.

c. Zinc (Zn)

Total zinc was identified as the contaminant of most concern on a mass loading basis in the 2006 study undertaken upstream of the current sampling event (Farrant 2006). It is also of great concern here (Fig. 27). Zinc levels rose to 0.521 g m^{-3} at 15:20, far in excess of the 80% ANZECC trigger value of 0.031 g m^{-3} . At the end of sampling, the level of total zinc during the storm event was close to that of baseflow, but still significantly above the 80% threshold.

Dissolved zinc was also above the 80% ANZECC threshold, but did not fall to baseflow levels (0.008 g m^{-3}) within the sampling period (Fig. 27). The European predicted no-effect concentration (PNEC) is set at $0.015\text{-}0.025 \text{ g m}^{-3}$ for dissolved zinc in a stream with low levels of trace elements at baseflow. That is, where there is little background concentration of zinc (in this case) during normal conditions, a high concentration such as that found in stormwater will be more toxic to biota than if the levels in the stream were higher at baseflow. Therefore, since the baseflow concentration at 0.008 g m^{-3} is within acceptable limits and below the 80% ANZECC trigger value, the high concentrations entering during storm events are more likely to be toxic to fauna in this section of the Okeover stream.

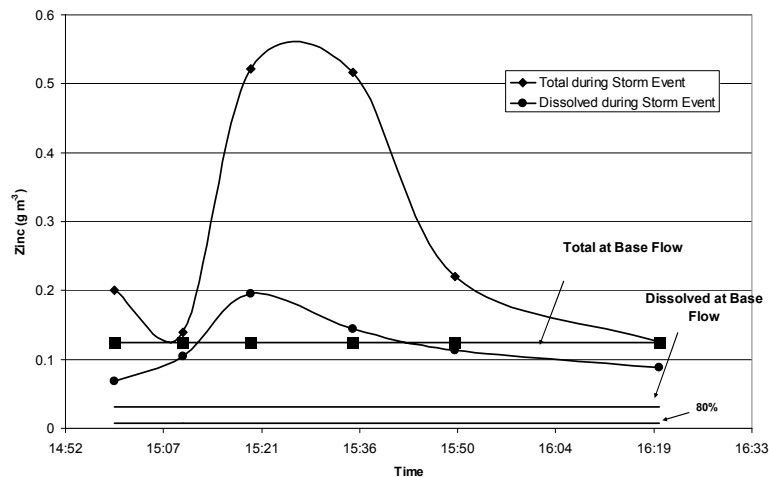


Fig. 27: Zinc at T5 during storm event and at baseflow

Zinc ingestion at high levels can interfere with gastrointestinal copper absorption. It is possible that the high zinc levels, although toxic, somewhat mitigate the bioavailability of the copper in the Okeover. Further ecotoxicological investigations would be required to validate this, but the preferred solution would be the reduction of both zinc and copper levels to below the 80% trigger level, thereby minimising potential ecotoxicity from these metals.

d. Aromatic Hydrocarbons

PAH stayed below detection levels at all times during the storm event (Table 12). BTEX levels were mostly below detection levels during the storm event, except for low levels of toluene, which peaked at 0.009 g m⁻³.

Toluene is used as a substitute for lead in petrol because of its high octane level and low vapour pressure (Shell Chemicals). It is therefore possible that petrol is the source of the toluene found in the Okeover Stream during the storm event. The ANZECC guidelines do not have trigger levels for toluene, because of insufficient data on its effects on aquatic ecosystems. Since no results were above detection levels at baseflow and only for one compound (toluene) at low concentrations during the storm event, it can be surmised that BTEX and PAH are

not contaminants of concern in this part of Okeover Stream. However, it would be interesting to conclusively determine the source of the toluene, and the levels required to have a detrimental effect on the ecological health of a freshwater stream.

3.2.4. Contaminant Loadings

Loadings represent the gross amount of contaminants expected to accumulate in a system. It is important to know expected contaminant loadings before any possible treatment systems could be considered for mitigating stormwater contaminants in the Okeover stream. This is because treatment systems are designed according to their expected contaminant loading and desired treatment efficacy and thus, their treatment performance would be compromised if this information was not known. Contaminant loadings were calculated for the flows corresponding to the highest concentrations of each metal of concern; and to the last recorded concentrations, which were also the lowest concentrations after the first flush peak. Peak concentrations occurred at slightly different times for each metal and metal speciation (Table 13). The lag time between heavy rainfall and contaminants exhibiting a peak concentration in the sampling was approximately 40 - 50 minutes, depending on the metal.

