Environment Waikato Technical Report 2005/58

Review of Science Relating to Discharges from the Kinleith Pulp and Paper Mill

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1 Introduction

The Kinleith Pulp and Paper mill, South of Tokoroa, is operated by Carter Holt Harvey Ltd (CHH). In 1994, CHH's precursor, New Zealand Forest Products Ltd (NZFP) applied to the Waikato Regional Council for an air discharge permit, under the provisions of the Resource Management Act 1991 (RMA). In 1996, CHH applied for consent for water-related activities. In line with requirements of the RMA, each application was accompanied by an Assessment of Environmental Effects (AEE). In order to characterise the potential impacts of mill discharges, the applicant had commissioned a reasonably comprehensive suite of interlocking scientific investigations and appraisals.

The consent application and its assessment was technically involved, comprising evidence from experts acting on behalf of the applicant, and scientific audit of this evidence and formulation of recommended consent conditions by experts acting on behalf of the Regional Council. After an open hearing, and an appeal, consent was granted by an Environment Court consent order. Consent certificates were last amended in 2003 [10, 11].

A number of safeguards were built in to the consent conditions. A central requirement specified in the two main consent certificates (authorising discharges of contaminants to water and air) is that the consent holder seeks to achieve continuous improvements in discharge quality, as far as practicable. Although impacts of the discharge to water in Lake Maraetai and downstream were judged to be relatively minor in terms of quantifiable adverse effects on aquatic organisms, the resource consent authorising the main contaminant discharge to water nonetheless requires that further scientific assessments be carried out on the health of the aquatic ecosystems in the receiving environment, to ensure that significant adverse effects are not being induced by the discharge during the consent period. Two rounds of effects assessments are scheduled during the consent period, for 2008 and 2015.

Despite having been subject to technical appraisal and an open consent process, and incorporation of safeguards in the consent conditions, discharges from the Kinleith mill continue to attract a certain amount of public concern. Such concern is likely to have been exacerbated by two recent operational failures experienced at the site—a sludge dam failure in December 2003, and a limited release of chlorine/chlorine dioxide gas to air in June 2004. There is also an awareness that science in the area of assessing the potential effects of pulp and paper mill discharges (particularly to water) has further developed since 1998, the date at which the last significant body of technical evidence was compiled.

As a matter of due diligence, Environment Waikato staff therefore perceived a need to review recent scientific information as it might relate to the Kinleith mill discharges, in order to assess whether there was any external evidence suggesting the existence of significant unmanaged environmental effects, and whether present consent conditions would still be regarded as suitably protective in the context of current scientific understanding.

This is the purpose of this review.

2 Scope, Structure and Sources

The scope of this review is to assess whether any new evidence exists which suggests that that there may be significant adverse effects resulting from the Kinleith Pulp and Paper mill's discharges, which have not been adequately considered as a part of the consenting process, or which are not being suitably managed through current consent conditions. It is not within the ambit of this review to discuss legal considerations or the Hearings Committee decision relating to the zone of reasonable mixing for the discharge to water.

For simplicity, key characteristics of the discharges to water and air are divided in to a number of areas which parallel those considered during the consenting process. These areas are outlined in **Table 1**.

Table 1 Discharge characteristics and effects reviewed in this report.

Topic	*Sub-topic*	*Report section*
Primary discharge to water	Wastewater quality—general wastewater quality and quantity	3.2
	Constituents of biological relevance: colour, biological oxygen demand, plant nutrients	3.3
	Constituents of biological relevance: potentially toxic elements and compounds	3.4
	Whole effluent effects assessments	3.5
	Human uses and exposure to contaminants	3.6
Primary discharge to air	Characteristics	3.7
	Potential effects to workers	3.8

Within each sub-topic (**Table 1**), information will be reviewed under three headings. These are:

- Prior evidence and assessment;
- Developments since the previous evidence was compiled; and
- An updated assessment.

Source materials relating to these headings are cited in **Section 6** (**Appendix 1**), and discussed further below. Numbers assigned to each publication will be used when referring to a given document.

2.1 Prior Evidence and Assessment—Sources

Resource consent certificates authorising discharges to water [10] and air [11] from the Kinleith Pulp and Paper mill were first issued in 2001 and 1999, respectively.

Evidence presented and assessed as part of the resource consent process which relates to the Kinleith mill's discharges to water and air is reasonably extensive. Source documents used for orientation and assessment as part of this review are listed in **Appendix 1** (**Section 6.1**) [references 1–11].

2.2 Developments Since the Previous Evidence was Compiled—Sources

2.2.1 Review of Relevant Recent Research

Two scientific search engines (SciFinder Scholar© and Current Contents©) were employed during 2005 to locate and categorise recent research that might have relevance to discharges from the Kinleith mill. During the consent period, the Kinleith mill has been employing the Elemental Chlorine Free (ECF) bleaching process. Search terms were targeted to capture both New Zealand related research, and overseas work relevant to effluent quality of ECF mills. Research studies located include papers published in international scientific journals which have been subject to scientific peer-review prior to publication, and conference proceedings. Conference proceedings often represent the most up-to-date work, but are not necessarily subject to peer-review. The most relevant recent peer-reviewed international conference was the *5th International Conference on Fate and Effects of Pulp and Paper Mill Effluents*, held in Seattle, Washington, June 1-4, 2003. Proceedings of this conference were forwarded to Environment Waikato for review.

Worldwide research

Worldwide, research relating to discharges to water from ECF mills is voluminous. In this document, a comprehensive review of worldwide research on discharges from ECF Mills research will not be attempted. Instead, most relevant work will be highlighted where it is deemed potentially applicable to the Kinleith discharge, in terms of providing any new insights that might be worth closer investigation.

New Zealand research

Research activity more closely focused on pulp and paper milling under New Zealand conditions relates mainly to the Kinleith mill (near Tokoroa) or the two Kawerau mills (primarily Tasman mill). A total of 90 research publications were located, with publication dates ranging from 1930 (an assessment of pulping and paper-making properties of selected New Zealand woods) through to 2005.[1] Breakdowns of these citations by publication decade and research area are provided in **Figure 1**.

[1] For personal research purposes (with regard to copyright restrictions), citations and abstracts are compiled in Environment Waikato document 991863.

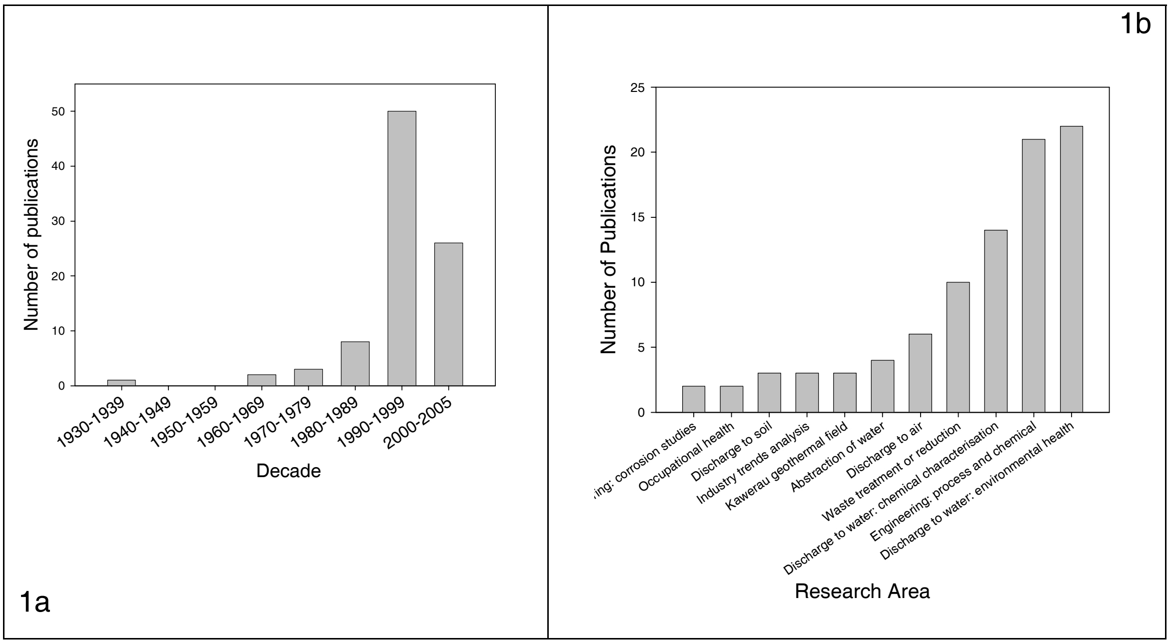

Figure 1 **Breakdown of 90 research publications located during this review relating to pulp and paper manufacturing in New Zealand.** Fig. 1a. Number of publications per decade. Fig. 1b. Number of publications in each research area.

In terms of prior evidence, publications [1] – [9] provide a comprehensive summary of effects assessments available to the mid 1990s. In the case of discharges to water, some research carried out before 1998 is not directly cited in the AEE [4] (dated 1996) or compilation of evidence in relation to the water resource consent applications for the Kinleith complex [9] (dated 1998). However, having reviewed these documents, it is the opinion of the authors that omission of the specifics of some research investigations did not compromise the assessment and evidence that was presented. Evidence provided to 1998 does accurately reflect the summarised state of knowledge of the discharge and its likely effects to the mid-to-late 1990s.

An upsurge of research beginning in the mid-1980s through to the present day (**Figure 1a**) was likely to have been caused by three inter-related factors:

- Progressive developments in the capability of analytical instrumentation capable of measuring organic and inorganic contaminants to trace levels;
- Worldwide interest in observed and potential impacts of pulp and paper mill effluents to aquatic receiving environments;
- The Resource Management Act (RMA), 1991: research was commissioned by New Zealand mill operators as part of the requirement to provide an Assessment of Environmental Effects in applying for resource consents.

In terms of research area (**Figure 1b**), publications most relevant to the wastewater discharge consent fall in to three categories:

- Those with a focus on chemical characterisation of the discharge or receiving waters, sediments or organisms (*e.g.* the chemical structures and concentrations of trace organic constituents);
- Those with a focus on potential effects in receiving environments.
- Those with a focus on wastewater treatment and reduction.

Together these three categories comprise just over half (51%) of the total publications. By contrast, only three (3% of) external publications since 1998 examine New Zealand pulp and paper mill discharges to air, and these relate to odour emissions from the Tasman Mill [28–30].

In this review, 1998 is nominated as the cut-off date for newer research. This is because the most recent summaries of evidence compiled in the resource consent process [8-9] were prepared in 1998. New Zealand pulp and paper related research papers identified in this review and published since 1998 are cited in **Appendix 1,** (**Section 6.2**) [references 12–47].[2]

Additional information was sought from some authors of newer research by direct conversation, for clarification of research findings and appraisal of potential issues. Where applicable, information sourced this way will be cited as a personal communication.

2.2.2 New or Updated Guidelines

Since the resource consent for discharges to water [10] was granted, two guideline documents which provide numerical values for protection of freshwater ecosystems from contaminants have seen increasing use in the Waikato Region [48, 49] (**Appendix 1,** (**Section 6.3**) [references 48-50]). These are:

- The ANZECC (2000) Guidelines [48], which update the ANZECC (1992) guidelines cited in the AEE [*e.g.* 4, p 86]. These provide numeric values for a wide range of major and trace contaminants in waters, and a more limited range of contaminants in sediments. These guidelines are an initial point of reference in resource consent appraisals.

- The Ontario Provincial Water Quality Objectives [49], which provide discharge quality objectives for two additional trace constituents of pulp and paper wastewater streams—dehydroabietic acid (DHA) and total resin acids. These values were recently adopted as part of consent conditions for the Blue Mountain Lumber resource consent (Environment Waikato file 61 25 51A).[18]

In the case of both documents, it should be noted that water and sediment guideline values should only be considered as numerical proxies for occurrence of potential adverse effects. Where a location-specific effects assessment has been carried out, its results would usually have precedence over an indicative guideline value.

In addition, in 2002, the Ministry of Health adopted a new tolerable intake figure for dietary dioxins [75], and in 2004, 14 National Environmental Standards for Air Quality were enacted [50]. Potential significance of these documents are discussed in relevant sections.

2.2.3 Compliance Monitoring Information

The third area of updated information relates to assessment of monitoring data to ensure consent compliance. Monitoring data is routinely submitted by CHH in keeping with conditions of its resource consents, and this is audited for compliance to consent conditions.[3]

In terms of routine discharge quality, the most significant compliance issues have been biological oxygen demand (BOD), volatile suspended solids (VSS) and total suspended solids (TSS). Through the resource consent framework, management processes are in place to deal with these issues. Factors leading to non-compliance of these parameters have been identified and control measures brought into place to re-establish compliance.[4] Effluent quality is presently regarded as generally being of high standard.

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[2] Two industry trends analysis publications written in Japanese are omitted from this list due to their limited relevance.
[3] For example, Environment Waikato document 927577.
[4] Environment Waikato document 990115.

Analytical results obtained from reports submitted in accordance with consent conditions are considered where applicable in relevant parts of this review – particularly **Sections 3.4** and **3.6**.

Compliance monitoring also extends to Council's knowledge of potentially adverse operational events and their management. These include a sludge containment dam failure in December 2003, and a limited (approximately 15 kg) release of chlorine/chlorine dioxide gas to air in June 2004.

- The dam failure has been reported on separately[5] to the Regulatory Committee of Council who considered the context, issues and management and opted to take no further action. The event is not further addressed in this report.

- Although accidental gas discharges were considered in the resource consent process, having previously been fairly frequent, such discharges incident are not specifically addressed or authorised in the resource consents granted. Such events are subject to debriefs and reviews. The June 2004 event was judged to be of relatively minor magnitude, not meriting enforcement action. Rather, appropriate steps have been taken to avoid a recurrence.[6] General comments relating to prevention and management of such events in overseas experience are provided in **Section 3.7**.

[5] Environment Waikato document 918039.
[6] Environment Waikato document 975569.

3 Assessments

3.1 Overview

The Kinleith Pulp and Paper mill's primary discharges to water and air are defined by a number of characteristics and potential effects, of which key areas are identified in **Table 1**. In this section, each of these areas will be reviewed to determine whether any new evidence suggests the existence of significant unmanaged adverse effects. In order to do this, it is necessary to first briefly summarise the prior state of knowledge and assessment for each area, and identify consent conditions designed to address potential adverse effects identified. Developments since the previous evidence was compiled can then be reviewed in context, and an updated assessment provided.

3.2 Discharge to Water: General Wastewater Quality and Quantity

3.2.1 Prior Evidence and Assessment

Wastewater volumes and location of the discharge point

Over 80% of the pulp and paper produced at the Kinleith mill is by the kraft process [9c, p 2]. This process relies heavily on chemical and water recovery and recycling, but generates large quantities of wastewater [9c, p 2].

Improving the efficiency of this process results in both environmental and market gains, and the historic approach of management at the mill has been to implement a process of ongoing improvement in water and chemical recovery [9a, p 7]. As a result of two modernisations (1991 and 1997-8), prior to resource consents being granted, the absolute volume of effluent discharged from the mill had already decreased significantly. The total volume of effluent being discharged is now about half the amount it was 15 years ago (**Table 2**).

Table 2 **Reduction in effluent volumes discharged from the Kinleith Pulp and Paper mill.**

Date	Effluent volume m^3/day	Reference
Feb-91	182000	[4] p 36
Dec-91	124000	[4] p 36
1996	118000	[9d] p 4
1998	90000	[9d] p 4

In expert evidence prepared in 1996 [9d], Galloway compared the Kinleith mill to 16 overseas pulp and paper mills. In 1996, Kinleith produced the second largest volume of effluent of the 17 mills. However, Galloway also estimated that as a result of the 1997 modernisation project, this ranking changed to first of the 17 mills. Estimated effluent volume per tonne of product was reduced from approximately 96 m^3/tonne to 56 m^3/tonne [9d, p 4 and p 20].

Kinleith mill's discharge consent allows for a wastewater discharge volume of up to 165000 m^3/d [10, schedule 1], of which it was originally expected that up to 155000 m^3/day may be discharged to the Kopakorahi Stream and 10000 m^3/d to the Waituna Stream [9b, p 7]. The latter meets the former just above the Kopakorahi arm of Lake Maraetai [7]. In original AEE evidence [4], the applicant (CHH) argued that the main discharge point for wastewater should be considered as the point where the

Kopakorahi Stream meets the Kopakorahi arm of Lake Maraetai, and most analytical data provided to date relates to this area and downstream. However as a result of legal deliberations and consent hearings, the discharge points were established as the two places where wastewater first entered each of the two streams. These are described in the resource consent [10] as:

- The discharge from the end of No. 1 Wastewater Treatment System into the Kopakorahi Stream, at map reference NZMS 260 T16: 612 163; and

- The discharge from the end of No. 2 Wastewater Treatment System into the Waituna Stream, at map reference NZMS 260 T16: 581 195.

More recently, the discharge to Waituna Stream has been discontinued, leaving the point where wastewater first enters the Kopakorahi Stream as the single discharge point.

Actual discharge volumes at time of consent application were lower than volumes applied for and granted in the resource consent figures, and were estimated in evidence as about 120000 m^3/d, with some seasonal variability [9c, p 13]. As a result of the 1996 modernisation the average wastewater discharge volume dropped further to about 90000 m^3/day (**Table 2**) and is now lower still, at about 85000 m^3/day.[7]

Treatment efficiency and relative effluent quality

Treatment system efficiency and the relative[8] quality of wastewater are inter-related. These aspects are addressed in a number of documents, most notably the AEE [4, p 36-42], Timperley's audit of the AEE [7, pp 10-12], the staff report [8], and evidence prepared for Environment Court [9, particularly 9c, 9d, 9e, 9h].

The majority of wastewater receives some primary treatment. This and other wastewater then undergoes secondary treatment in aerated stabilisation basins (ASBs) [8, p 11]. Galloway [9d] compared the relative efficiency of Kinleith's treatment system to those of overseas mills of similar age, technology and product. In Galloway's view, the contaminant removal efficiency of Kinleith's specific ASB system compared favourably to that of a state-of-the-art activated sludge treatment system [9d, pp 21-21].

At the time the consent evidence was compiled, modernisation had also seen substantial improvements in the quality of wastewater discharged from the mill. In his audit of the AEE, Timperley [7, p 10] notes:

> *"The quality of the wastewater discharged to the Waikato River from the Kinleith mill has improved dramatically over the last decade. The discharge that this AEE addresses is not the discharge of the 1970's and 1980's which caused very visible changes to the appearance of the Waikato River downstream of the mill. Rather, the present discharge contains much reduced amounts of waste matter and is more environmentally benign with less dramatic effects on the Waikato River. Several changes to the mill process have contributed to the improved wastewater quality. The most notable was the change from elemental chlorine bleaching to oxygen de-lignification and bleaching with chlorine dioxide..."*

[7] Mercer E, **2005**. Carter Holt Harvey, Personal Communication 13 July 2005.
[8] <u>Specific</u> contaminant types are addressed in **Sections 3.3**, **3.4**, and **3.6**.

Similarly, in subsequent evidence, Galloway [9d, pp 20-21] notes:

> *"When compared to overseas mills of similar age, technology and products, the Kinleith Mill has the lowest effluent volume, the lowest COD discharge, nearly the lowest BOD discharge, and about mid-range for AOX, TSS, nitrogen and phosphorus discharges. The modernisation projects carried out by CHH in 1991 and 1997-8 have reduced effluent volume and improved effluent quality significantly in spite of a 38% increase in production. Compared to pre-1991 operation, effluent volume has been reduced by 48%, COD discharge reduced by 30%, AOX by 82%, colour by 77% and chlorophenolic compounds by 96%.*

Stuthridge, a specialist in trace organic contaminants in pulp and paper wastewaters, also considered the Kinleith ASB system to be an effective and reliable means of secondary treatment for these constituents, with a performance comparable to those found in other well-operated softwood bleached kraft treatment systems [9h, p 7].

Relevant resource consent conditions

In managing discharge quality, a number of specific resource consent conditions were set in the resource consent [10] that relate to individual constituents of the wastewater stream, and these will be discussed in their relevant sections (mainly **Sections 3.3** and **3.4**). However, a condition relating to the general quality of wastewater was also set, this being that the consent holder shall seek to achieve continuous improvement [10, condition 1]:

> *"This consent is granted subject to the following conditions on the understanding that the consent holder will seek to achieve continuous improvement with the objective of reducing the effects of its operations on the Waituna Stream, the Kopakorahi Stream and the Waikato River including the Kopakorahi Arm. In so doing, the consent holder will continue to consult openly and fully with the community. In particular it will seek over time to reduce the discharge of contaminants authorised by this consent from the operations at the Kinleith Mill and adjacent activities to a practicable minimum by the maintenance and upgrading of the existing facilities, and the installation of appropriate control technology."*

For wastewater volume, an extreme limit of 165000 m^3/day has been set [10, schedule 2], although the usual volume discharged will be much lower than this, as outlined above (**Table 2**). For routine monitoring, the approach taken for contaminants in the resource consent is to focus mainly on mass loadings rather than concentrations. This seems reasonable: in terms of potential adverse effects, wastewater volume is of less relevance than concentrations (µg/L) and mass loadings (kd/day) of contaminants being carried in the wastewater.

3.2.2 Developments Since the Previous Evidence was Compiled

Research relating to general waste production or quality

In some of the studies outlined in this section, the explicit focus is waste volume and quality. In others, these aspects were not studied directly, but nonetheless indirectly relate to the research that has been reported. The following research was identified as having been published since 1997.

<u>1997: Wastewater volume and composition</u>

At approximately the same time as the last round of Kinleith consent evidence was compiled, Judd *et al* [51] published an assessment of wastewater flow and compositional data for the Tasman and Kinleith mills. For the Kinleith wastewater stream, this work examined dominant in-mill source areas of water, major and trace contaminants and acute toxicity [51, Tables 2 and 3].

- For example, in the untreated waste stream, over 50% of the total mill acute toxicity is attributable to the foul condensate wastewater, which had an EC50 of 2.6% using a Microtox™ test.

In comparing wastewater volumes and major constituents from the two mills, Judd *et al* noted a number of similarities, but also that Kinleith mill's bleach plant used substantially less water (at the time) than Tasman mill's as a result of the former's ECF bleaching modernisation [51]. Sampling apparently occurred before the latest modernisation, because wastewater flows are reported as being approximately 100 m^3/tonne of product for both the Kinleith and Tasman mills. As noted in **Section 3.2.1**, in the most recent round of expert evidence, Galloway estimated that the 1997 modernisation project would reduce Kinleith's effluent volume per tonne of product from approximately 96 m^3/tonne to 56 m^3/tonne [9d, p 4 and p 20].

Although Judd *et al* [51] make no specific recommendations, their work provides a basis for understanding how various process modifications or modernisations are likely to influence total wastewater volume (particularly) and potential toxicity after treatment, and are also useful for troubleshooting the likely sources of problem discharges.