Table 13: Times at which peak flow occurred during storm event

Metal	Metal type	Time	Sample Number	Flow (m ³ s ⁻¹) at:	
				Peak concentration	Last recorded concentration
Copper	Total	15:20	3	0.06	0.30
	Dissolved	15:10	2	0.03	0.30
Zinc	Total	15:20	3	0.06	0.30
	Dissolved	15:20	3	0.06	0.30
Lead	Total	15:35	4	0.12	0.30
	Dissolved	15:20	3	0.06	0.30

Total zinc was the dominant contaminant on a mass loading basis when compared with total lead and total copper concentrations (Fig. 28). These results are in accordance with the previous study (Farrant 2006). Zinc in its dissolved state was also substantially higher than lead and copper (Fig. 29). Again, this aligns with the results of the previous study (Farrant 2006).

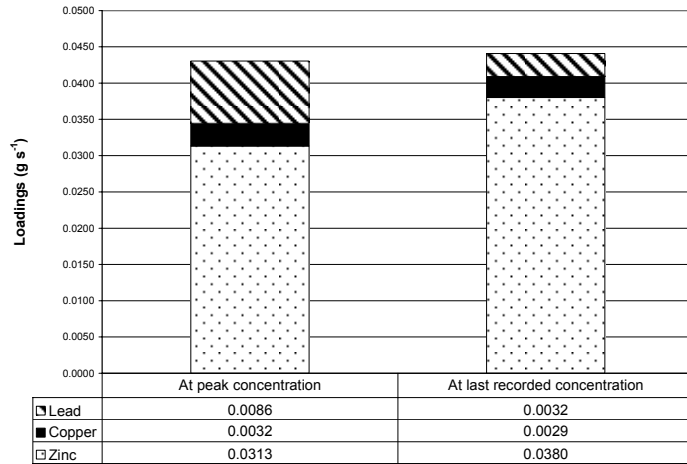


Fig. 28: Loadings of total metals during storm event

Due to the marked increase in flow of $0.302 \text{ m}^3 \text{ s}^{-1}$ when the final concentrations were recorded, compared to the lower flows where peak concentrations were observed ($0.0301 \text{ m}^3 \text{ s}^{-1}$ to $0.1169 \text{ m}^3 \text{ s}^{-1}$), there was an increase in loading for both dissolved and total metals (Figs. 28 & 29) after the initial ‘first flush’ concentrations peaks. This increase in loading also occurred in the previous study, and was followed by a decrease in loading values as flow decreased accordingly (Farrant 2006). This exemplifies how important it is to quantify both flow discharge and contaminant concentrations during stormwater sampling.

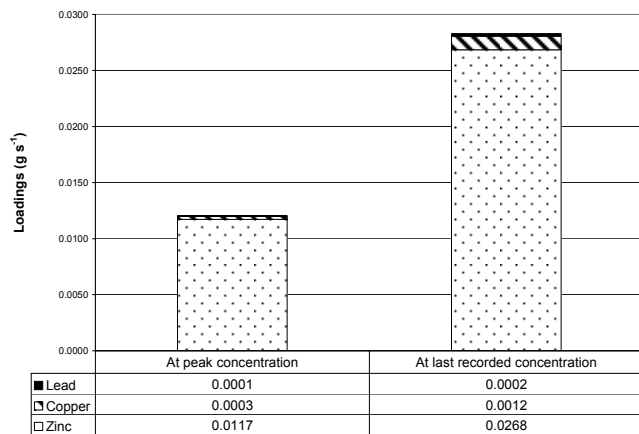


Fig. 29: Loadings of dissolved metals during storm event

4. RECOMMENDATIONS

From the results of this and previous studies, the water in Okeover has been shown to be in a degraded state, and is probably toxic to some aquatic biota. A successful rehabilitation plan that aims to improve the ecosystem requires a holistic approach to catchment management in the formulation of Best Management Practices (BMP). As part of this, an engineering solution is required to contain or divert contaminants (e.g. grassed swales, soakage basins, dry detention basins, extended wet period wet ponds, wetlands (CCC 2003)), while concurrently aiming to replenish some base flows. A system comprising a lime rock filter, swale, detention pond and surface flow wetland was discussed in the previous study (Farrant 2006). It has also been suggested that a detention pond could be constructed on Ilam field to contain contaminant loads from the first flush of a storm event (Pers. Comm. Dr. Aisling O’Sullivan, Natural Resources Engineering Group, UC). Ideally, the treatment system that is eventually implemented would have low maintenance requirements and would have to consider constraints imposed by the environment. These include available land area; current land-use; land topography and available slope, depth to ground water characteristic of the Christchurch area; and resources, both financial and human.