<u>1998-2001: Process closure and inorganic elements</u>

In a series of four papers, Ellis and various co-workers have examined the behaviour of inorganic elements in New Zealand kraft pulp mills, first at Tasman mill [34, 36] and then at both Tasman and Kinleith mills [39, 40]. A primary aim of these investigations has been to address a specific problem caused by improving the recovery and recycling of process chemicals and water inside modern ECF kraft mills, called process closure. Achieving more effective process closure is desirable from both an environmental discharge and economic viewpoint, but also raises new challenges. One of these is that with loss of purge-points and better recycling inside the process, inorganic elements accumulate to excessive levels and exert a negative impact on production, through reduced process efficiency, accelerated corrosion and increasing scaling [40]. Elements examined included potassium, calcium, aluminium, magnesium, manganese, iron, silicon and chlorine. Understanding points in the production process where these elements become most enriched helps to identify their most effective removal points. For example, potassium and silicon are enriched in precipitator dust with respect to weak black liquor, and for this reason the removal of precipitator dust has been widely recommended as a good means of controlling potassium and chloride concentrations in the recovery cycle [40]. The understanding of inorganic element behaviour gathered from these studies also facilitates the identification of viable options for further process improvements.

<u>1998-2000: Increase in eucalypt processing</u>

Since resource consents were granted, there has been a significant increase in the use of eucalyptus feedstock within the New Zealand pulp and paper industry [26, 35, 38]. The potential impact of this proportional increase (relative to pinus) on final effluent quality was initially unknown [26]. This topic was specifically investigated by Slade *et al* [26], who carried out mill surveys and laboratory simulations of wastewater production and treatment with eucalyptus feedstock. The authors report that increased eucalyptus processing does not decrease final effluent quality, but instead may actually result in some improvements.

2002-03: Pitch control

The term pitch is applied to suspended colloids and insoluble deposits that are extracted from wood during pulping and papermaking. These include compounds such as free fatty acids, resin acids and glycerides. Pitch can reduce process productivity through depositing and plugging washer screens, increasing bleach chemical consumption and reducing washer efficiency. Richardson *et al* [41, 44] have reported approaches adopted in managing pitch at Norske Skog's three Australasian mills (including the Tasman mill) during newsprint manufacture. These use a combination of purging, and adsorption of pitch to fibres, the second of which leads to its incorporation in the final product. Adsorption of pitch to fibres is facilitated by use of various chemical additives, and the authors investigate optimum dosing rates and pH conditions for use of medium molecular mass cationic polymers in the chemistry of fixation. Controlling pitch through adsorption to fibres is likely to increase the effluent quality to some degree, but it is unclear how much this would be, what system(s) are currently in place for pitch control at the Kinleith mill, and their impact on effluent quality. From the perspective of wastewater quality, the work of Richardson *et al* on the Tasman mill [41, 44] indirectly highlights that use of adsorption for pitch control is one means of improving wastewater quality.

2003: Black liquor evaporation performance

Ellis and Jensen [45] have recently reported success in improving production efficiency at the Kinleith mill by increasing the evaporation performance of the black liquor effects stages. Black liquor from pulp washing contains 15-17% solids, and needs to be concentrated to about 60-70% solids before it can be burnt in the recovery furnace [57]. Burning of organic compounds in the recovery furnace provides energy for the mill, and represents the first step in recovery and regeneration of sodium sulphide for use in the cooking process. Black liquor evaporation consumes a substantial part of the heat energy required in the kraft process [57]. Achieving increased evaporation for the same energy therefore translates to an increase in pulp production volumes. Ellis and Jensen [45] report that four small projects completed at Kinleith over a two year period have increased total black liquor evaporation capacity by almost 6%, while only expending minimal capital.

Although this efficiency improvement may be a net environmental benefit when expressed in terms of energy expended per tonne of product, potential downstream effects of efficiency improvements on discharge quality itself have not been reported. The upgrade is reported as having the positive benefits of reduced soda liquor loss in process condensates, and reduced colour to drain from the primary condenser condensate; on the other hand, sodium hypochlorite is now routinely dosed for two hours per day as a biocide to prevent microbial growth in the condenser tubes [45].

One might expect an increase in total pulp production volume to cause a concomitant increase in mass loadings of (for example) COD, BOD, and trace organic compounds exiting the secondary treatment system. In the case of Kinleith mill, it is possible that potential improvements in wastewater quality caused by the increase in eucalyptus processing (see above) may have been countered to some extent by increased mass loadings caused by production efficiency gains.

It is not particularly likely that such changes would be significant enough to trigger mean and extreme consented limits for specific wastewater constituents [10, Schedules 1 and 2], although a compliance issue with BOD has been noted (**Section 2.2.3**). However, production efficiency gains may have relevance in relation to the consent condition set for the general quality of wastewater, that the consent holder shall seek to achieve continuous improvement (**Section 3.2.1**).

This extant discharge consent condition implies that where process efficiency improvements lead to increased production volumes, corresponding measures may need to be taken to ensure that (at least) there is not also a net decrease in wastewater quality (*e.g.* tonnes contaminant/day).

Waste treatment

1999: Benefits of ASB treatment

Hunter and Slade [25] reviewed some of the benefits of an aerated stabilization basin (ASB) wastewater treatment plant, as operated at the Tasman mill. Advantages of Tasman mill's ASB system were said to include high treatment efficiency (BOD reduction of over 90%), lack of need for additional nutrients, and robustness—the ability of the system to cope with adverse conditions. These comments parallel claims made in consent hearing evidence for the Kinleith mill.

2001: Cyanobacteria in the ASB system

Kirkwood *et al* [27] examined the microbiological communities present in secondary waste treatment systems from pulp and paper mills in USA, Canada, Brazil and New Zealand (apparently, those of the Tasman mill [56]). All systems were found to contain dynamic cyanobacterial communities, some of which exceeded heterotrophic bacterial biomass. The authors note:

> *"Regardless of geographical location, Oscillatoriales including Phormidium, Geitlerinema, and Pseudanabaena were the dominant taxa. As well, Chroococcus (Chroococcales) was an important genus in Brazil and New Zealand. The possible impact of cyanobacteria on waste-treatment efficiency deserves further study given their large biomass and diverse metabolic characteristics."*

The findings of this research were unexpected, and the work raises three new possibilities for adverse effects of the Kinleith discharges to water that have not been previously explored or specifically quantified. These are:

- The possible impact of cyanobacteria (blue-green algae) on waste treatment efficiency itself (as noted by Kirkwood *et al* [27];
- The possibility that the secondary treatment system can provide a seed population of cyanobacteria to the Waikato River;
- The possibility that some of the dissolved chemical toxicity of the concentrated effluent may be attributable to cyanotoxins produced by the ASB cyanobacteria population.

The second possibility is the most potentially problematic. Occurrence of blue-green algae blooms in the Waikato River is an ongoing problem for contact recreation and public health. Although it is clear that blooms also occur upstream of the Kinleith discharge, it appears that that the severity of blooms occurring downstream can be worse [55]. However, proliferation of cyanobacteria (blue-green algae) is favoured by co-occurrence of several environmental factors. These include:

- Long water residence times caused by presence of the hydroelectric dams;
- Extended sunny periods;
- Relative responses of different microbial communities to dissolved nitrogen and phosphorus loads, which increase along the length of the Waikato River.

In the Kinleith AEE [4, p 83], data is presented for the total and fecal coliforms upstream and downstream of the Kinleith mill wastewater outfall. Bleached kraft effluent contains large numbers of *Klebsiella pnumoniae* which are included in these tests. Data suggests that the mill is not fully responsible for bacterial numbers in water discharging in to Lake Maraetai, and that bacterial die-off within the Kopakorahi arm is considerable. This may or may not also apply to cyanobacteria.

The corresponding author of the Kirkwood *et al* study [27] was contacted, and expresses the view that because cyanobacteria are ubiquitous, presence of favourable environmental conditions are the most significant factor in determining whether a bloom will develop. On the potential for the Kinleith secondary waste treatment system to act as a seeding population for cyanobacteria in the Waikato River, Kirkwood comments [56]:

> *"My belief in a nut shell is that the source of the cyanobacteria is not the problem, but rather the environmental conditions that promote their nuisance growth."*

Kirkwood's view is that the (likely) presence of cyanobacteria in the Kinleith secondary waste treatment system is probably of limited significance in terms of development of blooms in the Waikato River. This interpretation is supported by Timperley [99], who notes that:

> *"Irrespective of any "seeding" of the river from blooms in the ASB ponds, the conditions in the river will determine the potential for blooms in the river to occur."*

On the other hand, Vant [55] notes that it has not been established that the ASB ponds do *not* act a significant factor in the development of cyanobacteria blooms in the Waikato River. Absence of effect would be assumed if it could be shown that cyanobacteria blooms in the Waikato River are likely to be occur at the same frequency and severity whether the ASB ponds are present or absent. Obviously it is not possible to run a direct test on what would occur in the absence of the ponds, but Timperley [99] suggests that a good way to investigate the potential for effect would to be to establish the relative frequency at which blooms occur in the ponds, compared with the river:

> *"If blooms occur in the ASB ponds more frequently than blooms occur in the river, then the extended period of the year during which cyanotoxins are present in the river water could be of environmental and health interest."*

Therefore, on one hand there is no positive evidence that the Kinleith mill's secondary treatment systems may contribute to the severity of blue-green algal blooms in the Waikato River. However, the existence of such an effect has not yet been eliminated, but remains a plausible possibility.

Evidence available on this issue to date is not sufficiently definitive to warrant a review of consent conditions, but is such to recommend initiation of some specific research on this topic. This is supported by Timperley [99].

<u>2005: Potential problem with ASB treatment</u>

One potential disadvantage of ASB treatment systems are that they are characterised by anoxic zones (reducing environments), and these favour the production of certain resins acid derived neutral compounds [52]. These include the alkylated polycyclic aromatic hydrocarbon (PAH) retene, which is produced by anaerobic metabolism of abeitic acid. Fish exposed to diluted Kinleith effluent under controlled conditions show biochemical evidence of exposure to planar organic compounds, and these are most likely to be retene or similar alkylated PAHs: this evidence is discussed further in **Section 3.4.2**. The potential significance of such exposures in the field in terms of effects on the whole organism, or fish populations, is discussed in **Section 3.5.2**. The other option for secondary wastewater treatment at pulp and paper mills is the activated sludge (AS) system. Unlike ASB systems, AS systems do not produce significant quantities of alkylated PAHs [52].

3.2.3 Updated Assessment

Within the new research relating to general wastewater quality and quantity, and in relation to consent requirements, two areas stand out as being worth further investigation or clarification with CHH. These are:

1. Continuous improvement in discharge quality.

   - The extent to which CHH may be able to provide information which demonstrates that they have been addressing the discharge consent condition that the consent holder shall seek continuous improvement in discharge quality. Formal reassessments of the feasibility, costs and benefits of reducing effects of the discharge are programmed in to the resource consent conditions for 2009 and 2016, but do not preclude the consent holder seeking to make progressive improvements in the interim.

   - The extent to which production efficiency gains (such as the improvement in black liquor evaporation efficiency) may act to decrease wastewater quality through an increase daily loadings of some trace contaminants (such as resin acids), and whether strategies are in place to measure and counter any such increases given the above consent condition.

2. Potential significance of cyanobacteria in the secondary treatment ponds.

   - Confirmation of the presence or absence of (significant numbers of) cyanobacteria in Kinleith mill's secondary treatment ponds;

   - If cyanobacteria numbers are significant, investigation (desktop or otherwise) of their likely capacity to act as a seeding population for cyanobacterial (blue-green algal) blooms in the Waikato River when other environmental conditions are favourable.

3.3 Discharge to Water: Constituents of Biological Relevance: Colour, Biological Oxygen Demand, Plant Nutrients

3.3.1 Prior Evidence and Assessment

The dark **colour** of the Kinleith discharge is the parameter regarded as causing the most notable effects on receiving water quality [7]. This colour is caused by presence of organic compounds in the wastewater which strongly absorb light in the ultraviolet, blue and green wavelength ranges.

Although these organic compounds tend to be relatively non-toxic in themselves, their light absorption influences four optical water quality attributes—visual clarity, light penetration (euphotic depth), hue and brightness [9e, p 2]. However, Davies-Colley notes that the optical effect of the Kinleith discharge is largely masked by phytoplankton growth in the Waikato River [9g, p 8]. Effects on water appearance from the discharge colour are most evident in winter, when the plume remains on the surface of Lake Maraetai due to inter-related temperature and density effects [8a, 9f].

In summer, the plume is cooler and denser than surrounding water, and plunges to the bed of the Kopakorahi arm, where it flows towards the main body of the lake along the drowned river channel [9f, p 10]. The degree of mixing varies with season, but is not complete until after the water exits the Maratai I and II power station tailraces and enters Lake Waipapa.

As aerobic microorganisms metabolise assimilable organic compounds, they consume available oxygen. **Biological oxygen demand (BOD)** is an estimate of the capacity of wastewater to cause oxygen depletion in a receiving environment by this mechanism. Loss of dissolved oxygen is problematic for other organisms. Because oxygen consumption of this type presupposes the presence of aerobic microorganisms, laboratory measurements of BOD are best seen as a proxy for potential adverse effect that may be caused by oxygen depletion, and may or may not reflect an actual effect. The proportion of readily assimilable carbon in the Kinleith discharge (as measured by BOD) is only a fraction of the total carbon carried in the discharge [7, p 20]. The chemically oxidisable fraction (measured as COD) therefore greatly over-estimates BOD, and BOD is of most relevance when considering potential effects.

However, BOD and COD (chemical oxygen demand) are both standard measures of wastewater quality. Accordingly, evidence presented in the AEE on wastewater quality starts with BOD [4, p37]. BOD is reported as having improved significantly between 1990 and 1996 as a result of mill modernisation. BOD and COD are also reported by Marsh [9c, p 21].

Discharges from the Kinleith mill can also effect water quality through addition of the **plant nutrient** elements nitrogen and phosphorus. As noted by Vant [8b]:

> *"The waters of the Waikato River are nutrient-enriched and, as a result, contain high levels of phytoplankton biomass especially during the summer and autumn months. The major nutrients that limit aquatic plant growth are nitrogen and phosphorus."*

Before secondary treatment in the ASB system, nitrogen is mainly in the ammonium ($NH_4^+OH^-_{aq}$) form, and derives mainly from condensate wastewater, where volatile constituents tend to accumulate [51]. Most of this is oxidised to the nitrate ($NO_3^-{}_{aq}$) form during treatment, with the total mass of nitrogen being substantially reduced by microbial transformation to nitrogen gas or dinitrogen ($N_{2(g)}$) [9e] (denitrification). Nitrogen gas is lost to the atmosphere, which itself is about 80% nitrogen gas. Macdonald [9e] considers that the secondary treatment system is very effective at nutrient removal, achieving levels of total nitrogen and phosphorus better than most conventional biological or physico-chemical treatment plants can readily achieve. Nevertheless, the Kinleith mill discharge does make a contribution to the total nitrogen and phosphorus in the Waikato River system. Vant [8b] calculated that the Kinleith discharge is likely to contribute about 15% of the total nitrogen and 15% of the total phosphorus currently entering Lake Waipapa.

Resource consent conditions [10] include limits for colour, BOD, total nitrogen and total phosphorus in the Kinleith wastewater discharge. These are specified as mean and maximum permitted daily loadings (mass/day). Conditions that limit the discharge were designed to authorise the current level of discharge and hence authorise the current level of effect [8a, 8d], in the context of the general condition requiring the consent holder to seek progressive improvement. The resource consent also requires routine measurement and reporting, which enables compliance to be routinely audited (**Section 2.2.3**).

3.3.2 Developments Since the Previous Evidence was Compiled

No new research was identified that directly addresses colour, BOD, or nutrient loadings associated with discharges from the Kinleith mill. Two research papers include consideration of colour or dissolved oxygen issues associated with New Zealand pulp and paper mills.

Wilkins *et al* [12] investigated a possible secondary effect of pulp mill discharges to the Tarawera River. This was the suggestion that some pulp and paper contaminants were being carried in groundwater seepage from the Tarawera River to a nearby drainage canal (the Western drain). However, this work appears to have limited relevance for discharges from the Kinleith mill to the Waikato River. Groundwater systems and discharges to groundwater were also extensively studied and considered as part of the resource consent process for the Kinleith mill [4, 8c, 9l].

The work of Landman *et al* [22], who also investigated pulp and paper effluent associated with the Tarawera River, does have potential relevance to the capacity of the Kinleith surface water discharge to cause oxygen depletion (measured as BOD). These authors investigated the potential for contaminants in two pulp and paper discharges to enhance mortality of fish caused by low oxygen (hypoxia). Concentrations of effluent were at environmentally relevant levels—effluent from the Tasman mill was extracted directly from the Tarawera river, whereas that from the thermomechanical tissue mill at Kauwerau[9] was diluted to 15%, to represent the upper end of the range after mixing in the Tarawera River.

Using a series of controlled experiments on fry and juvenile rainbow trout (*Oncorhynchus mykiss*) and common bully (*Gobiomorphus cotidianus*), the authors found that presence of mill effluent at these concentrations **did not** cause a significant increase in hypoxia. Trout were significantly more susceptible to the effects of low dissolved oxygen than bullies, with mean LC50 values for dissolved oxygen being 1.43–1.83 mg/L for trout and 0.69–0.99 mg/L for bullies.

This research tested an hypothesis relating to interactions between potentially adverse environmental factors. In this case, no statistically significant additive or synergistic relationship was apparent between low oxygen and presence of diluted mill effluent. Results of this work further underline the potential impact of low oxygen itself, and the desirability of limiting the BOD of the discharge.

Kanber *et al* [14] have examined the capacity of filtration to reduce colour of Tarawera River water derived from the Tasman mill. It is expected that their results would be applicable to the Kinleith mill discharge also. These authors found that filtering does not reduce colour substantially. Standard filtering at 0.45 µm reduces levels of colour (measured as the absorbance at 270 nm) by only 15%, indicating that coloured compounds in the effluent are in the operationally dissolved fraction. About 75% of the colour still persisted in water filtered to 0.025 µm. These findings confirm that colour is predominant caused by truly dissolved water soluble chromophores, which are inherently difficult to remove.

3.3.3 Updated Assessment

In the areas colour, BOD and plant nutrients, no additional evidence has appeared since resource consent was granted to suggest the presence of additional unanticipated adverse effects. Current resource consent conditions appear appropriate to manage these aspects of the Kinleith mill's effluent quality.

[9] The pulp and paper mills at Kauwerau have undergone a number of name changes. The thermomechanical tissue mill has been known as Caxton mill, Carter Holt Harvey Tissue, and other names. The kraft mill is usually referred to as Tasman mill. The Tasman mill pulp operation is currently owned by Carter Holt Harvey, whereas the paper part is owned by Norske Skog.

3.4 Discharge to Water: Constituents of Biological Relevance: Potentially Toxic Elements and Compounds

3.4.1 Prior Evidence and Assessment

General

The mill wastewater contains a very large number of different chemicals [8d]. Organic constituents produced during pulp beaching are dominated by chlorinated and oxidised lignin degradation products [9h], with lesser quantities of other constituents. High molecular mass compounds in this mix are responsible for most colour and AOX (see below) content, whereas concerns around innate toxicity and persistence tend to focus on lower mass compounds, of which many hundreds have been identified [9h, 60].

In discussing the consent conditions requiring whole effluent toxicity testing, Timperley notes that the wastewater contains many more chemicals than are included in consent monitoring requirements [8d], and in fact it contains many more than could realistically be tested. In work leading up to preparation for the Kinleith water consents AEE [4], a total of 77 organic compounds over 13 compound classes were determined in either wastewaters or receiving sediments (excluding dioxins) [9h] (**Table 3**).

Table 3 Compound classes and numbers in each class tested for in Kinleith mill wastewaters and receiving sediments, excluding dioxins. Based on data in [9h].

Compound class	Number of compounds tested
Chloroacetic acids	3
Chlorocatechols	3
Chloroguaiacols	4
Chlorophenols	4
Chlorovanillins	3
Chloroveratroles	3
Diterpenes	10
Fatty acid alcohols	2
Monoterpenes	5
Fatty acids	13
Phenolics	3
Resin acids	22
Sterols	2

In terms of specific contaminant classes, pulp and paper wastewater constituents regarded as being of most interest with regard to their potential toxicity and/or environmental persistence are resin acids and some of their degradation/transformation products, halogenated (mainly chlorinated) organic compounds, and some trace elements such as copper. These classes are discussed further below.

Over time, new chemical reagents and feedstocks are also likely to cause subtle changes to the complex mix of constituents in wastewater. Examples might include increased use of polymeric cations for pitch control and tendency toward a higher proportion of eucalyptus feedstock, which might cause a shift in the relative proportions of different resin acids or other trace organic compounds (**Section 3.2.2**). According to Smith cited in Bright *et al* [60], traces of mono- and dichlorosyringaldehydes are present in bleaching effluent from eucalypt pulp. Here it is noted that in order to accommodate this complexity [8d], resource consent conditions stipulate the requirement for two further rounds of whole effluent toxicity testing, which integrates the impact of all contaminants in the waste stream, and effects-monitoring focused on the health of aquatic ecosystems in the receiving environment. These assessments are scheduled for 2008 and 2015. Other effects assessments carried out since the consent was granted are discussed in **Section 3.5**.

Resin acids and related compounds

Resin acids are natural plant compounds derived from the wood feedstock. Resin is a hydrocarbon secretion produced by plants, functions of which appear to include conferring resistance to insect and fungi attack, sealing wounds and eliminating excess metabolites. Resin is composed mainly of volatile terpenes, and non-volatile solids which include the compounds known as resin acids.

- Terpenes are employed in a wide range of biochemical functions in plants, derive through two main biochemical pathways from isoprene (C_5H_8) units, and have formulas that are multiples of this basic unit ($(C_5H_8)_n$). The most common terpenes are the two-isoprene unit monoterpenes ($C_{10}H_{16}$), which have numerous isomers. Addition of further units leads to sequiterpenes[10] ($C_{15}H_{24}$), diterpenes ($C_{20}H_{32}$), *etc*. The most important photosynthetic pigment in plants is carotene, which is a tetraterpene ($C_{40}H_{64}$). Over all, more than 30,000 terpenoids are known [58].

- Resin acids are structurally related to terpenes, and are derived from terpenes through partial oxidation. For example, the resin acid abietic acid is derived from a three-step oxidative pathway which starts with the terpene abietadiene [59].

The main significance of resin acids in relation to the Kinleith mill wastewater discharge is that a certain proportion of resin acids and their subsequent degradation or transformation products survive secondary treatment, and much of the inherent toxicity of pulp and paper mill wastewater is attributed to its resin acid content.

Concentrations of resin acids in Kinleith mill receiving waters were presented in the AEE [4] and subsequent evidence [9h].

At the time the last significant body of evidence was compiled, Stuthridge noted [9h] that the ability to assess the environmental significance of pulp and paper mill derived organic compounds was in the Kinleith mill receiving environment was hampered by lack of recognised water quality and sediment quality standards. As noted in **Section 2.2.2**, Ontario guidelines have been suggested as being suitable for dehydroabietic acid and total resin acids.

For many contaminants which strongly partition to sediments, this medium can serve as a useful index of time-averaged contaminant exposure. Contaminant build-up in sediments also has relevance as an exposure source for aquatic organisms. Resin acid concentrations in Waikato River in sediment samples collected in 1991–92 were low in sediments above the Kinleith mill wastewater discharge point, elevated immediately below the outfall, and then progressively decreased with distance [61]. Resin acids from the Kinleith mill were detected in sediments as far away as Hamilton [7, 61], which was the furthest sampling point.

Stuthridge notes in evidence [9h] that overall, resin acid concentrations detected in Waikato River sediments were generally lower than in other international cases, and would be expected to further decrease as a result of the mill modernisations. These modernisations apparently did translate to lower resin acid concentrations in mill wastewater. In his audit, Timperley [7] concurs with similar comments made in the

[10] Sesqui is a prefix meaning one and a half.

AEE [4], but notes that monitoring over several years is likely to be necessary to confirm a reduction in contaminant (including resin acid content) of sediments.

Expecting such a reduction in contaminant concentrations in sediments does presuppose that these had reached some form of steady state[11] prior to the mill modernisations. This seems likely but was not necessarily the case for some resin acids, and was never actually demonstrated as such. It may be that this concept was valid for some compounds with shorter environmental half-lives, but not others.

Chlorinated organic compounds

Most of the chlorinated organic compounds present in pulp and paper mill effluent come about through use of chlorine in pulp bleaching. However, the form of chlorine used has a marked influence on both the amounts and forms of chlorinated organic compounds produced. The Kinleith mill modernised to an elemental chlorine free (ECF) bleaching process in 1991. This process makes use of chlorine dioxide (ClO_2) instead of chlorine gas (Cl_2), which the pulp and paper industry usually refer to as elemental chlorine. Chlorine dioxide is a less aggressive reagent than elemental chlorine, and acts mainly as an oxidant. With chlorine dioxide, chlorinated products are only formed as a result of reaction of the byproduct hypochlorous acid with organic material [60].[12] Switching to ECF bleaching reduces the total amount of chlorinated organic compounds formed by 5-10 times, and also the relative mix in terms of composition towards compounds that are more environmentally benign [7].

Certain chlorinated organic compounds in pulp and paper mill wastewater can be analysed individually, but for others this is not possible due to their structural complexity and high molecular masses. The sum of this group of compounds is therefore assessed using a standard bulk measurement known as the AOX (Adsorbable Organic Halogen) test. At lower molecular mass and individually determinable are chlorophenolic compounds, and dioxins and furans.

Dioxins and furans are a structurally related family of 210 specific planar chlorinated organic congeners. The blanket term ‘dioxins’ is often used to cover 210 possible compounds, which fall into two main groups.[13] These are polychlorinated dibenzo-*p*-dioxins (PCDDs, 75 compounds) and polychlorinated dibenzofurans (PCDFs). PCDDs and PCDFs can contain from one to eight chlorine atoms. The reason this translates into a large number of compounds is that for each degree of chlorine substitution, there are several possible (geometric and stereoscopic) isomers possible. The term ‘congeners’ is used to describe the whole group of 210 compounds over both classes, and is broader than the term ‘isomers’, which would technically only cover specific isomers of either PCDDs or of PCDFs.

The most toxic PCDD and PCDF compounds are those with four chlorines at the 2, 3, 7 and 8 positions. Thus only 17 of all 75 dioxin and 135 furan congeners are significantly toxic. They all contain chlorine atoms in the 2, 3, 7 and 8 positions (**Table 4**).

The toxicity of dioxins varies widely depending on the congener, and in reporting is expressed as sum over all compounds known as a toxic equivalent (TEQ) (**Table 4**). Results are often reported based on international toxic equivalency factors (I-TEFs), but the general New Zealand policy approach is now to follow the World Health Organisation (WHO) TEF values, which vary from the international TEFs in the case of three congeners. In many cases, estimates made with one approach are close to

[11] The point of steady state is where the addition of new resin acids to sediments (by settling of resin-acid rich particulate material and adsorption processes) is matched by their relative loss rate. On a mass basis, resin acids should be mainly lost by degradation. On a concentration basis, they may also be lost through dilution with a proportionately higher load of clean sediment.

[12] Chlorine gas, by comparison, causes substantially more chlorination of organic compounds through nucleophilic attack and substitution.

[13] Although it is inconsistent, one specific member of the dioxin group, 2,3,7,8-tetrachlorodibenzo-p-dioxin (or TCDD), is also frequently referred to as ‘dioxin.’

those made using the other: differences emerge where a sample contains significant proportions of PeCDD, OCDD or OCDF.

Table 4 **Toxic equivalency factors for all PCDD/Fs that have a TEF>0.** Other congeners are not regarded as having dioxin-like effects.

Homologous group	Congener	International TEF	WHO TEF
PCDDs			
TCDD	2,3,7,8	1.0	1.0
PeCDD	1,2,3,7,8	0.5	1.0
HxCDD	1,2,3,4,7,8	0.1	0.1
	1,2,3,6,7,8	0.1	0.1
	1,2,3,7,8,9	0.1	0.1
HpCDD	1,2,3,4,6,7,8	0.01	0.01
OCDD	1,2,3,4,6,7,8,9	0.001	0.0001
PCDFs			
TCDF	2,3,7,8	0.1	0.1
PeCDF	1,2,3,7,8	0.05	0.05
	2,3,4,7,8	0.5	0.5
HxCDF	1,2,3,4,7,8	0.1	0.1
	1,2,3,6,7,8	0.1	0.1
	1,2,3,7,8,9	0.1	0.1
	2,3,4,6,7,8	0.1	0.1
HpCDF	1,2,3,4,7,8,9	0.01	0.01
	1,2,3,4,6,7,8	0.01	0.01
OCDF	1,2,3,4,6,7,8,9	0.001	0.0001

Dioxins and furans only appear at very low levels in Kinleith mill effluent, but are of special interest due to their environmental persistence and potential to accumulate in edible fish. From a regulatory perspective, this becomes a potential issue when set against the context that the adopted Tolerable Daily Intake (TDI) of such compounds is also very low. Due to the low concentrations involved (often parts-per-quadrillion or pg/g levels[14]), state-of-the-art analytical techniques are required to accurately measure dioxins; this is fairy expensive, and such tests are only offered at a limited number of analytical laboratories. The potential significance of human exposure to dioxins through fish sourced from Lake Maraetai is reviewed and updated in **Section 3.6**.

As a result of modernisation to ECF bleaching, prior to consent being granted, concentrations and mass loadings of chlorinated organic compounds (including dioxins and furans) in Kinleith mill wastewater had been substantially reduced [9h, 7]. Galloway [9d] presented evidence that the 1991 modernisation caused an 84% decrease in chlorinated organic compounds (measured as AOX) in bleach plant effluent, and a 97% reduction in the content of chlorophenolic compounds. Evidence was also presented which suggested that much of the dioxin load already present in sediments was likely to have been due to former use of pentachlorophenol (PCP) at the Kinleith mill [4, 7],[15] and that concentrations of AOX, dioxins and furans in sediments should decrease with time in response to lower loadings in wastewater [7, 9h]. As noted for resin acids, the latter is a likely but untested inference.

By mass, most of the chlorinated organic compounds are likely to be structurally complex and of high molecular weight. It is worth noting that since consents were granted, further evidence has been gathered that a wide range of chlorinated compounds are also produced as a result of natural processes [60 and references cited therein]. As a consequence of this natural background, organisms have evolved pathways for the biodegradation of chlorinated organic compounds [60]. Possibly as a result of the combined effect of natural background and biodegradation processes, previous evidence relating to the Kinleith mill discharge showed no significant difference in sediment loading of total organic halogens (TOX) between samples

[14] One pg/g is one part in one million million (1 in 10^{12}).
[15] This can be assessed on the basis of ratios of dioxin and furan congeners.

collected from above and below the discharge point [9h]. As noted above, this was not the case for some chlorinated compound types that are more characteristic of reaction conditions of the bleaching plant (mainly before modernisation), including chlorophenolics [61].

No specific evidence has been presented which demonstrates an adverse effect of chlorinated organic compounds from Kinleith mill wastewater on the Waikato River ecosystem. This lack of positive evidence is likely to be due to a combination of the following reasons:

- Adverse ecosystem effects from chlorinated organic compounds (if any) are not likely to be dramatic;

- Potential sub-lethal effects from resin acids may overshadow impacts from chlorinated organic compounds (for example, Stuthridge notes that resin acids may cause sub-lethal effects in fish at concentrations of 5-20 µg/L, which may be found at site K2, but at the time of his evidence not after further dilution in Lake Maraetai);

- Scientific methods needed to study the more subtle exposures and effects to specific compounds were (and are) still evolving.

Stuthridge's view [9h] was that that likelihood of more-than-minor adverse effects from trace organic compounds (including chlorinated organics) was low. Timperley [7] noted that the possibility of subtle chronic effects from chlorinated organic compounds in the Kopakorahi Arm could not be ruled out. However, if such effects had been occurring, the mill modernisations should result in progressive improvements [7] as 'historic' compounds work their way through the secondary treatment system, and receiving sediments recover in response to lower present day loadings.

Consent conditions require monitoring for both AOX on a routine basis, and dioxins and furans in specific media (wastewater, sediments, fish) less frequently [10].

EROD induction as an indirect marker of exposure

The cytochromes P450 are a family of catalytic proteins generated mainly in the liver (humans, fish and other animals) that react with certain classes of organic contaminants by inserting an atom of oxygen. This can cause oxidation, reduction or hydrolysis of the chemical and usually causes the product to be more water-soluble, detoxifying it, and enhancing its elimination *via* the kidney [53, 54].

One of these proteins is known as CYP1A. CYP1A has been found to be useful as a proxy for exposure, because its concentrations increase in response to uptake of certain organic contaminants. A multitude of chemicals can induce production of CYP1A in fish liver, but the most potent inducers are those with planar (flat) chemical structure. These include dioxins, furans, and polycyclic aromatic hydrocarbons (PAHs). The biochemical signal for generating more CYP1A is when a suitable organic compound binds with an aryl hydrocarbon receptor in the cell cytosol. Because CYP1A acts as a catalyst, its relative concentration can be determined by measuring how quickly it catalyses the reaction of a known compound. The compound used is 7-ethoxyresorufin. CYP1A catalyses the loss of an ethyl group from this compound (deethylation) to form the compound resorufin. The ethyl group loss-rate induced by the CYP1A enzyme is known as the ethoxyresorufin-o-deethylase (EROD) activity.

In short, measurement of EROD activity provides an indirect but sensitive index of the aggregated exposure of fish to organic chemical contaminants. Sensitivity and response is highest for planar halogenated hydrocarbons (PHHs) and PAHs [53, 54].

Trace elements

Though naturally occurring, both essential and non-essential trace elements are also capable of inducing toxicity when their concentrations become elevated. This can pose an issue both in terms of dissolved concentrations in the water column, and gradual accumulation in receiving sediments. Guidelines exist for both situations (**Section 2.2.2**).

Concentrations of trace elements discharged in wastewater from the Kinleith mill are not particularly high, based on a summary of wastewater composition [4, pp 40 and 85]. Average arsenic concentrations (9 µg/L) are near the drinking water standard (10 µg/L), but the mill wastewater would actually work to slightly dilute arsenic concentrations in the Waikato River (typically 25 µg/L[16]). The same occurs for boron [4, p 85].

Sediment records suggest that the Kinleith mill may have been a source of arsenic in the past, with a substantial increase starting at Lake Maraetai which peaks in Lake Waipapa. Arsenic concentrations of up to 1520 mg/kg have been measured in Lake Waipapa sediments [3]. In previous commentary [3, 7], localised natural geothermal inputs were suggested as one possibility that could account for this. This is possible but not confirmed: the Mangakino field sits to the east of Lake Maraetai, but appears a little distant from Lake Waipapa to be having a significant influence; geothermal sources in Lake Waipapa itself are unknown. By contrast, high concentrations of copper and chromium were found in Kopakorahi Stream sediments in the upper Waikato River study, and these were attributed to due to losses from copper-chrome-arsenic (CCA) treatment [3]. Arsenic does tend to move further than copper and chromium before being attenuated on sediments, and at first glance, the overall pattern of highest enrichment in Lake Waipapa might suggest that former CCA operations at Kinleith are likely to account for at least some of this additional arsenic in sediments of that lake.

However, further analysis of the same data suggests a more likely explanation for high arsenic in sediments of lakes Maraetai and Waipapa, which was not identified in previous evidence or commentary. This is outlined in **Section 3.4.2**.

When last measured, mercury concentrations were also elevated in Lake Maraetai sediments. This has been attributed to historical inputs of mercury from the chloralkali plant (shut down about 1978) [3], or may be an artefact of the high organic content of Lake Maraetai sediments [7, p 22].[17] Mercury does form very strong adsorptive complexes with organic matter. Timperley [7] suggests that when the sediment mercury results are expressed on a volume basis, the apparent differences between lakes for this element largely disappear.

Overall consensus [4, 7, 8] based on previous evidence was that the likelihood of significant adverse effects resulting from trace elements in the Kinleith mill wastewater discharge was less than minor. Accordingly, there are no resource consent conditions covering discharges of specific trace elements in Kinleith mill wastewater.

[16] This arsenic comes about from both natural geothermal discharges upstream, and the discharge of the Wairakei Power Station.

[17] This is significant because results are expressed on a weight/weight basis (mg mercury per kg sediment), and organic-rich sediments contain more volume and surface area per unit weight.

3.4.2 Developments Since the Previous Evidence was Compiled

Resin acids and related compounds in wastewater

A large subset of new research relating to the potential role of trace contaminants in the New Zealand pulp and paper mill wastewater is inter-linked with work assessing adverse effects of whole effluent on fish reproduction. Work assessing the extent of potential adverse **effects** is discussed in **Section 3.5**. In this section, the focus is on new work relating to either the **concentrations** or **physico-chemical nature** of specific contaminants in the wastewater discharge or receiving environment.

<u>Total resin acids – trends and comparison to Ontario guidelines</u>

In prior evidence [9h, p11], Stuthridge commented that the ability to assess the environmental significance of organic compounds in pulp and paper discharges was hampered by the lack of recognised water and sediment quality standards. As noted in **Section 2.2.2**, since the Kinleith mill consents were issued [10], Ontario's guidelines for dehydroabietic acid (DHA) and total resin acids in pulp and paper mill receiving waters were adopted as part of the Blue Mountain Lumber resource consent.[18]

In receiving waters of pH 7 (seen as appropriate for the Waikato River), the Ontario guideline values are **8 µg/L** for dehydroabietic acid and **25 µg/L** for total resin acids [49, p 24]. The Ontario guideline would generally be treated as an indicative value, a figure below which significant adverse effects are unlikely to occur, but above which they might begin to occur. This seems a reasonable threshold denoting possible significance of adverse effects, in the light of Stuthridge's evidence that resin acids may cause sub-lethal effects in fish at concentrations of 5-20 µg/L [9h].

Figures are not available for concentrations of DHA in prior evidence for Kinleith mill; however figures for resin acids have been provided [4, p 93 and 9h]. Over two studies, measured concentrations in the Kopakorahi Stream at the point it enters the Kopakorahi Arm of Lake Maraetai ranged from **7–55 µg/L** (parts per billion). Mean values for the two studies were **17** and **27 µg/L** [9h, p 7]. On dilution in the Kopakorahi Arm of Lake Maraetai, concentrations decrease rapidly, and at the Kopakorahi arm bridge were already commensurate with (presumably natural) resin acid concentrations measured in the upper Kopakorahi Stream (2.6 µg/L at the Kopakorahi arm bridge compares with 2.3 µg/L in the upper Kopakorahi Stream).

At the time previous data were collected for the point the Kopakorahi stream enters the arm of Lake Maraetai, average concentrations of total resin acids were therefore below or analytically indistinguishable from the Ontario guideline (25 µg/L), and maximum concentrations could exceed it by a factor of two, but would decrease rapidly on entering the lake arm. Comparison of previous data for resin acids with the (more recently adopted) Ontario guideline is therefore reassuring. The resource consent allowed for the discharge to this level, subject to the general condition of aiming to achieve continual improvement in wastewater quality.

In relation to current loadings and concentrations of resin acids, the former measurements should only be seen as indicative of the order-of-magnitude, and can not be taken to reliably reflect the present situation at either the discharge point or the point where the Kopakorahi Stream meets the arm of Lake Maraetai. Prior to consent being granted, the only data provided had been for the latter.[19] However, based on flow data provided in the Appendix – **Section 6.5**, it would appear that the amount of dilution experienced by the wastewater is fairly similar at the two points. When resin acid concentrations in the wastewater were last measured, water entering the lake arm

[18] Which itself has since been rescinded by the Environment Court.

[19] See **Section 3.2.1**. In original AEE evidence [4], the applicant argued that the main discharge point for wastewater should be considered as the point where the Kopakorahi Stream meets the Kopakorahi arm of Lake Maraetai, and most analytical data provided to date relates to this area and downstream.

(the measurement point) was only about 12% more dilute than after mixing at the upstream discharge point. Currently, it is estimated to be about 20% more dilute.

- On average the wastewater is now diluted by a factor of 2.0 as it enters the Kopakorahi Stream, and has become diluted by a factor of 2.4 by the time it reaches the Kopakorahi arm of Lake Maraetai. Under low stream flow conditions, and assuming the wastewater volume remained constant, the wastewater would be diluted by a factor of 1.4 as it entered the Kopakorahi Stream, and have been diluted by a factor of 1.6 by the time it reaches the Kopakorahi arm of Lake Maraetai (**Section 6.5**).

- There is uncertainty about what relationship might exist between lower mill wastewater volumes and resin acid concentrations. Figures presented in the AEE and subsequent evidence for resin acid concentrations were based on samples collected when effluent volumes were higher than they are now. Other factors being equal, a more efficient recycling of mill water might be expected to result in an **increase** in resin acid concentrations, expressed as µg/L.

- However, other factors have not been equal, and the mill modernisations that occurred since sampling for resin acids were said to have caused a significant **decrease** in resin acid mass loadings (**Section 3.4.1**) [9h]. The decrease in loads may have been sufficient to more than offset any increase in relative concentration caused by the more efficient use of water.

If previous data were had been all there was to go on, it would seem probable that average concentrations of resin acids in Kopakorahi Stream water were likely to be in the same order-of-magnitude as the Ontario guideline of 25 µg/L, rather than being substantially greater (*e.g.* 250 µg/L) or less (*e.g.* 2.5 µg/L).

However, more recent data is available, and suggests that this is not the case. As part of consent conditions, concentrations of trace organic compounds are reported on a six-monthly basis for both the primary discharge points to the Kopakorahi Stream (formerly E1 and E2, now only E1), and the Kopakorahi Stream at the point it enters the arm of Lake Maraetai (site K2). A summary of updated data for trace organic compound classes at site K2 is presented in **Appendix 6.6** (a full compilation of data for all three sites is archived in Environment Waikato document 1033009).

Data for total resin acids, fatty acids, phenolic compounds, total chloro-catechols, total chloro-guaiacols and total chloro-phenols was provided previously in the AEE [4, p 93] and subsequent evidence [9h]. Of these compound classes, concentrations reported after resource consent was granted are either commensurate with or below those reported previously for classes except the resin acids (**Appendix 6.6**).

Resin acids are behaving differently. The average and median values of seven total resin acid measurements on samples collected from site K2 since December 2001 are 245 µg/L and 109 µg/L, respectively. These are 14 and 9 times **higher** than corresponding mean and median figures presented in the AEE and subsequent (1998) evidence, based on samples collected in 1994-95. Concentrations of total resins acids reported for samples collected from sites E1 and K2 since 2001 are illustrated in **Figure 2**.

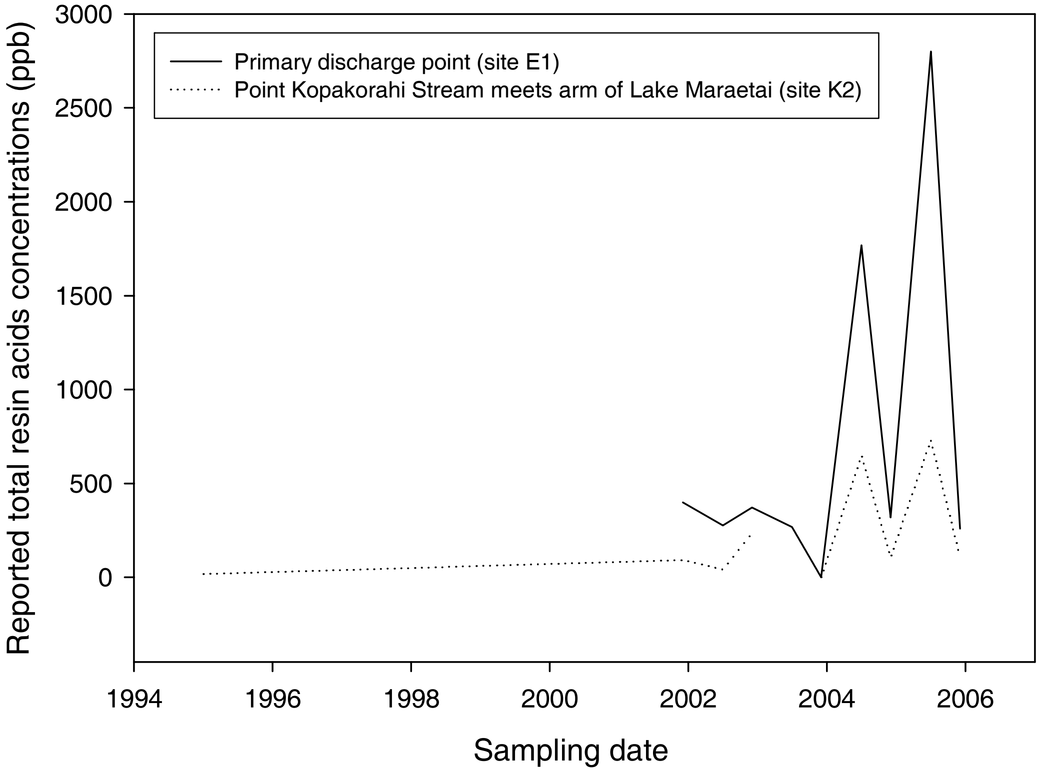

Figure 2 Reported concentrations of total resin acids (µg/L) in wastewater at sampling site E1 and Kopakorahi stream water at sampling site K2.

The data in **Figure 2** suggests that concentrations of resin acids are significantly higher now than they were in 1994-95, and that there may be a gradually increasing trend in concentrations. However, the interpretation of this data is subject to the following ambiguities and provisos:

- There is uncertainty about how temporally representative the pre-consent measurements of resin acids in Kinleith mill wastewater are likely to have been, and how much natural variation might be expected in output of resin acids over longer time periods. Data presented in the AEE [4] and subsequent evidence [9h] was based on a total of 16 samples collected in two studies.

- The data for individual and total resin acids shows a high amount of variability between sampling dates (**Figure 2**), which is not seen for most of the other organic determinands (**Appendix 6.6**). This raises questions over sampling and analytical precision (in particular), followed by average accuracy, of the reported results.[20] If sampling and analytical precision is good, then the data in **Figure 2** implies that the Kinleith mill effluent does show extreme fluctuations in its total resin acids content.

- It is evident that there have been variable periods between sampling of the wastewater and analysis in the laboratory, and there is some indication in analytical data reports that samples had not been preserved. Wilkins [98] indicates that it is appropriate to preserve such samples with sodium azide to ensure their stability prior to analysis. Kanber *et al* [14] have noted that variations in handling prior to analysis can have a significant impact on the concentrations measured, with significant losses occurring with longer sample storage times and lack of sample preservation, and other variations being introduced depending on the exact extraction systems employed. However, poor sample preservation is expected to

[20] Precision refers to the reproducibility of repeated analyses: how close the range of measured values for identical samples are to each other. In this case, precision might also include the reproducibility of sampling and sample preservation before analysis, as well as that of the actual analysis step. Accuracy refers to how close a reported result is to its true value. Results can show poor precision (wide spread) but good average accuracy.

result in losses of resin acids from solution before analysis (rather than increases), so would not explain the very high reported results for some sampling dates.