It is proposed that the second component of a successful integrated solution is the promotion of education and community awareness regarding stormwater management. A significant proportion of the contaminants originate from numerous small residential spills onto impervious surfaces, which are then washed into the stormwater system by rainfall. Alternatively, through ignorance or apathy, contaminants such as crude oils and detergents are disposed of by residents directly into stormwater drains. On an individual basis, the amount of contaminants might be negligible, but their cumulative effect is more serious. Educational programmes aimed at primary school children have been instituted in city centres (Auckland, Christchurch and Dunedin). These involve the children spray-painting a stencilled fish on the concrete next to stormwater drains in their area to reinforce that the drain discharges directly into the environment without passing through a treatment system. As highlighted by Farrant’s study 2006, heightened community awareness is necessary to dispel the belief that ‘dilution is the solution’. The general public is probably unaware that the amount of a contaminant required to adversely affect an ecosystem can actually be quite low. Publicity of the rehabilitation efforts on Okeover and other urban streams in

Christchurch and nationwide could help to address this, and could engender interest from groups such as community boards and nearby residents. Okeover is the subject of ongoing research and university field laboratory classes for Natural Resources Engineering, Biology and some Civil Engineering students. It might also be interesting to approach teachers from neighbouring primary schools to gauge interest in its use as an educational tool for younger children. This would have the effect of reaching pupils who might not be exposed to the project at a tertiary level.

Considerations for possible treatment technologies:

Something that will have to be considered in designing a treatment system for stormwater inputs is the particle size distribution of sediments in the stormwater. Stoke's Law governs the settling rates of larger, spherical particles under laminar flow conditions and is given by:

$$D = 3\pi\eta vd \quad \text{[Eqn. 6]}$$

where η = the dynamic viscosity of water ($1 \text{ mg mm}^{-1}\text{sec}^{-1}$)

v = settling velocity of a spherical particle (mm sec^{-1})

d = diameter of the spherical particle (mm)

While this formula can be used to determine the likely settling rate of suspended solids, thereby removing turbidity and concomitant particulate metals, it does not ideally apply to smaller particles, which are the predominant particles of concern in stormwater as metals are more likely to be adsorbed to them. These particles are also more likely to stay in solution and thus possibly defeat the purpose of a settling pond, which is to encourage the settlement of contaminated sediments (i.e. particulate metals). Therefore, it is recommended that an analysis of particle size fractions and their respective metal concentrations is conducted in order to ascertain the distribution of suspended particles that would be targeted in a detention-type treatment strategy. This information could be obtained in a once-off stormwater monitoring/sampling period targeting the 600 mm and 500 mm diameter culverts in the upper ephemerals and lower reach of Okeover simultaneously, as well as sediments in the stream bed.

It is also proposed that calculating the sediment-water partitioning coefficients (as per Farrant 2006) would be helpful to understand metal dynamics in the Okeover ecosystem. Partitioning coefficients represent a metal's preference to remain in a dissolved or particulate state in a solid/liquid matrix. This preference has implications for the type of treatment device that could eventually be implemented. Partitioning coefficients are calculated from the total and dissolved concentrations of the metals of concern, along with total suspended solids (TSS) concentrations. K_d , from which the partitioning coefficient, $\text{Log } K_d$, is found, is calculated with the following formula:

$$K_d = \frac{C(\text{particulate})}{C(\text{dissolved})} \quad (\text{m}^3 \text{ Kg}^{-1}) \quad \text{[Eqn. 8]}$$

Where: $C(\text{dissolved})$ = concentration of dissolved metals (mg m^{-3}); and

$C(\text{particulate})$ = concentration of metals in particulate form (mg Kg^{-1}):

$$C(\text{particulate}) = \frac{(C(\text{total}) - C(\text{dissolved}))}{TSS} \quad (\text{mg mg}^{-1}) \quad \text{[Eqn. 9]}$$

Where $C(\text{total})$ = concentration of total metals (mg m^{-3}); and

TSS = Total Suspended Solids (mg m^{-3})

In addition to further analysis of sediments in Okeover, it is recommended to continue monitoring the water quality during both baseflow (where available) and stormflow conditions in order to generate sufficient data for better understanding this highly modified ecosystem.

5.0 CONCLUSIONS

Water and sediment sampled from Okeover Stream were analysed for metals at baseflow along a five-point transect between Ilam Road and Clyde Road. Water from the fifth transect point (T5) was also analysed during a storm event that took place on 20 December 2006, to determine the quality of the stormwater and to provide a comparison with a study undertaken further upstream in the ephemeral regions earlier in 2006 (Farrant 2006).