Taking these limitations into account, it is not possible to be definitive about whether resin acid concentrations in the mill wastewater have been increasing with time, but the data to date is certainly suggestive that this may be the case. One possibility is that elevated resin acid levels may be linked to pond de-sludging operations. The likelihood and toxicological significance of this has yet to be assessed.

In the last two sample results, the Ontario guideline for total resin acids of 25 µg/L[21] was apparently exceeded by a factor of 109 times (June 2005) and 6 times (Dec 2005) in the primary discharge at site E1. The median exceedance factor for all sampling dates since 2001 at site E1 is **8 times**. Such guidelines relate to the situation after reasonable mixing, but the Kopakorahi Stream itself does not provide a lot of additional volume (**Section 6.5**). At site K2, the Ontario total resin acids guideline was apparently exceeded by a factor of 29 in the June 2005 sample and 2 times in the most recent Dec 2005 sample.[22] The median exceedance factor for all sampling dates since 2001 at site K2 is **3.2 times**.

For dehydroabietic acid, the Ontario guideline is 8 µg/L. In the Dec 2005 sample, this was exceeded by a factor of 3.6 in the primary discharge, and 1.8 at site K2.

These guidelines are only of indirect relevance to the conditions of the resource consent, because no specific limit is set for resin acids in the mill wastewater. Their significance comes about because, as guidelines, they denote a point below which adverse effects are deemed to be acceptably low in a jurisdiction that is familiar with pulp and paper mills (Ontario, Canada). Of more direct relevance to the Kinleith mill discharge is the general consent condition that the consent holder shall seek to achieve continuous improvements in discharge quality, given that resin acids are likely to constitute a significant portion of total wastewater toxicity. As noted in **Section 3.4.1**, much of the inherent toxicity of pulp and paper mill wastewater is attributed to its resin acid content.

Overall, a compilation of monitoring data provided since consents were granted **suggests** that resin acid concentrations in Kinleith mill wastewater may be showing a significant increase, and the apparent magnitudes involved are higher than the Ontario guideline value for total resin acids, a threshold that could be used to denote toxicological significance. Combination of the possible trend with the magnitude of effect means that this is an area that does warrant closer investigation.

<u>Chemical speciation and apparent degradation rates</u>

Kanber *et al* [14] have examined the speciation of resin acids in the Tarawera River derived from the Tasman mill. It is expected that their results would be applicable to the Kinleith mill discharge also. These authors make a number of observations about the measurement, form and behaviour of resin acids that are potentially useful in developing further management options for this class of contaminant. These include:

- Differences in analytical results for resin acids can occur depending on the form of chemical pre-treatment before analysis. The authors note [14]:
  "In recent years pH values ranging from 2 to 12 have been used in liquid-liquid extraction of resin acids from pulp mill effluents. Some workers advocate use of an acidic extraction medium to minimise dissociation of resin acids, while other worker

[21] These figures are calculated in this case using only a subset of resin acids classed as total resin acids for purposes of comparison to the Ontario guideline (**Section 2.2.2**). These are pimaric, sandaracopimaric, isopimaric, palustric, levopimaric, abietic and neoabietic acids. Dehydroabietic acid is considered separately.

[22] Although further dilution in Lake Maraetai will act to reduce this considerably, under the consent, the primary discharge point is considered to be E1, with the zone of reasonable mixing occurring fairly rapidly in the Kopakorahi Stream itself. The stream is therefore the first effected water body requiring consideration.

[sic] have recommended an alkaline extraction media in order to minimise resin acid isomerisation."

The protocol followed can have a modest impact on the results obtained, with a 20% reduction in the recovery of resin acids extracted at pH 4 compared with those extracted under more neutral and alkaline conditions (pH 7.6 and 10). Some significant differences are also apparent between extraction systems, with liquid-liquid extraction being shown to be reliable for Tarawera River water samples.

- Standard filtration (through a 0.45 μm filter) reduced resin acid concentrations substantially, by about 65%, irrespective of the extraction pH. Filtration at 0.45 μm is taken as the operational cut-off between particulate-bound and dissolved forms of an element or compound. This result was attributed to a significant proportion of the resin acids being bound to suspended solids such as sediment particles and macromolecular aggregates of lignans. Concentration-based guideline values are usually taken to apply most closely to the soluble form of a species, this being more readily available for uptake and assimilation in aquatic organisms. It could be argued that in future comparisons to the Ontario guideline, the soluble (<0.45 μm) resin acid fraction is most applicable. However, where the aim is to establish mass loadings of resin acids to the wider environment (including deposition of particle-bound forms in sediments), non-filtered samples would be more appropriate.
- Some loss of resin acids can occur in samples that are left for a period before analysis, presumably through biological and abiotic degradation processes. Over three days, a loss of about 6% was observed, but this figure is less than the usual precision obtained for replicate analyses of resin acids. However, the results imply that samples being tested for resin acids should be analysed within a few days of collection, to prevent this type of error. These results also provide some general indication that resin acids as a group are not particularly persistent, but concentrations of most resin acids in sediments should reach steady state in relation to discharge mass loadings (as had been previously assumed), rather than progressively increase with time (**Section 3.4.1**).
- Neutral non-polar (uncharged) resin-acid derived compounds such as retene tend to be strongly associated with the suspended particulate fraction, and are therefore more effectively removed by filtration than resin acids themselves. Resin acids themselves have some polar character due to presence of a carboxylate (—COO^-) group. The compounds fichtelite, dehydroabietin, tetrahydroretene and retene have 0, 1, 2 and 3 aromatic rings, respectively. As the aromaticity of the compound increases, so does its tendency to be associated with the particle fraction.

Exposure of fish to planar polycyclic aromatic hydrocarbons (PAHs) such as retene can be detected using a system that responds to subtle changes in the activity of specific enzymes in the organism, known as EROD induction (**Section 3.4.1**). The likely absence of such compounds from the truly dissolved phase but tendency to concentrate on suspended particulates (and in sediments) is consistent with recent observations by Tremblay *et al* [62]. These authors note that fish downstream of the Tasman mill show biochemical signs of exposure to PAH-like compounds, and this result is curious because Tasman mill effluent itself no longer causes elevated EROD activity in rainbow trout. They suggested that effects observed in the field may be through exposure of the fish to such compounds from downstream sediment, rather than the water column (see further discussion below under the **sediments** section).

Resin acids and related compounds in fish

Recently, Tremblay *et al* [62] have reported results of studies on fish populations upstream and downstream of several discharge sites on the Waikato River. Species chosen were brown bullhead catfish (*Ameiurus nebulosus*) and shortfin eel. Bullhead catfish are a pest fish, but useful as an indicator due to their presence throughout the length of the Waikato River.

Part of this work involved sampling at matched points upstream and downstream of the Kinleith discharge to Lake Maraetai, with backwater habitats being targeted for bullhead catfish. A range of physical, biochemical and chemical measurements were carried out, with bullhead catfish bile being analysed for the presence of resin acids. Concentrations of resin acids in pooled bile samples from bullhead catfish downstream of the Kinleith mill discharge were 37 times higher than those in upstream samples, showing that resin acids in the Kinleith mill discharge are taken up by fish.

By comparison to results of a previous sediment study, it is notable that differences between resin acids in fish bile samples upstream and downstream are in the same order as differences seen for resin acids in sediments downstream of the discharge compared with other reference sites [9h, p 9]. This suggests that these compounds may not be building up in fish, but instead reflect a steady state condition in relation to average concentrations from the mixed wastewater and sediments.

Exposure of fish to pulp-mill compounds was also indicated by elevated EROD activity [62], although differences in this parameter were more modest.[23] Eel and bullhead downstream of the discharge also had enlarged livers, an effect which is not necessarily adverse in nature, but has been demonstrated to occur in response to pulp mill effluent in other studies.

Despite these exposures, fish downstream of the discharge were also of greater size and significantly better condition than those from the upstream location. The authors speculated that possible negative effects associated with trace contaminants may be offset by beneficial effects of added heat and perhaps nutrients in the discharge.

Resin acids and related compounds in sediments

As part of resource consent conditions [10], CHH is required to measure and report trace organic compounds in bed sediments of the Kopakorahi Arm by 2001, 2008 and 2015, for the purpose of confirming the expected downward trend over time of these compounds in sediments. Such changes are expected to be gradual. Results for resin acids and related compounds were measured and reported in 2003 [71].

The main value of the 2003 sampling round [71] was in identifying suitable sampling sites and providing a benchmark for future trends analyses. Comparisons to an earlier sampling round (1999) were difficult to make, because the earlier samples were not collected from the most suitable depositional environments, and also had a far lower organic matter content. Sediment results are therefore not yet sufficient to draw any firm conclusions about a trend in resins acid levels [72], although the data contained some interesting features.

As noted above, van den Heuval [52, 62 p 35] has speculated that most EROD activity observed in fish downstream of the Tasman mill discharge may be caused by exposure of fish to certain resin-acid derived PAHs in sediments. This is because:

- Fish exposed to the whole effluent (in the dissolved phase) from the Tasman mill no longer show significant EROD activity. A previous modest EROD induction factor for Tasman effluent of 2.5 times [16] has now disappeared, apparently in response to process improvements [23, 62].

- However, fish in the field downstream of the Tasman discharge point still show additional EROD activity.

[23] Presumably reflecting the proportion of total resin acids and related compounds in the mix that show significant binding to the aryl hydrocarbon receptor.

- PAHs can be formed in ASB and stream sediments from resin acid precursors by microbial transformation. Retene, the dominant PAH in ASB sediments, is formed under low oxygen conditions, as may occur in sediments.

Confirming this for the Kinleith mill, the average retene concentration in sediments reported from the 2003 sampling round was 369 µg/kg (0.37 mg/kg) [71]. Monitoring data also shows that in cases where resin acid neutral compounds are detected in the mill wastewater (site E1 on some dates), positive detections are mostly accounted for by retene and tetrahydroretene.[24]

Judd *et al* [13] have published three papers on specific pulp-mill related organic compounds including resin acids in New Zealand sediments. Much of the data in the first paper of the series [61] was presented in previous evidence leading up to granting of Kinleith's resource consents. In relation to this review, the third paper of the series [13] is the most relevant. In it, the authors report concentrations of resin acids and their biodegradation products in shallow streams from remote forested areas.

- Two remote sediment sites were tested: one from a stream inside a *Pinus radiata* plantation, and the other from a podocarp/hardwood area. Both samples were found to contain significant concentrations of resin acids and resin acid derived neutral compounds. Although the relative proportions of different resin acids were different to those characteristic of pulp and paper discharges, consistencies were also observed. In the pine plantation sediments, *Pinus radiata* wood derived resin acids were detected (dehydroabietic acid, pimaric acid), as well as resin acids that would normally be associated with pulp processing (seco-dehydroabietic acids) and biological treatment systems (7-hydroxydehydroabietic acid). Relatively high concentrations of resin acid neutral compounds were also found in both samples.

Results suggest that in any small stream inside a forested area, there is a good chance that sediments will contain reasonable concentrations of natural resin acids and their biotransformation products, including some PAH compounds such as retene. This observation adds an additional layer of complexity to attempts to determine whether pulp mill derived resin acids and their biotransformation products are likely to cause significant adverse effects in sediment receiving environments.

Chlorinated organic compounds

Wastewater

The AOX class of compounds is subject to routine measurement and compliance audit against consented limits. These limits have always been met, and AOX will not be further considered here. At the low end of the range (sub parts per billion), concentrations of trace chlorinated organic compounds including chlorocatechols, chloroguaiacols, chloro-phenols and chlorinated phenolics have been reported in the mill wastewater on at least three occasions since resource consents were granted, and always found to be either below instrumental detection limits, or near instrumental detection limits.[24]

Also at the lowest end of the detection range (parts per quadrillion), CHH has tested and reported dioxins and furans in the Kinleith mill wastewater, using the most sensitive instrumentation currently available for this type of measurement. These results have been reviewed separately [63]. Concentrations of these compounds in the water are always much lower than those in particulate or sediment phases, because they are strongly hydrophobic and lipophilic. No dioxins or furans were detected in the wastewater to a detection limit of **2 pg/L** (2 parts per quadrillion, or 0.000000002 parts per million).

[24] Compiled data is available in Environment Waikato document 1033009.

However, an unusual problem exists with low-level measurement of dioxins in water, which is that the recommended guideline values are lower than detection limits that can be reasonably achieved without specialised techniques.[25] This problem has been recognised by the Ministry for the Environment in their report on organochlorines in New Zealand rivers, who note [64]:

> *"The technological requirements to measure such low concentrations of 2,3,7,8-TCDD and other PCDDs and PCDFs are considerable, as high-volume water sampling is usually required. As a consequence, the detection limits for PCDD and PCDF concentrations in the river water samples from the current study are well above the exposure criteria discussed above."*

Potentially applicable guidelines are a USEPA Water Quality Criteria (WQC) of **0.013 pg/L** for protection of human and wildlife health, and a Dutch recommended exposure limit of **0.1 pg/L** for aquatic systems. Of these, the Dutch limit is likely to be most applicable in a New Zealand regulatory setting.[26]

Overall:

- The results provided for the Kinleith mill wastewater to date do not show that there is an issue with dioxins and furans in the water samples tested, in relation to available guideline values.

- At the same time, results to date do not rule out the possibility that guidelines may be exceeded in the Kopakorahi Stream, where the average dilution factor on wastewater mixing is 2. Allowing for dilution in this stream still leaves a factor of 10 between the recommended Dutch guideline (0.1 pg/L) and the effective detection limit after mixing (1 pg/L).

- For context, it is worth noting that no specific limits have been set for dioxins and furans in wastewater from the Kinleith mill, and exceeding a guideline can not be taken as being equivalent to demonstrating an adverse effect. Such guidelines are usually taken as a trigger levels for further site-specific investigation.

<u>Sediments</u>

Ultra-trace level measurements of dioxin in water are difficult to undertake and reproduce, and the integrated sediment record is likely to represent a better indicator of environmental exposure. CHH is required to measure and report trace organic compounds in bed sediments of the Kopakorahi Arm by 2001, 2008 and 2015. Chlorinated compounds included in the schedule of trace pulp mill organic compounds are chloroacetic acids, chlorocatechols, chloroguiacols, total chlorophenols, dioxins and furans [10]. As noted for resin acids, the main value of the 2003 sampling round [71] was in identifying suitable sampling sites for future comparison. Although there is an expectation that modernisations at the Kinleith mill should have resulted in progressively lower concentrations of chlorinated organic compounds in sediments, there is not yet the empirical evidence to confirm this. Such an analysis may also be complicated by the sludge dam failure which occurred in December 2003 (**Section 1**), and is better left to (at least) the 2008 review.

Concentrations of total dioxins and furans reported in the 2003 sampling round were 57.4 ng/kg (I-TEQ, dry weight sediment), and apparent increase relative to the 1999 samples which contained 11.6 ng/kg. In raw terms, 2003 results exceed the Canadian sediment quality guidelines, which define a Probable Effects Level (PEL) for total

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[25] Involving preconcentration of dioxins through extraction from high volumes of water into small volumes of extraction solvent, and requiring a thorough pre-cleaning of all reagents used to ultra-trace levels. This type of approach is beyond what can be offered by commercial analytical chemistry laboratories, and would usually be undertaken only as part of specialised research on dioxins in a University or research institute.

[26] The US guideline is likely to be partly derived on the basis of a human lifetime excess cancer risk factor of 1 in 10^6, whereas New Zealand opts for 1 in 10^5.

dioxins and furans of 21.5 ng/kg and an Interim Sediment Quality Guideline (ISQG) of 0.85 ng/kg.

On closer examination of the data, however, this is attributable to the very high levels of organic carbon in 2003 samples compared with 1999 samples. Sediments sampled in 1999 had only 1.4% organic matter, whereas the 2003 sampling sites averaged 30% [71].

This is significant because the ANZECC (2000) guidelines for sediments [48] recommend normalisation of listed trace organic contaminant concentrations to 1% organic carbon. The ANZECC guidelines do not provide figures for sediment dioxins. However, contaminant classes covered include a range of PAHs and organochlorines, and, it would be difficult to argue that dioxins (which are organochlorines) should not also receive the same treatment as those contaminants for which New Zealand and Australian guidelines have been derived. On a 1% organic carbon normalised basis, dioxin and furan results from the 2003 sampling round are 1.9 ng/kg (I-TEQ), a figure well below the Canadian Probable Effects Level (21.5 ng/kg), and about double the Interim Sediment Quality Guideline (0.85 ng/kg).

When both 1999 and 2003 data sets are normalised to 1% organic carbon, there is an apparent fourfold **decrease** in dioxin and furan concentrations in sediments between 1999 and 2003. Such an outcome is in keeping with what would be expected after the change to ECF bleaching. Confirmation of a downward trend will need to wait for results of future sediment sampling rounds, where samples will be collected from the 2003 locations and so be more directly comparable than previously.

Chlorophenolic compounds were included in the three papers by Judd *et al* [13] on pulp-mill related organic compounds in New Zealand sediments. Data that appeared in the first paper on Waikato River sediments sampled in 1991/92 [61] has already been presented in the AEE [4] and other evidence [9h] leading up to granting of resource consents. The second and third papers are interesting in their own right, but add nothing additional to our understanding of chlorinated organic compounds in sediments upstream and downstream of the Kinleith mill discharge.

<u>Fish</u>

CHH is also required to test composite eel flesh samples, where dioxins and furans are the chlorinated organic compound classes of potential relevance to human health. The significance of results to date is discussed in **Section 3.6**.

Trace elements

Based on arsenic concentrations reported for the wastewater discharge (9 µg/L), the Kinleith mill wastewater would work to slightly dilute arsenic concentrations in the Waikato River (typically 25 µg/L[27]), but not detectably. In terms of additional mass loads, at a discharge volume of 90000 m^3/day, the Kinleith mill would contribute no more than an additional 0.2% to arsenic already being carried by the Waikato River.

However, as noted in **Section 3.4.1**, sediment records presented in previous evidence suggest that the Kinleith mill may have been a source of arsenic in the past, with an increase starting at Lake Maraetai which peaks in Lake Waipapa.

Concentrations of arsenic in Lake Waipapa sediments [3, 4] are well above levels where significant adverse effects on sediment dwelling organisms are expected [48, 69]. As noted by Vant [69], the Ontario Ministry of the Environment sediment quality guidelines define 'Low' and 'Severe' numbers, where the latter represent *"concentrations that could effectively eliminate most of the benthic organisms."*

[27] This arsenic comes about from both natural geothermal discharges upstream, and the discharge of the Wairakei Power Station.

Similarly, the ANZECC (2000) interim sediment quality guidelines [48] define 'Low' and 'High' levels of effect, where the latter corresponds to a probability of causing adverse effects to 50% of organisms. For arsenic, numeric values for the Ontario severe level and ANZECC ISQG-High are 33 mg/kg and 70 mg/kg, respectively [69]. By comparison, sediments of Lake Waipapa have been reported to contain between 859 mg/kg [4] to 1520 mg/kg [3] arsenic.

Based on these considerations, sediments of Lake Waipapa should be toxic to bottom dwelling organisms due to their high arsenic content. Direct evidence of the toxicity of Lake Waipapa sediments to benthic invertebrates has in fact been previously presented, and this is reviewed in **Section 3.5.2**.

Two explanations forwarded to account for high arsenic in Lake Waipapa sediments were localised geothermal inputs, and loss of arsenic from former copper-chrome-arsenic (CCA) operations at Kinleith. Supporting evidence is lacking for either explanation, and neither is particularly convincing. In peer-review of this document, Timperley [99] agrees that a CCA source is improbable, and identifies another reason why existence of a significant local geothermal source of arsenic is unlikely. This is that with such a source, we would expect to see discrete increases in the concentrations of arsenic and other geothermal marker elements such as lithium in Waikato River water downstream of Lake Maraetai, which are not observed [99]. This is because only a minor fraction of the arsenic flowing in the Waikato River is lost by adsorption to bed sediments at any given time; most remains with in the river water.

In the AEE [4], more elements were measured in sediments (17 elements) than in wastewater (5 elements). Of the additional elements measured in sediments [4, p 101], iron and manganese are of interest because they also show relatively high concentrations in Lake Maraetai and peak in Lake Waipapa, mirroring the pattern for arsenic.[28] Hydrated oxides of these two elements work to strongly attenuate certain elements: adsorption to iron oxides, in particular, plays a major role in environmental arsenic chemistry. Iron and manganese are also highly correlated with phosphate in Waikato River sediments, and this is also consistent with an adsorptive mechanism determining arsenic accumulation in sediments because the usual form of adsorbed arsenic (arsenate, AsO_4^{3-}) is isomorphous with phosphate (PO_4^{3-}). For the same reason, arsenate and phosphate also correlate with each other.

Concentrations of iron, arsenic and phosphorus reported for sediment samples collected from Waikato River lakes are shown in **Figure 3**. Co-occurrence of these elements provides the basis for an alternative explanation for high levels of arsenic in Lake Waipapa sediments. High arsenic in these sediments may not reflect an historic discharge of arsenic from the Kinleith mill, but the cumulative effect of iron and manganese precipitating as oxides in downstream sediments, then acting as a trap for some of the geothermal arsenic being carried by the Waikato River (which is in the order of 150 tonnes/yr).

If adsorption to iron and manganese oxides is the dominant operative mechanism behind arsenic accumulation in sediments of Lake Waipapa, this process may still be occurring. In relation to the possible influence of Kinleith mill on this process, two questions would be relevant:

1. Whether the Kinleith mill may represent a significant source of additional iron or manganese, relative to loads already being carried in the Waikato River.

2. Whether some aspect of the Kinleith mill discharge system encourages coagulation and settling of iron and manganese colloids being carried in the Waikato River.

[28] Although there are only six Waikato River sites where both iron and arsenic were reported, the log-Fe vs log-As correlation coefficient is $R = 0.909$, $p<0.02$. For manganese, the correlation is $R = 0.879$, $p<0.05$. A Spearman rank correlation for the iron-arsenic data set gives an $R = 0.943$, $p<0.01$.