Results from the storm event showed a high correlation with those of the earlier study: copper (Cu), zinc (Zn) and lead (Pb) were found at concerning levels in the stormwater samples. Furthermore, dissolved proportions of the total concentrations for each of these metals were high, indicating that they are relatively bioavailable. High, potentially toxic, levels of copper, zinc and lead were also found in water and sediment samples at baseflow.

Nickel, cadmium, BTEX and PAH levels were either below detection levels, or at levels low enough not to be of concern. We therefore recommend that they are not considered in future water and sediment quality sampling in Okeover Stream.

Stormwater is a challenging discharge to regulate because of its diffuse nature. It is submitted that a holistic approach is required to enhance ecosystem improvements in the Okeover stream. Sufficient preliminary data has probably been collected to explore the design of an ecological engineering treatment system such as a detention pond or treatment wetland. This could be the subject of future research. Additionally, community awareness of the problems associated with stormwater needs to be heightened, and involvement in a solution encouraged. Finally, the legislative regime perhaps needs revision in order to ensure it provides the best solutions for stormwater discharges. This point is connected to community awareness and involvement as the higher the profile of the problem, the more likely it is to receive attention at a national government level. It is further proposed that options for legislative change in relation to approaches in other jurisdictions might be an interesting subject for a law honours project or dissertation at the University of Canterbury.

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- Google Earth
<http://earth.google.com/>

APPENDIX A - Example of Hills Laboratories Chain of Custody

APPENDIX B - Example of Cation/Anion Balances

ANALYSIS REQUEST

CLIENT
 Name University of Canterbury 37559
 Address Private Bag 4800
 CHRISTCHURCH
 Client Phone 03 4223524x Fax 03 304 2999
 Client Reference CCC/Econ Storm H2O Pottery for Teaching
 Quote No 19058 Order No

Hill Laboratories
 R1 Hill Laboratories Limited - accredited by International Accreditation NZ
 1 Clyde Street, Telephone: +64 (7) 858-2000
 Private Bag 3205, Facsimile: +64 (7) 858-2001
 Hamilton, Email: mail@hill-labs.co.nz
 New Zealand, Internet: www.hill-labs.co.nz

RESULTS TO Mail Client Mail Submitter
 Fax Results
 Email Results ent32@shident.canterbury.ac.nz
 aising-osullivan@canterbury.ac.nz

CHAIN OF CUSTODY RECORD

Sent to Hill Laboratories Date & Time: 7-12-2006
 Name: ACS/ELIE TAPPS
 Signature: [Signature]
 Please tick if you require COC to be faxed back

Received at Hill Laboratories Date & Time: - 8-12-2006
 Name: [Signature]
 Signature: [Signature]

Condition
 Room Temp Chilled Frozen Temp:
 Sample & Analysis details checked
 Signature: [Signature]

PRIORITY Normal (up to 10 days) High (5 days) Urgent (ASAP, extra charge applies, please contact lab first)
 Date results required by: ASHT

SAMPLE TYPES

Waters	E Effluent	G Geothermal	P Potable	SW Surface Water
	GW Ground Water	L Leachate	S Saline	TW Trade Waste
Solids	ES Soil	Se Sediment	SI Sludge	PI Plant
Other	O Oil	M Miscellaneous	FS Fish/shellfish/biota	BM Biological Material