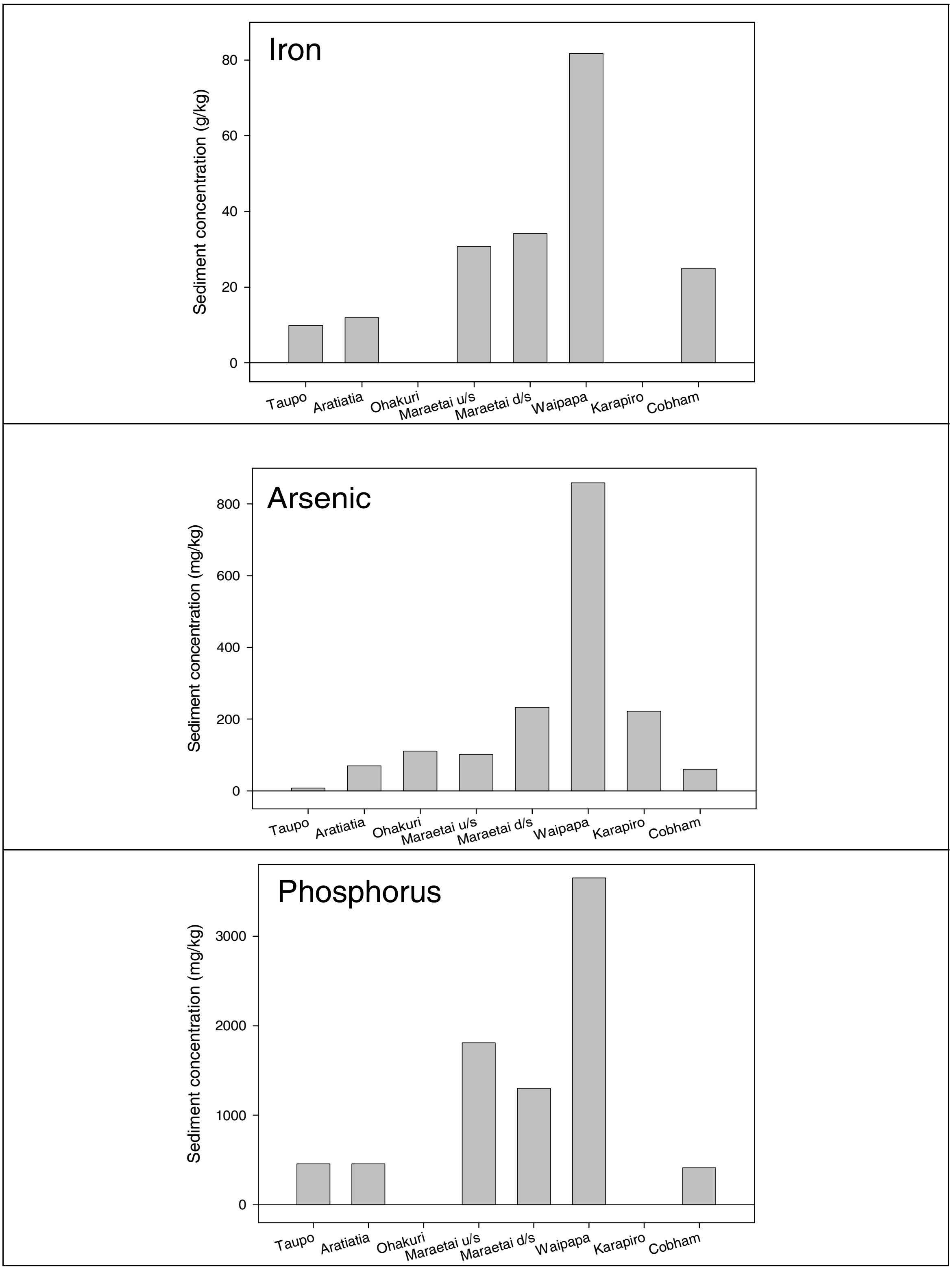

Figure 3 **Concentrations of iron, arsenic and phosphorus reported for sediment samples collected from Waikato River lakes in the AEE [4, p 101].** Arsenate (AsO_4^{3-}) and phosphate (PO_4^{3-}) share a similar adsorption chemistry and are strongly adsorbed by iron (and manganese) oxides.

In relation to the first question, concentrations of iron in Kinleith mill wastewater have not been reported as part of previous evidence. However:

- Kanber *et al* [14] have reported iron concentrations in the Tarawera River downstream of the wastewater discharge from the Tasman mill wastewater discharge point, and these were given as about 0.2 mg/L. This is within the natural range of concentrations for iron in freshwaters, and suggests that Tasman mill (which also operates a kraft process) does not contribute much by way of additional iron to the Tarawera River.

- The natural concentration of (total) iron in the Waikato River at Lake Maraetai is approximately 0.13 mg/L [65], and this would represent a daily mass load of over 2 tonnes.

- Commenting on quality of the water for drinking and irrigation, Timperley [7 p 27] notes: *"it is not likely that the mill wastewater contributes substantial amounts of iron to the river. No data were collected, however, to confirm this."*

The possibility that the Kinleith mill may contribute significant iron relative to natural loads being carried in the Waikato River therefore remains open, but appears unlikely.

In relation to the second question – whether some aspect of the Kinleith mill discharge system encourages coagulation and settling of iron and manganese colloids being carried in the Waikato River – three possibilities exist.

1. Some flocculation may be facilitated by interactions between Waikato River iron and suspended organic matter in the mill wastewater.

    - Lignins have previously been used as water clarifying agents in water treatment.

    - Kanber *et al* [14] have shown that a substantial proportion of resin acids in the Tasman wastewater discharge are present across a range of fine particulate size fractions from <0.02 µm to >3 µm. Suspended particulates in these size ranges have extremely high relative surface areas (expressed as m^2/g).

    - Iron oxides readily form fine colloidal coatings on available surfaces. Concentrations of arsenic and other geothermally sourced trace elements in Waikato river and Taupo Volcanic Zone plants are highest in those plants with the highest surface areas (such as *Myriophyllum propinquum* or parrot feather). On the basis of a tenfold difference between plant uptake of arsenic observed under controlled laboratory conditions and field observations, and inter-element correlations, this has been attributed to formation of colloidal iron coatings on the plant surfaces [66].

    - Environmental organic matter (mainly humic and fulvic material) also tends to carry a negative surface charge, whereas under normal environmental pH conditions, iron oxides are positively charged. They should therefore attract each other.

    - On charge and surface area grounds, it is therefore possible the fine suspended organic matter contributed by the Kinleith wastewater may attract a coating of colloidal iron oxides as it moves through Lake Maraetai. Some iron may then be deposited elsewhere in lake Maraetai and downstream in Lake Waipapa, where a proportion of the particulate organic load settles. Iron oxide coatings may also contribute to the organic particulate flocculation and settling process.

2. Some flocculation may occur when ever mill wastewater is slightly more alkaline than Waikato River water.

    - Iron in the Waikato River is expected to exists as a mixture of dissolved ferrous and ferric iron (as Fe^{2+}_{aq} and Fe^{3+}_{aq}) and fine suspended ferric oxide colloids. Raising the pH slightly would be expected to cause a proportional shift toward more and larger colloids in the vicinity of the plume.

    - Hydroxide (OH^-) is the reactive ligand in this instance. The consent limit range for pH of the mill wastewater ranges from 6.5–9.5 [10], representing a permitted range of hydroxide concentrations from 3.2×10^{-8} *M* to 3.2×10^{-5} *M*, a thousand-fold range. Recent data on the discharge pH gives a range from about pH 6.7

to 8.0. The average pH of the Waikato River at the Whakamaru Tailrace measured from 1990 to 2005 is 7.4, with a range of pH 6.6 to 8.1.[29]

3. It is also conceivable that the aeration units in the Kopakorahi arm of Lake Maraetai and further aeration of water at the Maraetai dam tailrace, may both work to facilitate iron and manganese oxide flocculation, with particle growth and settling occurring elsewhere in Lake Maraetai and downstream in Lake Waipapa.

   - Oxygen bubbling can facilitate the oxidation and precipitation of iron and manganese oxides. A standard laboratory synthesis of the manganese oxides birnessite ($Mn_{14}O_{27}.8H_2O$) and hausmannite (tetragonal Mn_3O_4) involves bubbling oxygen through an alkaline solution of divalent manganese (Mn^{2+}_{aq}) [67]. Similar synthetic approaches could be used for preparing iron oxides such as goethite (α-FeO(OH)) and haematite (Fe_2O_3) from ferrous iron (although, in practice, ferric iron and an alkali are used [68]).

   - Bubbling with oxygen may present a more oxidising environment than would be expected based on dissolved oxygen content of the water, because chemical reactions can occur at the air bubble-water interface.

If such mechanisms are responsible for elevated levels of iron, and thus arsenic, in Lake Waipapa sediments, it may prove difficult to apportion responsibility to any one party. Iron flocculation can cause smothering of benthic organisms where concentrations are high, but is normally be seen as being relatively benign. Presence of the Kinleith mill would be a necessary, but not sufficient, condition for arsenic accumulation in Lake Waipapa sediments. The other necessary condition is a elevated mass load of arsenic in the Waikato River. Currently, about half of the mass of arsenic being carried by the Waikato River can be accounted for by natural geothermal discharges, and half is attributable to operations of the Wairakei Geothermal Power Station.

In peer-review of this document, Timperley [99] considers the hypothesis that the Kinleith mill discharge may be causing iron flocculation (and thus arsenic trapping) downstream to be plausible, but also raises a question about whether the flow velocities in Lake Waipapa would be slow enough to allow flocculated colloids to settle:

> *"This is a credible process but given the relatively small volume of Lake Waipapa, I wonder if the river water velocities through this lake would be low enough to enable the flocculated colloids to settle. It would be relatively easy to test the formation and settling rates of the colloids."*

Assuming that the sediment sampling carried out to date is reliable and representative, the main unequivocal inference that can be made from the data to hand is that the arsenic is elevated in Lake Waipapa sediments specifically because the metal oxides (which act as an arsenic trap) are elevated in these sediments. The arsenic follows the iron. For this reason, any hypotheses primarily need to explain why there is such a high metal (iron, manganese and aluminium) oxide content of Lake Waipapa sediments. As specific sources of arsenic only, contamination from former CCA treatment and a local geothermal source are both considered unlikely.

Circumstantial evidence consistent with a hypothesis that some aspect of the Kinleith mill discharge may be facilitating iron oxide precipitation is summarised in **Table 5 (Section 3.4.3)**. At least two alternative mechanisms might go some way to explaining the high iron (and thus arsenic) concentrations in Lake Waipapa sediments [99]. These are that there may be a local source of iron to Lake Waipapa from groundwater, and that stratified waters in Lake Maraetai might seasonally deoxygenate, causing iron release to the overlying water and re-precipitation in Lake Waipapa [99].

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29 Environment Waikato spreadsheet 1007078.

With regard to the first possibility, Timperley notes [99] that iron rich groundwater seeping in to Lake Waipapa would mainly influence shallow sediments, and should have limited impact on deeper sediments. There is no data yet available to test this hypothesis, and it has not proven possible to identify to what depth the sediment samples (**Figure 3**) were originally collected.

The second mechanism would involve release of iron from bed sediments of the upstream lake by reductive dissolution,[30] followed by re-precipitation as it mixes with more oxygenated water (for example, at the dam tailrace). For the first part of this mechanism to operate, it would be necessary for the bottom waters of Lake Maraetai to deoxygenate during stratification to an extent that causes iron oxide reduction, and whether this occurs is presently unknown. Timperley [99] notes that Lake Atiamuri would be a suitable test case to assess the likelihood of this process, because Lake Ohakuri (immediately upstream of Lake Atiamuri) is already known for its deoxygenation, reductive dissolution of iron oxides, and arsenic release. Unfortunately, Lake Atiamuri is a 'forgotten lake,' and we are not aware of sediment sampling having been undertaken there.[31] Two observations that might tend to weaken this second hypothesis are that:

- Current sediment data shows a higher than average iron oxide content of Lake Maraetai sediments (peaking in Lake Waipapa), whereas a lower or similar content might perhaps be anticipated if there were significant annual loss of iron from the Maraetai sediment pool through reductive dissolution.

- Once solubilised, iron from sediments of Lake Maraetai should be indistinguishable from that being carried by the Waikato River. Given that the river transports about 2 tonnes of dissolved and colloidal iron each day all year, it would seem that a seasonal pulse from any given lake would have to be substantial to make much of a difference to the total quantity of iron oxide that settles in Lake Waipapa.

Currently these two alternative hypotheses come unaccompanied by any specific evidence or demonstrated existence of a mechanistic source,[32] but this is for lack of anyone actually looking. At this stage the hypothesis that Kinleith mill effluent plume can act to flocculate some of the colloidal iron being carried in the Waikato River would appear to provide the best internally-consistent match to external observations (**Table 5**), but further investigation would be required to establish whether this is actually the case.

3.4.3 Updated Assessment

Resin acids and related compounds in wastewater

A compilation of monitoring data suggests that resin acid concentrations in Kinleith mill wastewater may be showing a significant increase relative to earlier periods. Evidence for existence of such a trend is still equivocal, due to a wide variability in reported results raising uncertainty about how well previous and current measurements can be said to accurately reflect the true resin acid content of the wastewater. However, comparison of concentrations of resin acids recently reported with an Ontario guideline value suggests that the magnitudes involved may be of toxicological significance.

It would be useful to have more measurements carried on resin acids in the mill wastewater and Kopakorahi Stream out to define the boundaries of short and longer term variability, and establish whether or not the apparent increase in resin acid concentrations in recent measurements may be part of a longer-term upward trend, or relate to specific activities such as pond de-sludging.

[30] Ferric iron oxide $Fe^{III}O(OH)$ is reduced to soluble ferrous iron, Fe^{2+}_{aq}

[31] It should be noted that the Kinleith mill effluent might still have a role in such a process to the extent that it may cause lower oxygen than would otherwise be the case.

[32] For example, whereas existence of the Kinleith Mill is known and forms a part of a circumstantial picture for the hypothesis summarised in **Table 5**, presence of iron-rich groundwater in Lake Waipapa or seasonal deoxygenation in Lake Maraetai are both currently only speculative possibilities.

However, as a precursor to this it will be necessary to standardise and validate sampling, sample handling and analysis protocols for resin acids. The validation programme should involve establishing the accuracy and precision of replicate measurements for resin acids, and arriving at an agreed protocol that is at least precise (and preferably accurate).[33] Comments by Timperley [99] in peer-review of this document's draft are as follows:

> *"The much higher resin acid concentrations reported for samples collected since the AEE was produced are somewhat disturbing....Although pond de-sludging operations might have contributed to the latest concentration[34] reported of over 2500 ppb, the correspondence implies to me that the sampling, preservation and analytical protocols need to be urgently reviewed and a set of rigorous procedures established for future monitoring. It is not necessary that the procedures produce results of the highest accuracy although this would be desirable, rather the focus should be on the precision (the repeatability of the results) because the trends over time are, in my opinion, more important than the absolute concentrations.*
>
> *I also believe that a rigorous quality control procedure should be implemented using blind replicates to check the stability of resin acids in the samples. The concern is that if the latest result is not a consequence of pond-desludging, then resin acid concentrations in the discharge are clearly a probable hazard to aquatic life."*

The authors and Timperley [99] therefore both recommended analytical validation of the resin acids sampling programme as a high priority, after which more reliable inferences can be made about whether there has been a real increase and its potential significance.

Depending on results, as part of the 2008 round of assessments, it may be advisable to define an appropriate site-specific target for resin acids based on what can be inferred about toxicity in the field. This might involve review of data defining toxicity thresholds from laboratory or tank studies on resin acids and whole effluent.

Resin acids and related compounds in fish

In previous evidence [4, 8], it was shown that resin acids (and chlorophenols) were not detected in trout flesh to a detection limit of 4.4 µg/kg (wet weight). Recent sampling of bullhead catfish confirms that fish downstream of the discharge do take up resin acids, with concentrations in pooled bile samples downstream of the discharge being 37 times higher than those in upstream samples [62, p 49]. Exposure of fish to pulp-mill compounds was also indicated by elevated EROD activity, although differences in this parameter were more modest.

These findings show that downstream fish are exposed to resin acids and related compounds (as expected), but can not in themselves be considered as evidence of significant adverse effects on the fish. Fish downstream of the discharge were also of greater size and significantly better condition than those from the upstream location. Potentially negative effects associated with trace contaminants are likely to be offset by beneficial effects of added heat and perhaps nutrients in the discharge.

(One point also worth noting is that resin acid levels in bile samples are always expected to be substantially higher than those in flesh. The new results for pooled bullhead catfish bile samples do not contradict earlier findings of undetectable levels of

[33] Measurements made in analytical chemistry are always estimates of an underlying 'true' value. In analytical chemistry, the term **accuracy** denotes how close the average is to the 'true' value, whereas **precision** refers to the reproducibility or spread of replicate results. A given set of replicate tests can be both accurate and precise (which is ideal), accurate but not precise, not accurate but precise, or not accurate and not precise.

[34] Timperly's reference here is to results from the June 2005 sampling round, which were the latest results at time of peer-review. Results for the December 2005 sampling round were forwarded in January 2006, and have been included in this report.

resin acids in trout or eel flesh, or suitability of trout and eel flesh for human consumption.)

Research is ongoing in to the significance of elevated EROD, but at this stage, there is no new evidence from these monitoring studies to suggest the existence of adverse effects from resin acids and related trace compounds that have not already been considered as part of the resource consent process.

Resin acids and related compounds in sediments

Evidence now exists to suggest that where elevated EROD activity is observed in fish downstream of New Zealand pulp and paper discharges, it is likely to be caused through their increased exposure to certain resin-acid derived PAHs that have accumulated or formed in sediments, rather than the wastewater itself. The PAH retene may be responsible for much of the observed EROD activity.

Retene is produced by anaerobic metabolism of a resin acid precursor (abeitic acid) and should be formed in reasonable quantities in sediments of the Kinleith mill ASB treatment system. Once formed, retene is expected to associate strongly with the particulate and sediment fraction due to its aromatic nature [14]. An unknown proportion may be formed in sediments of the arm of Lake Maraetai.

This preliminary evidence would need further work for confirmation, and does not indicate existence of an unmanaged significant adverse effect. Rather, the new work provides a plausible mechanism by which a known effect—EROD induction—is most likely to be mediated. This may prove useful in the event that future work were to determine that EROD induction is associated with definite harm to an organism.

Evidence also now exists that resin acids and related compounds such as retene are abundant in sediments of areas in forested areas (both natural and plantation). This observation adds an additional layer of complexity to attempts to determine whether pulp mill derived resin acids and their biotransformation products are likely to cause significant adverse effects in sediment receiving environments. Where compounds occur naturally and are potentially harmful, organisms have evolved metabolic processes to mediate their detoxification and breakdown.

Chlorinated organic compounds

Since the Kinleith mill discharge consent was granted, the only new work relating to chlorinated organic compounds has come about as a result of monitoring required as part of CHH's consent conditions. This includes testing and reporting dioxins in wastewater and fish, and dioxins and other trace organic compounds in bed sediments of the Kopakorahi Arm of Lake Maraetai. Results provided to date for wastewater and sediments do not show the existence of significant unmanaged effects. Results for dioxins and furan in sediments suggest a downward trend is likely to be occurring (when normalised to 1% organic carbon). Results for dioxins in fish are discussed in **Section 3.6**.

For dioxins and furans in water, there is a problem that available guidelines for freshwaters are lower than the analytical detection limits for these compounds, despite the latter being extremely low (2 pg/L). Therefore, on one hand analytical results provided for the Kinleith mill wastewater to date do not show a problem in relation to trigger values for further investigation. On the other hand, results to date do not yet rule out the possibility that a trigger value might be exceeded. However, for context, it is worth noting that no specific limits have been set for dioxins and furans in wastewater from the Kinleith mill, and exceeding a guideline would not be taken as being equivalent to demonstrating an adverse effect. Such guidelines are usually taken as a trigger levels for further site-specific investigation. In addition, when normalised to

1% organic carbon, dioxin and furan levels in sediments do not appear to be particularly elevated in relation to available guideline values.

Trace elements

A reassessment of previous evidence suggests that some aspect of the Kinleith mill discharge may be causing arsenic to accumulate in bed sediments of Lakes Waipapa (mainly) and Maraetai (to a lesser extent). Concentrations of arsenic in these sediments are well above levels where significant adverse effects on sediment dwelling organisms are expected. Evidence of significant adverse effects in bottom dwelling invertebrates that may be attributed to arsenic in Lake Waipapa sediment has in fact been previously presented (**Section 3.5.2**).

It is speculated that some aspects of the Kinleith mill wastewater encourage flocculation of a small proportion of iron (and manganese) being carried in the Waikato River, with some this material subsequently being deposited downstream in Lake Waipapa, and a smaller proportion settling elsewhere in Lake Maraetai. Mechanisms may involve a slightly higher pH of the wastewater (relative to the Waikato River) from time to time, the ability of fine suspended organic matter in the discharge plume to attract a coating of colloidal iron oxides, and aeration of water in the Kopakorahi arm and Maraetia dam tailrace.

Alternative explanations for the high levels of arsenic and toxicity of Lake Waipapa sediments have included former use of CCA at the Kinleith mill, and possible natural geothermal sources of arsenic in Lake Waipapa. However, as hypotheses, these possibilities lack supporting evidence and fall short of addressing a number of ancillary observations. Observations that a wastewater-facilitated iron flocculation hypothesis would adequately explain are outlined in **Table 5**.

At least two alternative mechanisms have been proposed that might also account for iron accumulation in sediments of Lake Waipapa [99]: these are a significant localised input of iron in groundwater of that lake, and periodic deoxygenation of Lake Maraetai bottom waters causing the reductive dissolution of iron oxides (followed by their reprecipitation in Lake Waipapa). Data has not yet been collected that would enable assessment of the validity of either hypothesis. Other limitations are that the groundwater hypothesis would only apply to shallow sediments (and it is not known the depth to which original samples were collected from), and the reductive dissolution hypothesis seems less plausible when placed within the context of the natural iron load already being carried of the Waikato River (about 2 tonnes per day).

Currently, the authors consider that wastewater-facilitated iron flocculation is the most likely cause of high arsenic in sediments of Lake Waipapa, but note that alternative possibilities have not been eliminated. If confirmed, this process would result from the unusual circumstance of a pulp and paper mill having the geographical misfortune of being located downstream of significant sources of arsenic.

Table 5 Observations relating to high levels of arsenic in Lake Waipapa sediments that may be explained by an iron flocculation mechanism.

Observation	Explanation if observation is attributable to an iron flocculation mechanism
Iron and manganese concentrations in Lake Waipapa sediments substantially higher than other Waikato Lakes	Flocculation of a small proportion of iron and manganese carried in the Waikato River is initiated through mixing with mill wastewater. Mechanisms may involve pH of the water being slightly more alkaline than the Waikato River, and/or adsorption of iron and manganese colloids on fine organic matter as mill wastewater mixes with Waikato River water. Process possibly assisted by aeration (Kopakorahi Arm aerators and Maraetai dam tailrace).
Iron concentrations in Lake Maraetai sediments also elevated	Residence time of water in Lake Maraetai (and partial circulation) sufficient to allow some settling of iron flocs
High concentrations of arsenic in Lake Waipapa sediments	Adsorption of Waikato River arsenic to iron and manganese oxides that have settled (or as they settle). Adsorption to iron oxides is known chemistry dominating arsenic retention Waikato River sediments.
Correlation between iron, arsenic and phosphate	Arsenate and phosphate are isomorphous and share parallels in adsorption behaviour.
Low concentrations of copper and chromium in Lake Waipapa sediments	Copper and chromium mass loads in Waikato River water are substantially lower than those of arsenic: copper is more likely to strongly adsorb to organic matter than iron oxides.
Decline in benthic invertebrate numbers with distance from the Kinleith mill discharge point in Lake Maraetai. Lake Waipapa sediments show acute lethality to benthic invertebrates.	*Possible* explanations: direct effect of iron-organic flocs settling and smothering benthic invertebrates; more suitable habitat for benthic invertebrates caused by more muddy sediments closer to the discharge point [7]; increasing toxicity of sediments with distance due to increasing arsenic, peaking in Lake Waipapa.

Research in this area is recommended. In sequence, a recommended research programme could include:

- A more detailed assessment of arsenic in sediments and sediment interstitial water of Lake Waipapa, and invertebrate abundances, in order to determine whether low invertebrate abundances are still evident, and if so whether these are likely to be directly attributable to arsenic toxicity, and if so;

- An investigation focusing on whether or not the Kinleith mill wastewater effluent plume plays a significant role in causing elevated iron, manganese and aluminium oxides in Lake Waipapa sediments (which act as sediment traps for arsenic), and if so;

Investigation of mitigation options. A preliminary desk-top investigation of the feasibility of mitigation options (making the assumption that the wastewater plume is implicated) might also help to direct some useful aspects of the research programme [99].