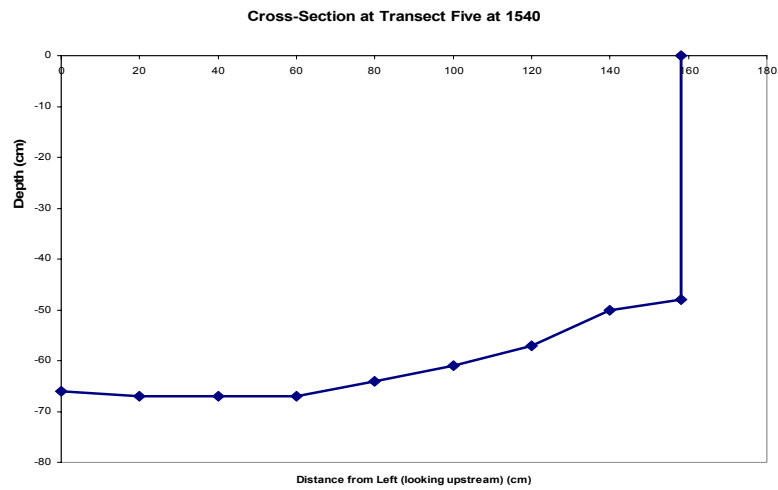
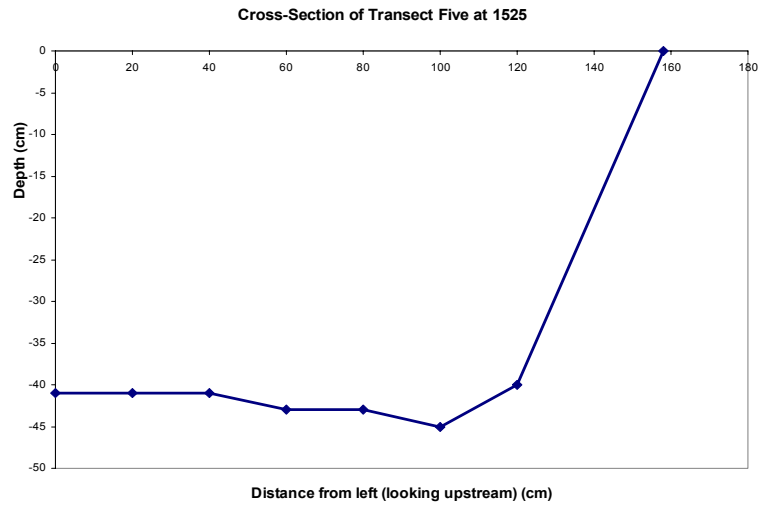
No.	Sample Identification	Sample Type	Tests Required	Date Sampled
1	T2-061206 (a)	SW	Dissolved metals (Zn, Cu, Pb, Ni, Cd) CATION SUITE (Ca, Mg, K, Na, SO4)	6-12-06
2	T2-061206 (b)	SW	TSS	↑ 6-12-06 ↓
3	T2-061206 (c)	SW	Total metals (Zn, Cu, Pb, Ni, Cd)	
4	T2-061206 (d)	SW	PAH	
5	T2-061206 (e)	SW	BTEX	
6	T2-061206 (f)	SW	BTEX	
7	T3-061203 (a)	SW	Dissolved metals - same as 1	
8	T3-061206 (b)	SW	"	
9	T4-061206 (c)	SW	"	
10	T4-061206 (d)	SW	"	

Cation/Anion Balance for Baseflow data

Transect	Anion/Cation Balance			
	Total Anions mEq/L	Total Cations mEq/L	Total mEq/L	% Difference
1	1.68	1.66	-0.01	-0.60
2	1.86	1.83	-0.01	-0.81
3	1.72	1.69	-0.01	-0.88
4	1.64	1.60	-0.01	-1.23
5	1.96	1.91	-0.01	-1.29

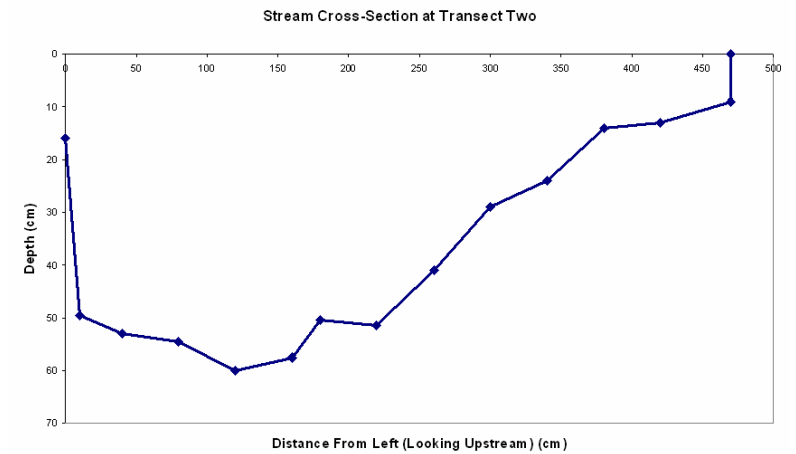
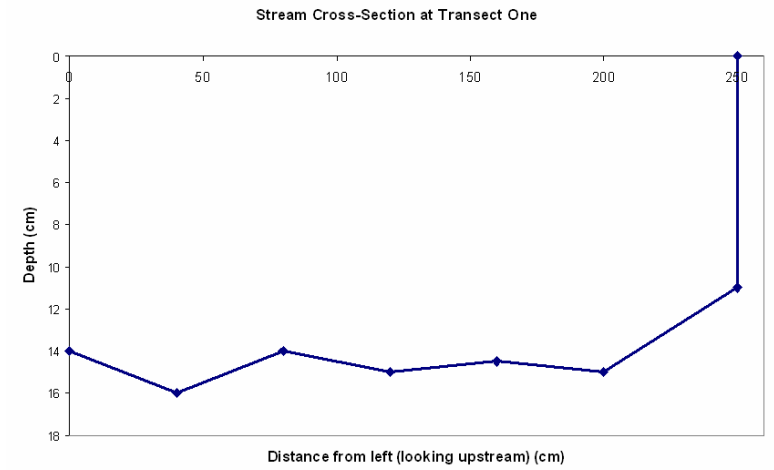
APPENDIX C - Storm Event