3.5 Discharge to Water: Effects Assessments

3.5.1 Prior Evidence and Assessment

Prior to the resource consent application, a number of studies were carried out to characterise and quantify the range of adverse effects the Kinleith mill discharge might be having on receiving environment ecosystems [9k]. These included studies of aquatic plants, invertebrates and fish.

Aquatic plants

Given the complexity of processes going on in the Waikato River hydro-lakes, it is difficult to be definitive in attributing observed effects to specific causes. The only effect on aquatic plants that can be attributable to the Kinleith mill discharge with reasonable confidence [7] is a reduction in depth range. This is associated with reduced light penetration caused by the wastewater colour (**Section 3.3.1**).

Colour has the potential to raise the depth range of vascular aquatic plants in those parts of the lake where it can cause the euphotic depth to become shallower than the pressure limit for vascular plants (which is about 6 m). For Lake Maraetai, the estimated loss of occupied depth zone attributable to colour in the wastewater was estimated as approximately 14.5% of the 1-6 m usual depth zone for vascular plants. Boubée [9k] summarises:

> *"The reduced depth zone of macrophytes in the main body of Lake Maraetai which has been recorded is likely to be related to the discharge of colour in the Kinleith wastewaters. However, given the number of factors influencing plant growth and distribution, the extent to which the Kinleith wastewater contributes to this effect it [sic] is not clear."*

Invertebrate fauna

Two distinct macroinvertebrate communities exist in Lake Maraetai.

- Communities in the lake weedbeds contain a diverse range of fauna dominated by larval chironomids (midges), tubificid oligochaetes (worms), gastropods (snails), amphipods (small crustacea) and damsel and caddis fly larvae. The abundance of these species is influenced by the extent of weedbeds [4]. Invertebrates in the weed beds are likely to comprise a significant part of a lake food web. Wastewater probably affects invertebrate communities in these beds indirectly, by reducing the area of habitat available [4, 7].

- On the lake bottom, the invertebrate community has much lower diversity, and is numerically dominated by midge larvae, ephydrid (shore flies) and worms [4]. In previous surveying of Lake Maraetai bottom sediments, populations of these invertebrates were found to be abundant, but show a decline with distance downstream of the Kinleith discharge.

Timperley [7] suggested that this decline with distance from the discharge point was likely to be related to the volume of organic-rich benthic habitat contributed by the wastewater discharge. An increase the amount of organic-rich sediment creates more habitat for worms and midge larvae that inhabit soft bottom sediments. In summary, Timperley noted:

> *"Overall, the only obvious effects of the wastewater on invertebrates is the greater area of organic-rich benthic habitat suitable only for worms and midge larvae in the Kopakorahi Stream and Arm and the reduced spatial extent of weed bed habitat in the Arm, lower Lake Maraetai, Lake Waipapa and probably also Lakes Arapuni and Karapiro."*

A second possibility that could account for lower benthic invertebrate numbers with distance from the discharge point is that sediments become increasingly toxic with distance due to accumulation of arsenic in iron oxide precipitates. Evidence consistent with this idea is outlined in Section **3.5.2**.

Fish

A series of investigations carried out on the fish of Lake Maraetai are summarised in the AEE [4], Timperley's audit of the AEE [7] and subsequent evidence from Boubée [9k]. After the 1991 mill modernisation, definitive evidence that the mill wastewater might be causing adverse effects to either fish health or the Lake Maraetai fishery appears to be relatively marginal. Comparison between fisheries in Waikato lakes upstream and downstream of Lake Maraetai is complicated by the fact that each is quite different for reasons other than presence of the Kinleith mill. Circumstantial factors suggested that the Kinleith discharge was probably contributing to a slightly poorer condition of fish downstream of the discharge point at the time the AEE was lodged. These ideas are summarised by Timperley [7, p 26]:

> *"...it can be concluded that Lake Maraetai has a viable and productive trout fishery although it is not possible to directly compare this fishery with those in the immediately upstream and downstream lakes. Fish in the Kopakorahi Arm of Lake Maraetai and Lake Waipapa (and probably also in lower Lake Maraetai) have slightly poorer health than the fish in Lakes Whakamaru and Arapuni. Although it is not possible to confidently attribute this effect to the presence of the mill wastewater, it is a reasonable assumption based on present knowledge for the Kopakorahi Arm. The possibility that the Mangakino sewage discharge[35] has an adverse effect on downstream fish health cannot be ruled out."*

Overall

At the time previous evidence was compiled, post modernisation effects of the Kinleith mill discharge to the receiving ecosystem were found to be relatively minor and equivocal in nature. They appear to have been less significant than had been anticipated based on the mill's history. Boubée [9k] summarises:

> *"The ecosystems in the main body of Lake Maraetai and the downstream Waikato River appear generally healthy and no major effects of the wastewater discharge have been identified. Due to the complexity of natural systems, it has been difficult to determine cause/effect relationships between the wastewater discharge and the receiving environment. In my opinion, the main effect on biological resources that can be directly attributed to the discharge occurs within the Kopakorahi Arm of Lake Maraetai due to the wastewater discharge. However, since modernisation in 1991, marked improvement in this area is evident."*

> *"Given that the Kinleith Mill has been operating since the early 1950's I consider the results of the studies on the aquatic ecology of the receiving waters are very encouraging. Any adverse effects of the discharge will no doubt continue to reduce as mill modernisation progresses."*

[35] Note: since this comment was written, the Mangakino sewage discharge to Lake Maraetai has been discontinued.

3.5.2 Developments Since the Previous Evidence was Compiled

Invertebrate fauna

In previous evidence, it was noted that the lake bottom invertebrate community (dominated by midge larvae, shore flies and worms) shows a decline with distance downstream of the Kinleith discharge (Section 3.5.1). One possible explanation for this was that sediments nearest the discharge point are richest in organic-rich bottom sediments that form a habitat only suitable for these species [7].

A second possibility that has become evident on review is that with distance from the discharge point, sediments may become increasingly toxic due to accumulation of arsenic in iron and manganese oxide precipitates, and possibly also smothering due to iron oxide settling. The possibility that some aspect of the Kinleith mill discharge works to facilitate the downstream flocculation of iron and manganese oxides and consequent trapping of Waikato River arsenic is outlined in **Sections 3.4.2** and **3.4.3** (**trace elements** subsection). This hypothesis is consistent with results of sediment toxicity tests for Lakes Maraetai and Waipapa that were also reported in the AEE [4, p 118]:

> *"Hickey & Roper (1993) reported the results of toxicity tests using amphipods, cladocerans (crustacea) and sphaeriids (finger-nail clams) on sediments from the Waikato Lakes includeing Kopakorahi Arm sediments. Hickey & Roper (1993) showed that the pulp and paper mill affected sediment showed no marked lethality in short term exposure for all three species tested. In comparison, downstream Lake Waipapa sediments displayed some significant lethality. It was considered that this was probably caused by the very high concentrations of arsenic (possibly of natural geothermal origin) measured in the sediments."*

In the field, flocculation and settling of iron oxides can also cause a more direct effect on sediment dwelling organisms, by smothering [70].

Fish

Effects assessments carried out since the Kinleith mill resource consents were granted have focused on fish. These include one paper [15] published in 1998 (about the same time as the last evidence for Environment Court was assembled), and nine papers [16-24] and one report [62] published during the period 2002-2005, with Dr Mike van den Heuval (previously of Forest Research/Scion) being a common author of all ten publications.

Improvements in water quality and the receiving ecosystem caused by the Kinleith mill modernisation were noted in the abstract of the 1998 paper by Sharples and Evans [15]:

> *"In 1991 the Kinleith mill undertook substantial process modifications which have resulted in improvements in the water quality of the discharge. Secchi disc visibilities have increased markedly at the most effluent-exposed sites since modernisation of the mill and similar improvements have been observed in light transmittance. A seasonal trend in water temperature not previously observed was recorded at the most effluent-exposed sites following modernisation, and dissolved oxygen levels at these sites rose markedly. Improvements in the water quality of the recipient* [environment] *since the mill modernisation are reflected in changes in the sampled fauna in particular the occurrence of trout at sites from which they were previously absent."*

Work by van den Heuval and colleagues has mainly focused on the potential impact of pulp and paper mill effluents on fish reproduction. This body of research forms part of a larger worldwide effort to understand the more subtle effects to fish that pulp mill effluents may cause. It has generally been assumed that such effects may be mediated by trace compounds in the discharge which are capable of interfering in normal hormonal signalling processes, through more than one mechanism. Other possibilities also exist. The current state of work in this area has been recently (2004) summarised by van den Heuvel in [21]:

> *"Since 2000, pulp and paper fish health studies have continued to focus on the impacts of effluents on reproduction. Three separate classes of compounds found in effluents have been identified as having endocrine-disrupting potential: polyphenolics (lignins), implicated in reduction of steroidogenesis; androstane metabolites of plant sterols, suspected of causing androgenic responses; and flavones such as genistien, identified as estrogenic substances. Though most studies have utilized in-vitro receptor binding to identify potential endocrine disrupting substances, one new study shows compelling evidence that gonadal apoptosis could be an alternative mechanism for some of the reproductive impacts."*

Most of the New Zealand pulp work in this area has involved exposing developing and mature fish to diluted Tasman mill effluent in large tanks over extended periods, and comparing results with fish from parallel control tanks. Measured variables ranged from general parameters that can be used to describe fish condition through to analysis of trace contaminants and biochemicals. Use of EROD as an indicator of an enzymatic response that occurs on exposure to planar compounds in pulp mill effluent has already been discussed (**Section 3.4.1**).

In absolute magnitude, effects observed to date that may be attributable to trace constituents in the Tasman mill (and by extension Kinleith mill) discharge are at the minor end of the scale, and are not easily related back to possible population level impacts in the field. Most of the effects observed are fairly subtle, and some may appear in the research setting but not be evident under environmental conditions. Some effects require fish to be exposed at a certain time during their development. For example, from [17]:

> *"Male trout showed significant induction of vitellogenin and lower 11-ketotestosterone during the experiment (only the eight-month group was examined), but this did not result in any significant differences in testes development. Thus, this study has shown an impact of pulp mill effluent exposure on the reproductive physiology of female trout that appeared to be hormonally mediated. Furthermore, the effect could only be manifest when the exposure was initiated before the start of gonad development."*

To some extent, scientific work in this area is being hindered by the fact that pulp mill effluent quality has continued to improve. In many cases, this has meant that effects that may have occurred are disappearing before researchers get a chance to properly document them. The field as a whole is still active, and the current state of such research worldwide has been summarised by van den Heuval as follows:

> *"New observations of reproductive effects continue to be documented, with an increase in the use of mesocosms to study these effects. Also many studies are describing recoveries in reproductive health, or are finding effects only at nonenvironmentally relevant concentrations. From the collective data it can be surmised that there are very likely a variety of mechanisms and causative agents for reproductive impacts that act in a manner specific to the species and timing of exposure. However, these effects are continuing to disappear as measures to improve effluent quality continue. In fish health field studies, the Canadian Environmental Effects Monitoring data is likely to make a significant impact on our knowledge of risks to fish, once it has been fully interpreted. Unfortunately, with the continued focus on reproductive physiology, few studies are being conducted at the community level, a deficiency that must be addressed to fully understand impacts on fish health."*

Overall, work carried out in New Zealand in this area is the type of research that stood the best chance of identifying any substantial unmanaged environmental effects of pulp mill discharges on local fish populations. However, whereas results to date have identified a range of effects on reproductive physiology and biochemistry of fish under controlled conditions, effects observed are apparently not sufficient to dominate the viability of fish populations in the field. Instead, in recent work by Tremblay *et al* [62], fish downstream of the Kinleith mill discharge were actually of greater size and significantly better condition than those from an upstream location. The authors speculated that in the Waikato River, potentially negative effects associated with contaminants in the mill discharge are likely to be offset by beneficial effects of added heat and perhaps nutrients (see **Sections 3.4.2** and **3.4.3** subsection on **resin acids**).

Pest fish

Recently, an assessment has been carried out on resident bullhead catfish upstream and downstream of four discharge points on the Waikato River: these were Wairakei Geothermal Power Station, Kinleith Pulp and Paper mill, Hamilton City municipal sewage effluent outfall, and Huntly Power Station [62]. Shortfin eel were also sampled at most sites, but are not present in Lake Aratiatia. A new idea to emerge from this work is that the additional heat associated with three of these Waikato River discharges may provide a favourable habitat for pest fish, at the expense of native species. Tremblay *et al* note [62 p 49]:

> *"Size range, relative density, length at age, and condition of bullhead [catfish] downstream of the discharges with a significant heat components (all except Hamilton) suggest that bullhead [catfish] benefit from the added heat, as would be expected given their preference for temperature of approximately 30°C (Cranshaw, 1974)."*

Whether this would be regarded as a significant adverse effect would probably depend on the contribution made by these favourable thermal habitats to overall numbers of pest fish in the Waikato River and its lakes. At this stage, the answer to this question is not known. However, on the basis of the evidence to date, Tremblay *et al* recommend the following [62 p 50]:

> *"Given the severe pest fish problems in the Waikato, more emphasis should be placed on reducing the impacts of thermal pollution."*

3.5.3 Updated Assessment

Research related to the direct toxicity of the Kinleith mill discharge has not demonstrated any unequivocal significant adverse effects. Despite extensive new research on the potential effects of trace constituents in pulp mill discharges on fish, those biophysical effects identified in controlled settings appear relatively minor in the context of other environmental stressors. Such effects are apparently not significant enough to threaten the overall health of fish, or viability of fish populations in the field. However, a pest fish (bullhead catfish) appears to derive some benefit from heat (and possibly nutrients) downstream of the Kinleith mill discharge, and this may be at the expense of native species that would otherwise inhabit this area. This is an area that might also benefit from further research, as to whether such an effect could be considered substantial enough to constitute a significant adverse effect in relation to the total pest fish population of Lake Maraetai.

In terms of possible indirect effects, reassessment of previous evidence suggests that the Kinleith mill discharge may indirectly effect the viability of benthic invertebrates in Lake Waipapa (in particular), by facilitating the accumulation of arsenic in bed sediments to levels that may be strongly ecotoxic. As noted in **Section 3.4.3**, some targeted research in this area is recommended.

3.6 Discharge to Water: Human Uses and Exposure to Contaminants

3.6.1 Prior Evidence and Assessment

General

In previous evidence leading to granting of resource consents, a range of factors that might potentially affect human uses were considered [7, 4 p 149–]. Water quality parameters considered overlap with those already discussed and include colour, microbiological quality, inorganic constituents and organic compounds. Water uses considered included aesthetic issues (mainly relating to colour), human consumption of fish, stock watering and irrigation.

In relation to this review, the only significant area not already considered, and where there have been some developments, is human consumption of fish sourced from Lake Maraetai. In the AEE [4], and subsequent evidence [9i], data was provided relating to analysis for trace organic compounds and contaminant elements in trout sourced from Lake Maraetai and nearby. Of compounds tested for, chlorophenolic compounds and resin acids were not detected in trout flesh. Dioxins and furans were detected at trace (pg/g) levels, with the highest concentrations being found in trout sourced from Lake Maraetai [4 p 137]. Toxicological evidence was provided to demonstrate that these were unlikely to constitute a health concern [9i].

As a result of deliberations, one consent condition put in place was that the consent holder should determine concentrations of trace organic compounds in eels, which had the potential to accumulate dioxins to higher concentrations than trout [10, condition 20]. Six eel-flesh composites – three from Lake Maraetai and three from Lake Waipapa – were to be collected and analysed during the years 2001, 2008 and 2015. Results of the first round of these tests showed no detectable concentrations of chlorophenolic compounds or resin acids from any of the sampling sites [73]. Further discussion in this review will therefore focus on the potential significance of dioxins and furans (hereafter grouped together as ‘dioxins’ for convenience) in trout and eel flesh sourced from Lake Maraetai.

In addition to the more recent measurements of dioxins in eel flesh, there have been two policy developments that assist in interpreting the significance of the analytical numbers. Firstly, the Ministry of Health adopted a new tolerable intake figure for dioxins in 2002, which sits at the lower end of the international range. Secondly, this comes with a policy shift in the manner that toxic equivalents should be calculated, with the WHO system (**Table 4**) now being preferred [75]. Estimating whether potential health risks from dioxins in Lake Maraetai fish are tolerably low requires the reconsideration of all previous data for dioxins in Lake Maraetai trout and eels in the light of these developments.

Dioxins in Lake Maraetai fish

Four reports exist in which potential human exposure to risks associated with dioxins in eel and/or trout sourced from Lake Maraetai are assessed. These are a preliminary assessment of risk based on potential excess cancer risk presented in the AEE [4 p 160], a more thorough assessment prepared for CHH by toxicologist Michael Bates [9i], a report based on the results of consent-related testing for dioxins and furans in eels by consultancy Kingett Mitchell & Associates (KMA) [73], and a further assessment of these figures by ESR toxicologist Jeff Fowles [74].

Interestingly, there are minor errors in the dioxin figures for trout and/or eel flesh reported in each of the more detailed risk assessments, [9i] and [74]:

- In the first case, the median concentration used (0.49 pg/g I-TEQ wet weight) and assumed to apply to trout in Lake Maraetai is actually a median over eight analyses of trout flesh based on samples sourced from Lakes Maraetai, Whakamaru, Waipapa and Arapuni [4 p 136]. For Lake Maraetai samples only, the median for dioxins in trout from 1996 was actually **0.586 pg/g** I-TEQ (mean **0.547 pg/g** I-TEQ).[36]

- In the second case, the median concentration used (0.474 pg/kg I-TEQ) for eel flesh from Lake Maraetai is actually a median from samples from Lakes Maraetai and Waipapa. The true Maraetai median for eel caught in 1999 was **0.525 pg/g** I-TEQ (mean **0.528 pg/g** I-TEQ). In addition, figures reported for trout as deriving from the KMA report [73] represent only part of the Lake Maraetai samples, and are actually based on the earlier samples as reported also in the original AEE [4 p 136].

It is worth noting that all reports to date have been based on analysis of only seven trout samples (with one being analysed twice) [4 p 136] and six eel flesh composites. Of these, four trout and four eel flesh samples analysed were from Lake Maraetai. However it is also worth noting that when the figures for Lake Maraetai only are used, concentrations of dioxins reported for trout and eel flesh (sampled 1996 and 1999, respectively) are remarkably similar. This may be because dioxin levels in eels were higher than those in trout, but both have been falling with time (given that trout were sampled in 1996 and eels in 1999); or it may be that dioxin levels in both trout and eels are genuinely similar. For the purposes of these estimates, concordance of the analytical results means that the two types of fish can be grouped together.

Approaches used to quantify risk to this point have included assessing excess cancer risk, comparing with tolerable levels in fish from other jurisdictions, comparing with dioxins in fish flesh from other New Zealand studies, and assessing dioxin intakes against international tolerable intake levels [4, 9i, 73, 74]. The number of approaches applied to date reflect the difficulty in being definitive about the potential low level risks that might be associated with dioxins in fish.

3.6.2 Developments Since the Previous Evidence was Compiled

Dioxins and furans in fish flesh and the tolerable intake level

It was noted in **Section 3.4.1** that four reports exist in which potential human exposure to risks associated with dioxins in eel and/or trout sourced from Lake Maraetai are assessed, and within these a range of approaches to the risk assessment have been adopted. The overall outcome of these multiple approaches has been ambiguity: after the most recent assessment [74], the question of whether risks can be regarded as sufficiently minor is still left open.[37]

From a regulatory perspective, there is no longer a need for multiple approaches in order to ascertain whether risks may or may not be tolerable. This is because in 2002, the New Zealand Ministry of Health adopted a new tolerable intake for dioxins which is at the lower end of the international range, and this can be regarded as the official New Zealand health-based figure. This is expressed as an Interim Maximum Monthly Intake (IMMI) value of **30 pg TEQ/kg body weight/month**. This value was established as a result of a WHO reassessment of toxicological data for dioxins [75].

At the same time, it should also be noted that when estimating toxic equivalents of dioxin, preferred New Zealand policy is to use WHO toxic equivalency factors (TEFs). Data provided in all reports to date has been based on international TEFs. For differences between the two systems, see **Table 4**. Raw analytical data for dioxins in trout were not available for review during the writing of this report, but the more recent

[36] Environment Waikato spreadsheet 1010924.
[37] This is due to due to an apparent conflict between international tolerable intakes and New Zealand's preferred excess cancer risk threshold: see Environment Waikato document 985583.

(1999) data for dioxins in eels does appear in the KMA report [73]. Original and adjusted data are provided in **Table 6**.

Table 6 **International and WHO toxic equivalents (TEQs) for dioxins and furans in eel flesh sourced from Lakes Waipapa and Maraetai.** TEQs are in units of pg/g (wet weight).[38]

Sample label	I-TEQ	WHO-TEQ	Sample location
990351/1	0.239	0.323	Lake Waipapa
990351/2	0.308	0.431	Lake Waipapa
990351/3	0.466	0.615	Upper Lake Maraetai
990351/4	0.567	0.752	Lower Lake Maraetai
990351/5	0.597	0.761	Kopakorahi Arm Lake Maraetai
990351/6	0.482	0.611	Kopakorahi Arm Lake Maraetai
Lake Maraetai eel flesh median	0.524	0.683	Lake Maraetai
Lake Maraetai eel flesh mean	0.528	**0.685**	Lake Maraetai

In this case, application of WHO-TEFs consistently increases the calculated TEQ by about one-third. This increase is attributable to the higher weighting placed on the congener 1,2,3,7,8 PeCDD in the WHO system (WHO-TEF of 1.0 compared to the International TEF of 0.5, **Table 4**).

Given the consistency between I-TEQ values for trout and eels caught in Lake Maraetai, it would be reasonable to assume the average WHO-TEQ for eel flesh is likely to also adequately represent the situation for trout. For this reason, the authors suggest that until further sampling is undertaken, the most appropriate figure to represent dioxins in Lake Maraetai trout is **0.685 pg/g WHO-TEQ** (wet weight).

Background dioxin intakes

When estimating exposure from a particular source in relation to a tolerable intake, it is desirable to subtract background exposure. For consistency, this should also be expressed as a WHO-TEQ value. Food is expected to represent the main background source of human exposure to dioxins. Dietary intakes of dioxins have been estimated in 1998 as part of the Ministry for the Environment's orgaochlorines programme. According to Buckland *et al* [76]:

> *"Dietary intakes estimated for an 80 kg adult male consuming a median energy (10.8 MJ/day) diet, were, for PCDDs and PCDFs, including half LODs, 14.5 pg I-TEQ/day (0.18 pg I-TEQ/kg bw/day) and, excluding LODs, 3.72 pg I-TEQ/day (0.047 pg I-TEQ/kg bw/day)."*

Using half limits-of-detection (LODs) in estimating dietary intakes probably gives an over-estimate of the true background exposure, because most dioxin and furan congeners were not detected in most foods.[39] However, the alternative approach of setting non-detected results to zero probably results in an under-estimate of real intakes. (The same comment applies to measurements of dioxins in fish from lake Maraetai: the values derived should be regarded as conservative best-estimates, but may well be over-estimates.)