Storm Event Flow Cross-Sections

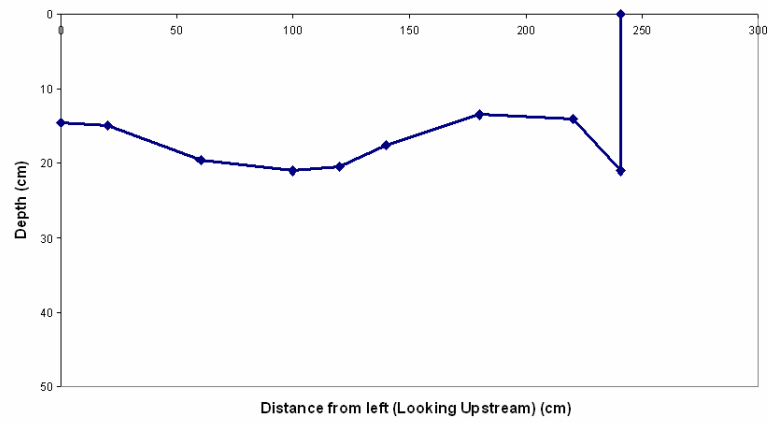


APPENDIX D - Baseflow

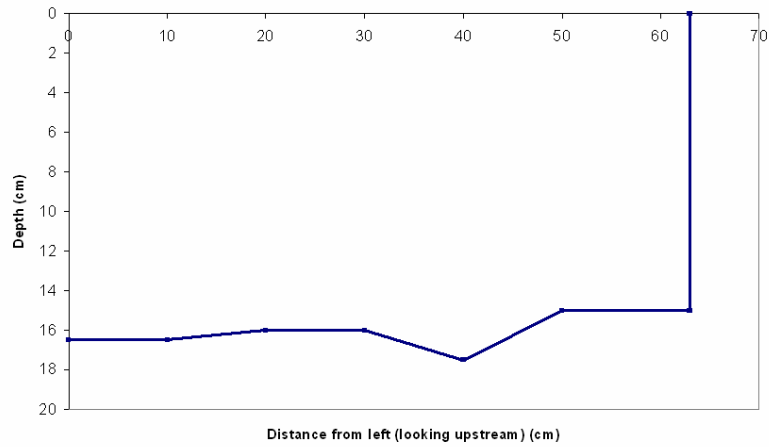
i. Baseflow Cross-sections



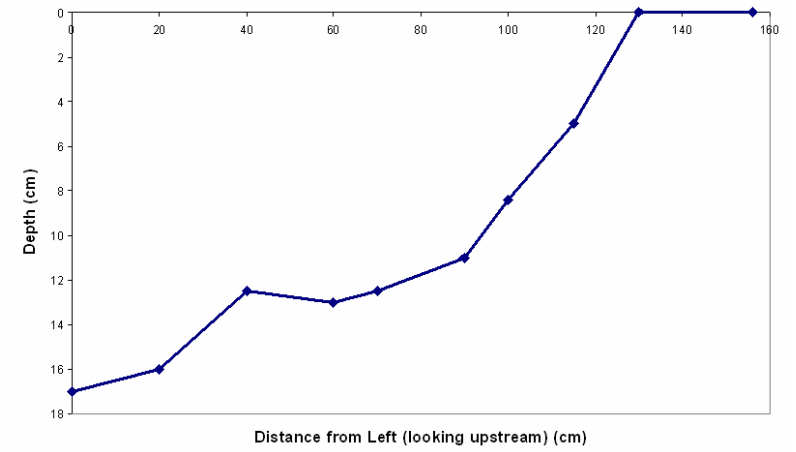
Stream Cross-Section at Transect Three



Stream Cross-Section at Transect Four



Stream Cross-Section at Transect Five



ii. Example of Velocity and depth values used to calculate discharge

Flow Gauging Results on Okeover Stream		
Transect Two		
Conditions: Fine weather. Flow curves around to RH bank but is very slow on that side.		
Date & Time: 6/12/06, 09:53		Width: 470 cm
DfL (looking upstream) (cm)	Depth of water (cm)	Average velocity (m/s)
0	16	0.005
10	49.5	0.005
40	53	0.005
80	54.5	0.06
120	60	0.04
160	57.5	0.08
180	50.5	0.005
220	51.5	0.005
260	41	0.005
300	29	0.005
340	24	0.005
380	14	0.005
420	13	0.005
470	9	0.005
Total Area (m ²)=		1.7935
Total Mean Stream Velocity (m/s)=		0.0168
Flow/Discharge (m ³ /s)=		0.0301

APPENDIX E - ANZECC Guidelines

ANZECC Interim Sediment Quality Guidelines		
Contaminant	Trigger Values (mg kg ⁻¹ dry wt)	
	Low	High
Arsenic	20	70
Copper	65	270
Nickel	21	52
Zinc	200	410

Table 3.4.1 Trigger values for toxicants at alternative levels of protection. Values in grey shading are the trigger values applying to typical *slightly–moderately disturbed systems*; see table 3.4.2 and Section 3.4.2.4 for guidance on applying these levels to different ecosystem conditions.

Chemical	Trigger values for freshwater (µg/L ⁻¹)				Trigger values for marine water (µg/L ⁻¹)			
	Level of protection (% species)				Level of protection (% species)			
	99%	95%	90%	80%	99%	95%	90%	80%
METALS & METALLOIDS								
Aluminium pH >6.5	27	55	80	150	ID	ID	ID	ID
Aluminium pH <6.5	ID	ID	ID	ID	ID	ID	ID	ID
Antimony	ID	ID	ID	ID	ID	ID	ID	ID
Arsenic (AsIII)	1	24	94 ^C	380 ^C	ID	ID	ID	ID
Arsenic (AsV)	0.8	13	42	140 ^C	ID	ID	ID	ID
Beryllium	ID	ID	ID	ID	ID	ID	ID	ID
Bismuth	ID	ID	ID	ID	ID	ID	ID	ID
Boron	90	370 ^C	680 ^C	1300 ^C	ID	ID	ID	ID
Cadmium H	0.06	0.2	0.4	0.8 ^C	0.7 ^B	5.5 ^{R,C}	14 ^{R,C}	36 ^{R,A}
Chromium (CrIII)	H	ID	ID	ID	7.7	27.4	48.6	90.6
Chromium (CrVI)	0.01	1.0 ^C	6 ^A	40 ^A	0.14	4.4	20 ^C	85 ^C
Cobalt	ID	ID	ID	ID	0.005	1	14	150 ^C
Copper H	1.0	1.4	1.8 ^C	2.5 ^C	0.3	1.3	3 ^C	8 ^A
Gallium	ID	ID	ID	ID	ID	ID	ID	ID
Iron	ID	ID	ID	ID	ID	ID	ID	ID
Lanthanum	ID	ID	ID	ID	ID	ID	ID	ID
Lead H	1.0	3.4	5.6	9.4 ^C	2.2	4.4	6.6 ^C	12 ^C
Manganese	1200	1900 ^D	2500 ^D	3800 ^D	ID	ID	ID	ID
Mercury (inorganic) B	0.06	0.8	1.9 ^C	5.4 ^A	0.1	0.4 ^C	0.7 ^C	1.4 ^C
Mercury (methyl)	ID	ID	ID	ID	ID	ID	ID	ID
Molybdenum	ID	ID	ID	ID	ID	ID	ID	ID
Nickel H	8	11	13	17 ^C	7	70 ^C	200 ^A	560 ^A
Selenium (Total) B	5	11	18	34	ID	ID	ID	ID
Selenium (SeIV) B	ID	ID	ID	ID	ID	ID	ID	ID
Silver	0.02	0.05	0.1	0.2 ^C	0.8	1.4	1.8	2.6 ^C
Thallium	ID	ID	ID	ID	ID	ID	ID	ID
Tin (inorganic, SnIV)	ID	ID	ID	ID	ID	ID	ID	ID
Tributyltin (as µg/L Sn)	ID	ID	ID	ID	0.0004	0.006 ^C	0.02 ^C	0.05 ^C
Uranium	ID	ID	ID	ID	ID	ID	ID	ID
Vanadium	ID	ID	ID	ID	50	100	160	290
Zinc H	2.4	8.0 ^C	15 ^C	31 ^C	7	15 ^C	23 ^C	43 ^C
NON-METALLIC INORGANICS								
Ammonia D	320	900 ^C	1430 ^C	2300 ^A	500	910	1200	1700
Chlorine E	0.4	3	6 ^A	13 ^A	ID	ID	ID	ID
Cyanide F	4	7	11	18	2	4	7	14
Nitrate J	17	700	3400 ^C	17000 ^A	ID	ID	ID	ID
Hydrogen sulfide G	0.5	1.0	1.5	2.6	ID	ID	ID	ID
ORGANIC ALCOHOLS								
Ethanol	400	1400	2400 ^C	4000 ^C	ID	ID	ID	ID
Ethylene glycol	ID	ID	ID	ID	ID	ID	ID	ID
Isopropyl alcohol	ID	ID	ID	ID	ID	ID	ID	ID
CHLORINATED ALKANES								
Chloromethanes								
Dichloromethane	ID	ID	ID	ID	ID	ID	ID	ID
Chloroform	ID	ID	ID	ID	ID	ID	ID	ID
Carbon tetrachloride	ID	ID	ID	ID	ID	ID	ID	ID
Chloroethanes								
1,2-dichloroethane	ID	ID	ID	ID	ID	ID	ID	ID
1,1,1-trichloroethane	ID	ID	ID	ID	ID	ID	ID	ID