In a subsequent 2001 report, these intakes were recalculated using WHO TEFs [81]. The current best estimate of daily dioxin/furan exposure for an 80 kg adult male consuming 10.8 MJ/day of food is 17.7 pg/day. Removing the (non canned) fish component of this intake (32 g/day) reduces the background intake estimate to 16.6

[38] For source data and working, see Environment Waikato spreadsheet 1010924.
[39] There is no particular reason to assume that where a congener is not detected, is true concentration is likely to be equal to half the limit of detection. More likely that it will be somewhere less than half the detection limit.

pg/day, which is **0.21 pg WHO TEQ/kg body weight/day**, or **6.4 pg/kg/month** for an 80 kg individual.[40]

Starting with the Ministry of Health Interim Maximum Monthly Intake (IMMI) value of 30 pg WHO TEQ/kg body weight/month, subtraction of the background dioxins intake from all sources other than fish fillets leaves **23.6 pg/kg WHO TEQ/kg body weight/month** available for exposure from other sources, before the tolerable limit is exceeded.

Fish consumption

In order to estimate potential exposure to dioxins from fish caught in Lake Maraetai, an assumption needs to be made about how much fish is consumed. The KMA report [73] assumed ingestion of **32 g/day** of fish, the same as that used by the Ministry for the Environment in estimating background dioxins exposure from food based on a 10.8 MJ daily diet (**32.4 g/day**) [76] (tinned fish was treated separately, being estimated as 5.3 g/day).

This figure is consistent with (conservative in relation to) estimated fish intakes for adult males used in simulated diets as part of the 1997/98 New Zealand Total Diet Survey [77]. Consumption of fish fillets (terakihi) and battered fish together summed to 21.4 g/day, rising to 26.4 g/day when canned salmon was included.

By contrast, Fowles [74] uses median and 95% fish intakes of 70 g/day and 321 g/day, respectively for Australian and New Zealand adults, and cites ANZFA (1999). It is unclear where this data is derived from, because the citation is not accompanied by a reference. However, it appears to be sourced at least in part from Australia's 1995/1996 National Nutrition Survey. The average fish consumption over all age groups was given as 30 g/day in reference [78] and 26 g/day in reference [79].

The apparently high median fish intake figures used in the latest review [74] appear to relate to data from the 24 hr recall component of the Australian survey, and apply only to those people who had actually eaten fish in the previous 24 hr period (14% of those surveyed) [80].

- Consumption figures within this group from the Australian 1995 National Nutrition Survey are given as 115 g/day of finfish and 70 g/day of canned fish—totalling 185 g/day, *but only on days when fish was eaten* [80].

- Australian survey results also implied that about 14% of respondents may eat fish on a given day. When averaged over the whole population (185 x 14/100), this figure works out to the 26 g/day provided by the Australian Bureau of Statistics [79]. (Note that this figure does include canned fish, so that the New Zealand estimate of 32 g/day for non-canned fish is still quite conservative as an average.) Based on the same data, a high consumption (95th percentile) figure for non-canned fish only would be **43 g/day**.

The limitations of using median intake data from the Australian nutrition survey is outlined by Rutishauser in a document entitled: *Getting it right:-–how to use the data from the 1995 National Nutrition Survey* [82]. In relation to data tables provided in the Australian survey, Rutishauser notes:

> *"Information on median daily intake is provided in tables 2, 5, 8, 11, 14, 17 and 20. The tables of median intake, unlike the tables of mean intake which average values over both consumers and non-consumers, show the median intake of consumers only. That is the median values represent the median or middle value of observed*

[40] Note that due to the long-term nature of dioxin exposure and the idea of lifetime risk, it could be argued that there is no specific need to consider shorter term childhood or adolescent exposure, characterised by lower relative body weights or higher energy intake levels, respectively.

intakes only for those individuals who actually consumed one or more foods from the food groups shown in the table."

On this basis it is suggested that the median intake data derived from ANZFA (and used in the last risk assessment [74]) is therefore useful for dietary work requiring knowledge of food portion sizes, but does not give an accurate indication of longer term average intakes of a given food group, on which estimates of chronic exposure and risk should be based.

Because risks associated with dioxins are of the long-term variety, average fish intakes across weeks and months are more applicable than a daily intake on those days when fish is consumed. In this assessment, **32.4 g/day** (**986 g/month**) of fish is assumed as an average consumption, following the figure used in the previous New Zealand estimate of dietary exposures [76], and **43 g/day** (**1.3 kg/month**) is assumed as a 95th percentile consumption based on data provided in [80].

Exposure estimates

Estimated intakes of dioxins that could be experienced by persons sourcing all their dietary fillet fish (excluding canned) from Lake Maraetai are provided in **Table 7.**

Table 7 Estimated potential exposure to dioxins from ingestion of fish caught in Lake Maraetai in relation to tolerable intake levels, assuming a person only eats this type of fish (excluding fish from cans), and the amount of fish ingestion required to approach tolerable intakes.[41] The body weight assumption follows that used in the previous national assessment [76].

Parameter	Unit	Adopted or derived value
Interim Maximum Monthly Intake of dioxins (Ministry of Health IMMI)	pg WHO-TEQ/kg/month	30
Background dioxins intake, excluding fillet fish	pg WHO-TEQ/kg/month	6.4
Available limit per kg body weight	pg WHO-TEQ/kg/month	23.6
Body weight assumed	kg	80
Available dioxins limit	pg WHO-TEQ/month	1888
Dioxins concentration in fish	pg WHO-TEQ/g	0.685
Average fish consumption	g/month	986
High fish consumption	g/month	1308
Average dioxins ingestion estimate if all fish sourced from Lake Maraetai	pg WHO-TEQ/month	675
High dioxins ingestion estimate if all fish sourced from Lake Maraetai	pg WHO-TEQ/month	896
Amount of fish ingestion required to reach the tolerable threshold	g/month	2756
	g/week	634

From this data it can be seen that an individual with an average fish intake who sourced all their fish from Lake Maraetai might reach up to 36% of the Interim Maximum Monthly Intake (IMMI) when background exposure from other dietary sources is also taken in to account. A 95th percentile fish consumer might reach about 47% of the IMMI.

Potentially exceeding the IMMI would require ingestion of at least 2.75 kg of Lake Maraetai fish per month (634 g/week), an intake rate about three times that of the average fish consumer. In review of this document, Timperley [99] notes that

[41] For source data and working, see Environment Waikato spreadsheet 1010924.

consuming this amount of fish on a weekly basis is not out of the question, but doing so every week for a significant part of a person's lifetime is very unlikely.

The term *potentially* is used here due to the conservative approach adopted in estimating the WHO-TEQ for both background food sources and Lake Maraetai fish, where non-detected results were set equal to half their detection limits. As noted above, this approach is likely to overestimate relative to true intakes.

- For example, when non-detected results are set to zero for the Maraetai fish, their mean dioxin content falls from 0.685 pg/g (WHO-TEQ) (**Table 6**) to 0.572 pg/g (WHO-TEQ). At the 'actually detected' end of estimates, an individual would have to eat about 4 kg of fish per month to reach the IMMI—this is about four times the typical intake.

For relating back to daily consumption and portion size, a single fish meal is taken as 150 g [80]. On this basis the amount of fish required to reach the IMMI (if all caught from lake Maraetai) would be equivalent to between 18–27 fish meals per month.

Interestingly, based on the average mercury content of shortfin eels caught from throughout the Waikato River (0.18 mg/kg),[42] a tolerable intake specified for mercury in Australian women[43] would be reached before the IMMI for dioxin, after ingestion of 2.5 kg of fish per month (approximately 17 fish meals). This means that natural mercury is more likely than dioxins to be the limiting contaminant in Lake Maraetai eels. Comments about the potential significance of mercury have also been made by Fowles [74].

Given that the dioxins in the Lake Maraetai ecosystem are expected to be mainly historic due to the mill's modernisation to ECF bleaching (**Section 3.4.1**), expectations for the future are that natural mercury is likely to be more significant than residual dioxins in terms of any limits that might be recommended for fish consumption.

One aspect still missing from this assessment is information about how much fish a keen lake-side fisherman would be likely to consume on both a weekly basis, and over an extended time period, and how this compares with the figure of 634 g/week (**Table 7**) [99]. Although this assessment shows that an individual would need to have three times the average fish consumption on a long-term basis to consistently reach the IMMI, it is unknown what proportion of local residents (if any) might consume fish sourced from Lake Maraetai at this rate. However, a counter-argument can be advanced that in a situation where natural mercury has become the limiting contaminant, the high fish-consumption behaviour would be the primary cause of any risk, rather than the low levels of residual dioxins in the lake sediments.[44]

3.6.3 Updated Assessment

A reassessment of all data to date for dioxins in trout and eels sourced from Lake Maraetai shows that total dioxin intakes of individuals eating all their (non canned) fish from Lake Maraetai are likely to fall well below the tolerable threshold of 30 pg/kg body weight/month.

Exceeding the tolerable threshold would require fish consumption at about three to four times the average rate (18-27 fish meals per month), with all fish being sourced from Lake Maraetai. Under these circumstances, natural mercury is likely to be the limiting contaminant in terms of recommended fish intakes, rather than dioxins. Given this finding, an argument can be advanced that if an individual managed to routinely reach

[42] Environment Waikato document 854666.

[43] 1.6 µg/kg body weight/week @ 66 kg body weight, equivalent to 460 µg/month [80]

[44] This parallels the approach taken when estimating risks associated with ingestion of soil and dust by children from contaminated land, which is normally taken as 100 mg/day. A limited number of children who exhibit pica behaviour may ingest several grams of soil each day, but in this case the behaviour itself has become the primary risk.

the tolerable threshold for dioxin on a long-term basis, the primary risk-factor would be that individual's high fish consumption, rather than the relatively low residual concentrations of dioxins in Lake Maraetai sediments.

Analytical data gathered to date shows no difference between dioxins in trout compared with eels. Based on differences between survey years, it is possible that dioxin concentrations in both types of fish may have been decreasing with time, but firm evidence for this is not yet available. The significance of dioxins in the Lake Maraetai ecosystem should diminish with time.

3.7 Discharge to Air: Characteristics

3.7.1 Prior Evidence and Assessment

In anticipation of the expiration of their air discharge permit in March 1995, Carter Holt Harvey (CHH) applied for a resource consent to discharge to air in 1994 [2]. The application was accompanied by an Assessment of Environmental Effects (AEE) that identified **odour** emissions, from the discharge of reduced sulphur (TRS) gases, as the key air quality issue. Plant technology upgrades planned for future years were anticipated to reduce the odour emissions and this requirement was later included in the resource consent conditions [11]. As part of Condition 1, the consent holder is particularly required to continually seek to reduce odour discharges.

Other contaminant discharges, including particulates, were regarded in the AEE to be within guideline levels at the time or to have insignificant environmental effects. Emissions were determined from Kinleith stack test results, tests from Tasman Pulp and Paper mill and from published emission factors. Data from literature were used for estimates of aldehydes, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), dioxins, trace elements, oxides of nitrogen (NOx), SO_2, particulates and combustion gases. The main literature sources were two reports published by the National Council for Paper Industry Air and Stream Improvement (NCASI).

Additional information provided in 1996 [5] updated the AEE with further monitoring and modelling data, following improvements to mill technology and processes. Again, when considering effects, odour emissions received the most attention. Further plant upgrades were anticipated for future years, with the expectation of continual odour emission reductions. Since the initial AEE, investment in equipment had also been made to augment monitoring capability that included TRS, particulates, carbon monoxide (CO) and chlorine gases. Ambient monitoring proposals were limited to odour surveys and modelling, along with meteorological monitoring of windspeed and direction. Chlorine storage and gas release risk assessment were also addressed in this report. It was concluded that only the Tokoroa community was exposed to risk of accidental chlorine gas release and it was suggested that some basic contingency measures would mitigate this risk to an acceptable level.

To assist Environment Waikato in the consenting process, Woodward-Clyde (NZ) Ltd was commissioned to provide technical advice and an audit of the AEE was completed in 1997 [6]. This report agreed with the conclusion that odour would be the main air emission of concern and some recommendations for future improvements were made. Additional recommendations included ambient monitoring programmes for odour, particulates, sulphur dioxide (SO_2) and meteorological parameters. Recommendations were also made for monitoring emissions of PAHs and odour, along with guidelines and standards for testing emissions of particulates, TRS and chlorine.

Woodward-Clyde also suggested the AEE risk assessment for accidental chlorine gas release was inadequate and recommended the development of appropriate operational planning and emergency response procedures. Accidental release of hazardous substances was recognised as *"the most serious potential air quality effect of the existing operations"*.

In 1999, Environment Waikato granted Carter Holt Harvey a consent to discharge contaminants into the air [11]. The consent included 43 conditions relating to discharge limits, discharge controls, monitoring, reporting, reviews and some general requirements including continual improvements to contaminant emissions. Discharge limits apply to particulate emissions, TRS, chlorine, chlorine dioxide (ClO_2), hydrogen chloride and oxides of nitrogen (NOx).

3.7.2 Developments Since the Previous Evidence was Compiled

Peer-reviewed literature

There is a paucity of literature relating to air quality issues associated with pulp and paper mills in New Zealand since the CHH air discharge consent was granted. The authors are aware of only three references that were published after or around this time and these relate to odour from Tasman mill [28,29,30]. No new research was identified that directly investigates the discharges to air from Kinleith mill.

The first of these three papers described the development of a model for assessing odour dispersion at Tasman mill [28]. The second paper [29] was an application of the model, combined with monitoring data, to assess various odour reduction options at Tasman mill. It was discovered that some capital intensive options were less likely to provide odour benefits than some previously lower-priority, cheaper options. Taller stacks were also rejected as an effective odour mitigation measure. The final of the three papers [30] used olfactometry and community surveys to assess odour emissions. It was concluded that hydrogen sulphide (H_2S) did not contribute to the perceived odour from the mill. Perceived odour was instead sourced from the other TRS emissions: methyl mercaptan, dimethyl sulphide and dimethyl disulphide.

This research was summarised in a non-peer reviewed report of odour management at Tasman mill [84]. It was demonstrated that TRS emissions, odour emissions and associated community annoyance all decreased significantly between 1994 and 2001.

TRS emissions from Kinleith mill have also decreased significantly over this period (**Figure 4**), in a similar fashion as a consequence of plant and process improvements. This is very likely to represent a reduction in odour emissions, however as Jenkins (2001) [84] cautions, this information needs to be verified by community surveys before conclusive statements can be made about mitigation of odour effects.

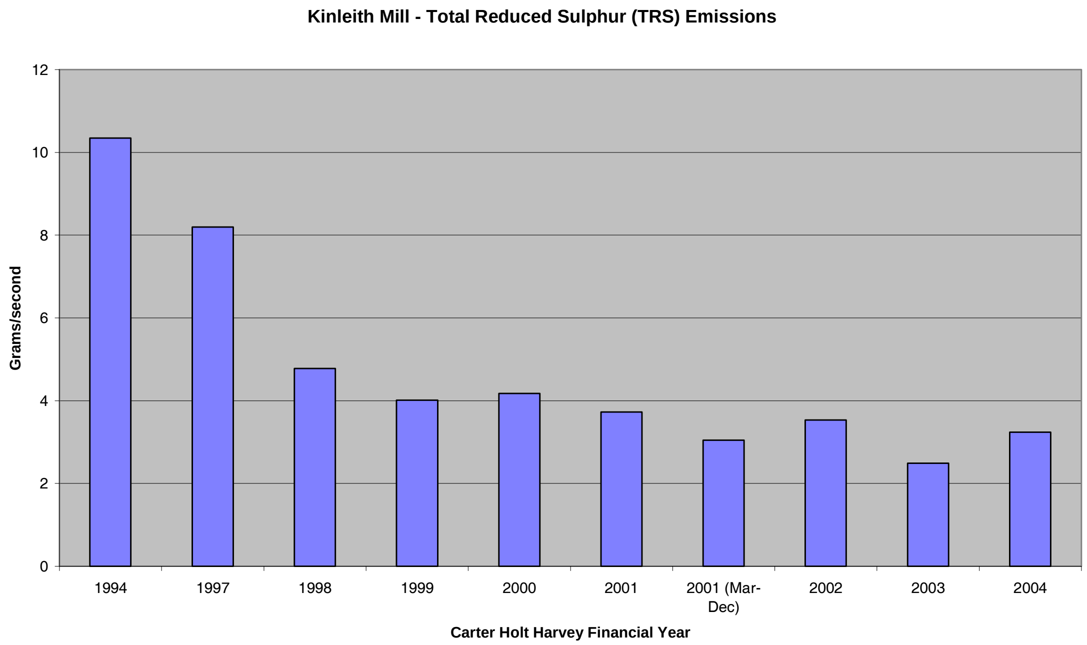

Figure 4 Mill-wide TRS emissions from Kinleith mill between 1994 and 2004.

Application for consent changes 2002

CHH later submitted an application to change consent conditions and the requests were mainly related to variations in fuel use. Environment Waikato commissioned a review of the application in 2002 [85] and the consent was modified in 2003. The use of alternative fuels was approved and discharge limits for particulates and TRS were modified as appropriate.

International emission limits

Since the consent was initially approved in 1999, there have been various international emission limits and emission factors published. However, it is not always a straightforward process to directly compare the Kinleith discharge limits to international standards for several reasons:

- Combustion discharges depend upon the mix and variations of fuel types, which are often not applicable to the unique mix of fuels at Kinleith. Sometimes there is a range of emission limits offered, depending on fuel types, but these limits appear to be changing fairly frequently over time as standards are developed.
- Emissions depend upon pulp feedstocks and some published values apply to eucalypt pulp mills, which are not applicable to the Kinleith mill's emissions. Even though the use of eucalypt feedstock is increasing at New Zealand pulp and paper mills, the dominant source at Kinleith is still pinus.
- International published values often apply to greenfield (new) mills and in these cases the authors are clear that the emission limits are too stringent and unrealistic for older mill retrofits.
- International regulations are often based on technology requirements, rather than effects-based criteria that are relevant to New Zealand legislation.

A paper published in 2003 summarises international trends in air emission limits at pulp and paper mills [97]. Some of the trends for world class mills are suitable for comparing to the Kinleith discharge limits (**Table 8**), however it should be noted that the range of international limits includes those applicable only to new mills.

Table 8 demonstrates that Kinleith discharge limits are sometimes outside the range of the published international limits and it is recommended that the discharge limits be re-evaluated at the next consent review. All mills used to identify the range of international limits were either new mills or had undergone extensive modernisation within the past 10-15 years, so it would be reasonable to assume that even the upper end of the range of international limits may be considered world-class for existing mills. Therefore it is perhaps not too alarming that some Kinleith limits exceed the international range in **Table 8**. It should also be noted that the lower end of the range of international limits includes limits for greenfield mills and these are not appropriate for comparison with existing mills.

Given that the emission limits are evolving, and because it is only 2 years since the Kinleith discharge limits were reviewed, it seems reasonable to defer any comparison with international standards until the next review of conditions scheduled for 2008. A review of effects could then be undertaken to assess Kinleith discharge limits within the context of appropriate international standards that may have been developed over this time.

Table 8 **Published mill emission limits (from Bruce and van der Vooren, 2003) [97] and corresponding Kinleith consent discharge limits.**

Source and contaminant	Kinleith limit	International limit range
Particulate Matter		
No. 2 Lime Kiln	250 mg m^{-3}	50-180 mg m^{-3}
No. 3 Lime Kiln	500 mg m^{-3}	50-180 mg m^{-3}
No. 4 Recovery Boiler	200 mg m^{-3}	60-240 mg m^{-3}
No. 5 Recovery Boiler	50 mg m^{-3}	60-240 mg m^{-3}
No. 8 Primary Boiler	100 mg m^{-3}	40-120 mg m^{-3}
TRS		
No. 3 Lime Kiln	45 mg m^{-3}	15-38 mg m^{-3} [a]
No. 5 Recovery Boiler	20 mg m^{-3}	5-14 mg m^{-3} [a]
No. 4 Recovery Boiler	45 mg m^{-3}	N/A [b]
Oxides of Nitrogen		
No. 8 Primary Boiler	300 ppm	100-200 ppm

Notes: a. Converted from the international limits published in units of ppm TRS as H_2S equivalents.
b. The published limits are for low-odour recovery boilers and not applicable to the conventional No. 4 recovery boiler.

Dispersion modelling

The most recent modelling exercise related to Kinleith was dispersion modelling of particulate and SO_2 conducted in 2003 [86].

The maximum average 24-hour contribution at Tokoroa of fine particulate air pollution (PM_{10}) from Kinleith was estimated to be 4 μg m^{-3}. The current National Environmental Standard (NES) for 24 hour PM_{10} concentration is 50 μg m^{-3} and it is estimated that domestic home heating contributes 85% of PM_{10} in Tokoroa during winter when the NES is exceeded [87]. Using meteorological data to identify periods when Kinleith emissions could contribute to Tokoroa PM_{10}, it has been concluded that PM_{10} from Kinleith is unlikely to significantly contribute to Tokoroa concentrations on days when the guideline (NES) was exceeded in 2004 [87].

Dispersion modelling of SO_2 indicates that discharges from Kinleith would not cause the NES to be exceeded in Tokoroa or other neighbouring communities. It is possible that the NES SO_2 threshold of 350 μg m^{-3} may be exceeded at a remote location 1 km from Kinleith, in a forest where public are excluded.

NES and Ministry for the Environment Guidelines

In September 2004, the Ministry for the Environment (MfE) introduced National Environmental Standards for Air Quality (NES). This includes ambient standard concentrations for contaminants including PM_{10}, SO_2 CO, NO_2 and ozone. Monitoring and emissions inventory assessment of these contaminants indicates that only PM_{10} concentrations are expected to exceed the NES in nearby Tokoroa [87]. Concentrations of the other contaminants are unlikely to be exceeded unless emission sources are significantly increased. Therefore the relevance of the NES to Kinleith emissions chiefly applies to PM_{10} and, as stated above, the best information available indicates that Kinleith is not a significant contributor to PM_{10} in Tokoroa [87].

Stockholm Convention and New Zealand implementation

The Stockholm Convention on Persistent Organic Pollutants (POPs) aims to protect human health and the environment from some very toxic chemicals. The Convention was ratified by New Zealand in September 2004. Chemicals listed as POPs that are most relevant to pulp and paper mills are polychlorinated dibenzo-p-dioxins or PCDDs, and polychlorinated dibenzofurans or PCDFs (dioxins and furans). Some action may be required to reduce the discharge of PCDDs and PCDFs to air from Kinleith mill, however improvements have already been made to New Zealand's pulp and paper mills, including the upgrade of Kinleith to the elemental chlorine free process. Dioxin emissions to air from pulp and paper mills rank at the lower end of source lists produced by the MfE [91]. (Refer to **Sections 3.4** and **3.6** in relation to dioxin and furan emissions to water.)

The Ministry for the Environment intends to release a draft National Implementation Plan during 2005 for public consultation and a final Plan will be submitted to the Stockholm Convention Secretariat by December 2006. The draft Plan will identify how New Zealand proposes to meet convention obligations, such as reducing dioxin releases. Rather than making recommendations here regarding dioxin emissions at Kinleith, it is recommended to wait until Government has released the implementation plan, so that if action is required this can be coordinated with national policy and response.

Eucalypt processing

As mentioned in Section 3.2.2, there has been an increase in the use of eucalyptus feedstock within the New Zealand pulp and paper industry since the Kinleith resource consents were granted [26, 35, 38]. This is unlikely to have an adverse effect on air quality, as emissions from pulp production from eucalyptus are considered to be lower than from conifers [83]. As with effluent discharges, it is possible that increased eucalyptus processing may result in air emission improvements.