APPENDIX F: IPCS Monograph for Copper

Inchem: Copper (EHC 200, 1998)

Responses expected for various concentration ranges of copper ^a	
Total dissolved Cu concentration range (g m ⁻³)	Effects of high bioavailability in water
0.001-.01	Significant effects are expected for diatoms and sensitive invertebrates, notably cladocerans. Effects on fish could be significant in freshwaters with low pH and hardness
0.01-0.1	Significant effects are expected on various species of microalgae, some species of macroalgae, and a range of invertebrates, including crustaceans, gastropods and sea urchins. Survival of sensitive fish will be affected and a variety of fish should show sublethal effects.
0.1-1.0	Most taxonomic groups of macroalgae and invertebrates will be severely affected. Lethal levels for most fish species will be reached
> 1.0	Lethal concentrations for the most tolerant organisms are reached

^a Sites chosen have moderate to high bioavailability similar to water used in most toxicity tests.

APPENDIX G: Analysis performed by Hill laboratories and detection limits for water samples

Parameter	Method used	Detection limit
Sample filtration for metal analysis	Sample filtration through nitric washed 0.45 µm membrane filter	N/A
Total (nitric) acid digest for low level metals	Nitric acid digestion	N/A
Total Suspended Solids	Filtration (GF/C, 1.2 µm) retained residue dried at 103-105°C. Gravimetric	3 g.m-3
Dissolved Cadmium	Filtered sample. ICP-MS	0.00005 g.m-3
Total Cadmium	Nitric acid digestion. ICP-MS	0.00005 g.m-3
Dissolved Chromium	Filtered sample. ICP-MS	0.0005 g.m-3
Total Chromium	Nitric acid digestion. ICP-MS	0.0005 g.m-3
Hexavalent Chromium	Diphenylcarbazide colorimetry. Discrete analyser.	0.01 g.m-3
Dissolved Copper	Filtered sample. ICP-MS	0.0005 g.m-3
Total Copper	Nitric acid digestion. ICP-MS	0.0005 g.m-3
Dissolved Nickel	Filtered sample. ICP-MS	0.0005 g.m-3
Total Nickel	Nitric acid digestion. ICP-MS	0.0005 g.m-3
Dissolved Lead	Filtered sample. ICP-MS	0.0001 g.m-3
Total Lead	Nitric acid digestion. ICP-MS	0.0001 g.m-3
Dissolved Zinc	Filtered sample. ICP-MS	0.001 g.m-3
Total Zinc	Nitric acid digestion. ICP-MS	0.001 g.m-3

APPENDIX H: Analysis performed by Hill laboratories and detection limits for sediment samples

Parameter	Method Used	Detection Limit
Dry and sieve sample	Air dry (35°C), sieved to pass 2 mm	N/A
Total Recoverable Digest	Nitric/hydrochloric acid digestion	N/A
Dry Matter	Dried at 103°C, gravimetric (removes 3-5% more water than air drying at 35°C)	0.1 g/100g as recvd
Total Recoverable Cadmium	Nitric/hydrochloric acid digestion, ICP-MS	0.01 g/100g as recvd
Hexavalent Chromium	Diphenylcarbazide colorimetry. Discrete Analyser, screen level	2 mg/kg dry wt
Total Recoverable Copper	Nitric/hydrochloric acid digestion, ICP-MS	0.2 mg/kg dry wt
Total Recoverable Nickel	Nitric/hydrochloric acid digestion, ICP-MS	0.2 mg/kg dry wt
Total Recoverable Lead	Nitric/hydrochloric acid digestion, ICP-MS	0.2 mg/kg dry wt
Total Recoverable Zinc	Nitric/hydrochloric acid digestion, ICP-MS	0.2 mg/kg dry wt