Hazardous events

While the accidental gas release of June 2004 was relatively minor and did not warrant enforcement or further action, steps are being taken as a precautionary assurance of appropriate management of future accidental discharges. As part of this process, it is understood that CHH Kinleith has commissioned an external consultancy to prepare an updated risk assessment.

The Woodward-Clyde audit of AEE [6] recognised accidental release of hazardous substances as *"the most serious potential air quality effect of the existing operations"* and this belief has been echoed in international literature: at a Canadian mill, chlorine-dioxide storage was acknowledged as the single largest potential environmental threat to a surrounding community [92]. Given the serious nature of the consequences of this potential threat, some recommendations are made for consideration in the updated risk-assessments:

- Consideration of changes made to Canadian mill design, operating procedures and emergency response measures following a catastrophic chlorine dioxide (ClO_2) release at the Canadian site [93]. Integration of this knowledge would include an assessment of tank design and monitoring, with measures to **contain** a spill of a size 1.4 times the volume of the largest storage tank. This commonly involves a bund or berm that surrounds storage tanks and allows for containment and neutralisation of an entire tank of spilled chlorine dioxide. The literature also recommends **vapour suppression** methods, of which an oil skim has been recognised as most effective [94]. Finally, the most suitable **neutralisation** and disposal methods for Kinleith's operation and environment should be identified and installed. It is noted that dilution with water is not an effective means of avoiding chlorine dioxide cloud formation and neutralisation is essential. At NorskeCanada's Crofton mill, concentrated sodium thiosulphate was chosen as the most suitable neutralisation method, however this may not be universally appropriate for all locations [92].

- Experience from risk management assessment conducted at another Canadian mill as part of ISO14001 process, where the probability of occurrence and potential impact of a major chlorine dioxide spill was reduced [92, 94]. This resulted in substantially improved safety for mill personnel and people in the community. The literature recommends that risk assessment includes a comprehensive study of the risks of storing chlorine dioxide and the development of robust policies to mitigate potential risks. It is also recommended that documentation be maintained throughout the development process, to provide evidence of due diligence and as a record of the work aimed at reducing the risk of environmental damage. Once the systems are operative, their effectiveness must be maintained by testing and auditing [94]
- Risk evaluation of piping and other equipment failure, with special attention to any fibre reinforced plastic (FRP) components. Failure of FRP piping at a chlorine-dioxide-stage bleach tower in a pulp mill has been reported, where the line broke in a catastrophic manner after only about six years of service, despite being high quality and designed according to current norms [95].

3.7.3 Updated Assessment

There is a paucity of literature relating to air emissions from New Zealand pulp and paper mills and there is no known evidence since the resource consent was granted that might suggest the presence of unanticipated adverse effects. Unless significant new evidence is published in the meantime, current consent conditions appear to be adequate to manage Kinleith discharges until the next review in 2008.

However following the (albeit minor) accidental release of chlorine dioxide gas at Kinleith in June 2004, and with international literature highlighting the serious potential threat of future catastrophic release, a review of risk assessment and emergency response procedures is appropriate. It is recommended that any updated risk assessment evaluates risk of component failure (especially FRP piping) and also embraces the lessons and responses of Canadian mills that have completed similar reviews of risk management processes [92-95].

3.8 Discharge to Air: Potential Effects to Workers

3.8.1 International Evidence and Assessment

Workers in the pulp and paper industry are exposed to a number of potentially hazardous substances, most of which are either gases or can exist as suspended particulates.[45]

The most frequently identified specific exposures in production areas of ECF mills are reported as those associated with simple chlorine and sulphur compounds. Compounds present in work areas may include chlorine dioxide, elemental chlorine (from breakdown of chlorine dioxide), other organochlorines, sulphur dioxide, and reduced sulphur compounds.[46] An example of an organochlorine compound currently lost to both air and wastewater is chloroform [89]. However, production of chloroform is much (>30 times) lower in ECF mills than those still using elemental chlorine as part of the beaching process [89]. Other exposures in production areas may include wood dust and calcium oxide [90]. Chemical exposures in non-production areas may include asbestos, copper, mercury, chromium(VI) compounds, ozone, styrene, sulphur dioxide, trichloroethylene, nitrogen dioxide, welding fumes, carbon monoxide, and silica [90].

In most cases where significant exposure might occur, inhalation would be the dominant exposure pathway. Within this review, most workplace exposure therefore comfortably sits inside a wider context of air quality.

Internationally, a range of epidemiological investigations have examined the potential for adverse health effects that might be associated with working in the pulp and paper industry. Approaches have included proportional mortality, case control and cohort studies. As noted by Matanoski *et al* [88]:

> *"Many of these studies have had limitations. Most cohort studies have included small populations. Case-control studies have had few cases exposed. Many of the reported risks of disease do not reach biostatistical significance....Most of the studies have not been controlled for smoking even though all of the diseases reported except for lymphosarcoma are thought to be associated with cigarette use..."*

The population of workers and former workers available for a cohort study on a given mill has often been limited by the fact that although they can be significant local employers, in relation to significant national sectors such as farming, pulp and paper mills have comparatively few workers, and also a fairly stable workforce [88]. A further limitation in work to date has been that workplace exposures have been inferred retrospectively, based on job type and period of employment, and external risk factors have frequently not been accounted for. Non-workplace factors that may be higher among mill workers (depending on circumstance) range from voluntary activities such as smoking [88] to involuntary factors such as a higher incidence of hepatitis B and consequent potential for liver cancer in workers of Mäori and Pacific Island ethnicity [47]. Shift-work is a workplace factor not usually considered that can also be associated with poorer health [93].

Epidemiologists quantify the risks of death from various causes using a standardized mortality ratio (SMR), defined as the ratio of the number of observed deaths to the

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[45] It should be noted that National Environmental Standards for ambient air – discussed in **Section 2.2.2** and **3.7.2** – do not apply inside the consented area; various Workplace Exposure Standards may apply.

[46] Compounds measured in a total reduced sulphur (TRS) assay are hydrogen sulphide H_2S, methyl mercaptan CH_4S, dimethyl sulphide $(CH_3)_2S$, and dimethyl disulphide $(CH_3)_2S_2$. Carbon disulphide (CS_2) and carbonyl sulphide (COS) may also be present.

number expected for members of a control population of equivalent age, calendar time,[47] race and sex. For interpreting the SMR, the following should be noted:

- The SMR is not without error and is based on assumptions about the nature of how well the sample population (the study group) may be taken to describe the underlying population (all mill workers). Error around the SMR is expressed as a 95% confidence interval, which is the interval within which the true SMR for the underlying population (all mill workers) is likely to fall with a 19 out of 20 chance.

- Death rates in mill workers can be said to be statistically higher than those of the control group when the lower boundary of the 95% confidence interval exceeds 1.0. Conversely, an SMR statistically less than 1.0 indicates a lower risk of death in members of the study population.

- However, because this is a 95% interval, it is likely that 1 in 20 apparent differences between mill workers and members of the general population will still be spurious. Some of the differences between epidemiological investigations on pulp and paper mill workers, where an effect identified in one study is not borne out in the next, are likely to be due to this cause. For this reason, reviewers [90] are more interested in consistent patterns between studies, rather than irreproducible or one-off findings.

A useful review of epidemiological studies on health effects on pulp and paper mill workers has recently been written by Driscoll [90]. Reasonably consistent findings from epidemiological investigations on pulp and paper mill workers are as follows:

1. Deaths from all causes, and deaths from all cancers, are fewer in pulp and paper mill workers than in members of the general population [88, 90]. This is not a special aspect of the pulp and paper industry, but rather a common epidemiological observation for working populations. Matanoski [88] notes:

   "In general, working populations are healthier than the general population, and the paper industry is no exception."

   However, the fact this observation also holds for the pulp and paper industry does suggest that the aggregate sum of any health effects that may come about as a result of workplace exposure is not very substantial, because otherwise it would cause a deviation from the normal pattern.

2. Although mill workers show a lower or similar incidence of, or mortality from, all cancers combined [90], a number of studies have found an increased incidence of **certain types** of cancers in mill workers – particularly lung cancer, mesothelioma and stomach cancer. However, most of the increased incidence of lung cancer and mesothelioma has been attributed to historic exposure to asbestos, although other causes are not excluded. The significance of greater incidence of stomach cancer is also equivocal, due to the possibility of confounding dietary variables in the study populations [90]. Of potential relevance to the Kinleith and Tasman mills, the largest study to date [88] did identify a statistically significant 35% increased mortality from lung cancer among workers employed at kraft mills, although this was not corrected for smoking as a confounding variable.

3. There is now reasonably good evidence that pulp and paper mill (including ECF mill) workers are (or were) at increased risk of developing respiratory disorders [90]. Chlorine, chlorine dioxide, sulphur dioxide, hydrogen sulphide, methyl mercaptan, dimethyl sulphide and ozone are all respiratory irritants [90]. The magnitude of these effects are not necessarily large, but statistical significance of a number of elevations relative to expected background rates has been demonstrated with reasonable consistency. Symptoms and effects can include

[47] Calendar time refers to the specific years a given cohort of individuals has lived through. A group born during the five year period 1955-1959 may have experienced a different set of background exposures than an otherwise identical group born between 1975-1979.

increased incidence and mortality from asthma, increased wheezing and chest tightness, increased airways inflammation, and decreased lung function. Such effects are more likely to occur in workers who have experienced high exposures as a result of uncontrolled releases (have been ‘gassed’). There is an ongoing question over whether bronchial hyper-responsiveness induced by such exposures is permanent or reversible [90].

Overall, international evidence suggests that in terms of death from all causes and deaths from all cancers, mill workers fare better than the general population. Some types of cancers (lung, stomach) may show a higher incidence among mill workers, but these findings are still somewhat equivocal in some cases or may be due to historic exposures in others. The potential for respiratory disorders (item 3) is therefore probably of greatest significance to modern pulp and paper mill workers.

Depending on the exact process and control measures in-place, exposures to vapours and dusts may range from the long-term/low-concentration to short-term/high concentration. In 1996, Toren *et al* [96] suggested that exposure to respiratory irritants may be an important, probably overlooked, aspect of working in specific areas of pulp and paper mills:

> *“Workers with repeated exposure peaks to chlorine, e.g., bleachery workers, seem to have an impaired lung function and an increased prevalence of respiratory symptoms. Exposure to high levels of paper dust, (> 5 mg/m^3) causes impaired lung function...”*

but also noted:

> *“However, before any definite conclusions can be drawn, the impact of important confounders, such as shift-work and smoking habits have to be further evaluated.”*

3.8.2 New Zealand Epidemiology

Pulp and paper mill workers

In 2002, the *New Zealand Medical Journal* published an epidemiological investigation examining mortality and cancer incidence in New Zealand pulp and paper mill workers carried out by McLean *et al* [47]. This came about as part of a collaborative international study organised by the International Agency for Research on Cancer.

The study population comprised 8456 workers employed for at least one year between 1978 and 1990 at one of New Zealand’s three pulp and paper mills, with an average period of employment of 12.1 years. Study subjects were traced forward in time to 1992. Mortality records and the cancer register were used to determine cause of death, cancer incidence and type of cancer where diagnosed. Confirmation that those not registered as having died were still living (‘vital status’) was also ascertained where possible using other methods.

Limitations of this study were:

- The small number of cases of specific diseases, making it difficult to examine associations between inferred exposures and diseases [47];
- The relatively short follow-up period (until 1992 only). Cancer incidence and mortality is ideally examined in cohorts decades after exposure, to allow for the latency period between exposure and cancer development [90];
- With the exception of cancer, any adverse health outcomes that did not result in death of the study subject prior to 1992 were excluded. As noted above (**Section**

3.8.1), working in some parts of some pulp and paper mills may be associated with increased incidence of certain respiratory disorders, only a small proportion of which might result in fatal outcomes.

- The fairly small sub-populations that result when data is broken down to smaller components, such as workers exposed to particular chemicals or who worked in a particular department. Although 8456 workers is a large sample size for New Zealand workers in any industry, it is small when attempting to be definitive about exposure-linked diseases that may only show a marginal increase in exposed subgroups. Inclusion of individuals who only worked in the industry for a fairly short time (e.g. 1–3 years) is also a potential issue. By comparison, due to the size of the US industry, the largest US study to date was able to track 63025 long-term workers (each with 10 or more years of employment) over 51 mills from 23 corporations [88].

Despite these limitations, the New Zealand study showed the following statistically supported outcomes [47]:

1. Deaths from all causes, and deaths from all cancers, were fewer in pulp and paper mill workers than in members of the general population (314 deaths observed compared with 394 expected giving an SR of 0.8 and 95% confidence interval of 0.71–0.89). This is attributed to the 'healthy worker effect,' that healthy people are more likely to gain employment and remain in employment. Part of the reason also appears attributable to statistically fewer than expected deaths from two external causes – traffic accidents and suicides.

2. Incidence of all cancers combined was lower in the mill workers than the general population, whereas all-cancer mortality was indistinguishable from that of the general population.

3. Statistically significant increases in mortality from lung cancer were observed among workers classified as ever being exposed to pulp and paper dust (SMR 1.45) and talc (SMR 3.15), and those ever employed in the non-production department (SMR 1.44). The authors note:

   "Much of this increase could be explained by smoking and asbestos exposure, but the effect of other exposures including talc and pulp and paper dust cannot be excluded."

4. A significant ($p<0.01$) trend exists between the SMR describing mortality from all causes and the year since first employment, whereas no such trend is evident between the same SMR and duration of employment. In other words (as an example), there is some evidence that on average, a group of people employed for a 5 year period from 1978-1982 may have fared worse in a subsequent follow-up period than a similar group employed for 5 years from 1985-1990. This suggests that the types of exposures that might eventually lead to premature deaths may have decreased with time.

Items 1 to 3 are consistent with findings from international research on workers in the pulp and paper industry (**Section 3.8.1**). Item 4 suggests that improvements in occupational hygiene in the New Zealand industry may have resulted in lower exposures, and progressively fewer adverse health outcomes over time. This interpretation is consistent with developments in occupational safety and health over time, many of which were specifically designed to minimise worker exposure. In its most recent form in New Zealand, this translates to the HSNO Act, under which the Environmental Risk Management Authority will progressively review and implement Workplace Exposure Standards.

No comments can be made from New Zealand work to date about whether the incidence of respiratory disorders may be higher in particular groups of pulp and paper workers, than in members of the general population.

Inferences about nearby populations

It has been suggested that findings of better health among pulp and paper mill workers might be used to demonstrate that any exposures from mill discharges to air are unlikely to result in adverse health outcomes to nearby members of the general population. For example, better health at workers from the Kinleith mill might mean better health in Tokoroa than other comparable towns.

Unfortunately, the methodology used precludes making such an inference. The reason for this is that the health status of the New Zealand population, and nearby populations by inclusion within this group, has already been considered in deriving standardized mortality ratios (SMRs). Given that the population of Tokoroa is a subset of the control group, the finding of lower mortality in mill workers can not be reversed to infer better health of Tokoroa residents.

3.8.3 Assessment

Findings of a New Zealand epidemiological study on health of pulp and paper mill workers is consistent with international findings. In general, pulp and paper mill workers show lower total mortality, and equivalent or lower incidence and deaths from cancers, when compared with members of the general population. Lower total mortality is a general finding for working cohorts, known as the ‘healthy worker effect.’

There is some evidence that the types of exposures that might eventually lead to premature deaths in some mill workers have decreased with time, and this would be consistent with lower worker exposures through improvements in occupational hygiene that have been made over the years.

New Zealand findings can not be used to infer anything about the health status of Tokoroa residents, and whether the mill might contribute to better or worse health in some small part.

New Zealand work to date has not examined the relative incidence of non-fatal respiratory disorders among workers, which would appear to be the most likely occupationally-influenced adverse health outcome that might be associated with working in some parts of a mill, depending on the extent to which workers are exposed to and inhale various gases and dusts. This idea has indicative (non-definitive) epidemiological support from some overseas studies, and mechanistic support in that most of the gases and dusts that can become elevated in a mill environment are respiratory irritants.

4 Summary

4.1 Water

The focus of this review has been to identify whether developments in scientific understanding since resource consents were granted indicate that there may be areas that require additional investigation or management. Overall, consent conditions relating to the wastewater discharge from the Kinleith mill still appear appropriate and sufficient to manage most potential adverse effects. A summary of findings relating to potential adverse effects and associated recommendations is provided in **Table 9**.

Table 9 Possible unmanaged effects relating to the Kinleith mill wastewater discharge, and associated recommendations.

Wastewater quality—general wastewater quality and quantity (Section 3.2)			
Area	*Possible significant unmanaged effects*	*Possible effects that may warrant closer investigation*	*Recommendation*
Continuous improvement in discharge quality	None identified	Extent to which increased mass loadings that may come about through production efficiency gains are offset by improvements elsewhere.	As part of the 2008 review, the consent holder should provide evidence outlining how they have sought a continual improvement in wastewater quality over time.
Cyanobacteria	None identified	Potential for secondary treatment ponds to act as a seeding population for blue-green algal blooms in the Waikato River downstream.	A desktop review should be carried out by a microbiologist within the next six months to assess the potential for this to occur.
Constituents of biological relevance (Sections 3.3 and 3.4)			
Area	*Possible significant unmanaged effects*	*Possible effects that may warrant closer investigation*	*Recommendation*
Colour, BOD, nutrients	None identified	None identified	None
Resin acids in wastewater, fish or sediments	Apparent upward trend in reported concentrations to levels that may be toxicologically significant.	Relationship between pond de-sludging and the resin acid content of wastewater, and whether high transient concentrations are of toxicological concern.	It is of high priority to validate the resin acids sampling, preservation and analysis protocol to ensure that results are robust, accurate and reproducible. One this is done, work should be carried out to identify factors leading to fluctuations in concentrations of resin acids in the wastewater stream, with a focus on identifying means of minimising real loadings (and toxicity) as far as practicable, and establishing that concentrations are not trending upwards. A specific resin acids effects assessment is suggested as part of 2008 review.
Chlorinated organic compounds in wastewater	None identified	None identified	None

(Table 9 continued..)

Constituents of biological relevance (Sections 3.3 and 3.4) continued...			
Area	*Possible significant unmanaged effects*	*Possible effects that may warrant closer investigation*	*Recommendation*
Trace elements	Iron, manganese and arsenic accumulation in sediments of Lake Waipapa (in particular): possibility that this is linked to an aspect of the Kinleith wastewater discharge	Capacity of the Kinleith plume to cause flocculation of a some iron being carried in the Waikato River. (Possible international significance in relation to iron oxide smothering and sediment manganese toxicity.)	A targeted research project should be undertaken to further investigate the significance of arsenic in Lake Waipapa, and identify whether aspects of the Kinleith mill discharge and specific receiving environment initiate flocculation of a portion of iron and manganese being carried by the Waikato River. If this is the case, options for mitigation should be identified. It would be preferable for this to be done either before, or as part of, the 2008 review.
Whole effluent effects assessments (Section 3.5)			
Area	*Possible significant unmanaged effects*	*Possible effects that may warrant closer investigation*	*Recommendation*
General	Toxicity of Lake Waipapa sediments to benthic invertebrates	As above: capacity of the Kinleith plume to cause flocculation of a some Waikato River iron and associated arsenic adsorption.	As above
General	None identified	Potential for warm water plumes to encourage spread of pest fish at the expense of native species by providing a favourable habitat.	As part of 2008 review, a qualitative or quantitative assessment of this nature should be carried out by an appropriate specialist, to define the potential magnitude of such an effect when considered in the wider context of the Waikato River system.
Human uses and exposure to contaminants (Section 3.6)			
Area	*Possible significant unmanaged effects*	*Possible effects that may warrant closer investigation*	*Recommendation*
Dioxins in fish flesh	None identified	None identified	Future risk assessments on this topic (2008, 2015) need to make use of the Ministry of Health IMMI and WHO-TEFs, or whatever is current at that time.

4.2 Air

Overall, consent conditions relating to the air discharge from the Kinleith mill appear appropriate and sufficient to manage most of the potential adverse effects of air discharges. A summary of findings relating to potential adverse effects and associated recommendations is provided in **Table 10**.

Table 10 Possible unmanaged effects relating to the Kinleith mill discharges to air, and associated recommendations.

Air quality (Section 3.7)			
Area	*Possible significant unmanaged effects*	*Possible effects that may warrant closer investigation*	*Recommendation*
Accidental release of hazardous gas	None identified	The risk assessment and emergency response procedures may possibly be outdated in light of the recent accidental ClO_2 release and international experience.	A review of risk assessment and emergency response is currently in preparation by URS. It is recommended that this review recognises international experience and adopts similar responses as appropriate.
Resource consent conditions - discharge limits	None identified	As part of the consent condition that requires continual improvements, discharge limits should be guided by international trends and best practice as appropriate.	Unless monitoring results demand more immediate effects-based action (following Conditions 39-41), it is recommended that Kinleith discharge limits be reviewed in 2008 (Condition 42), with consideration of international limits at the time.
Dioxin emissions	None identified	May need to reduce PCDD and PCDF emissions to align with national strategy to meet requirements of Stockholm Convention on POPs.	A review of dioxin and furan emissions should be considered in 2006, to align with a national implementation plan scheduled for release by MfE at that time.
Odour	None identified	TRS emissions have been substantially reduced in recent years, however this may not be linearly related to effects on community.	Continue monitoring effects on community and upgrade operations as appropriate, with aim to reduce to minimum practical effects (Condition 1).
Worker health	None identified	Incidence of non-fatal respiratory illness.	Industry may choose to commission their own investigation.

5 Recommendations

5.1 Water

Six recommendations relating to various aspects of the Kinleith mill wastewater discharge are made in **Table 9**. Of these, three could (or will be) accommodated as part of future work, in particular the 2008 review. The remaining recommendations are that:

- A desk-top review is undertaken to investigate the potential for Kinleith mill's secondary treatment ponds to act as a seeding population for blue-green algal blooms in the Waikato River downstream. This is based on the finding by Kirkwood [27] that pulp and paper waste treatment ponds can contain unexpectedly high populations of cyanobacteria, as reported in 2001.

- A review is undertaken to identify factors leading to fluctuations of resin acids in the wastewater stream, with a focus on establishing a robust sampling and analytical protocol and identifying means of minimising real loadings (and toxicity) as far as practicable.

- Research is initiated to investigate the levels and significance of arsenic in sediments of Lake Waipapa, factors leading to high concentrations of iron, manganese and arsenic in these sediments, and whether or not the Kinleith wastewater discharge is likely to be contributing to this process by causing a small proportion of Waikato River iron to flocculate and settle. This is based on a reconsideration of previous evidence, and would account for a number of observations that are otherwise difficult to explain (**Table 5**). If such a mechanism is operative, the focus could move to options for future management, such as reductions expected in the arsenic output of Wairakei Power Station, and closer matching of the Kinleith mill wastewater pH with that of the Waikato River.

5.2 Air

Four recommendations relating to various aspects of the Kinleith mill discharges to air are made in **Table 10**. Two of these recommendations will be accommodated as part of the 2008 review of consent conditions.

The most immediate attention is required toward the assessment of risk and emergency response to catastrophic chlorine dioxide (ClO_2) gas release. Some recommendations are offered to guide the URS review that is currently in preparation.

The other issue that may require attention is a review of dioxin emissions, depending on how current emissions align with MfE implementation plan to meet requirements of the Stockholm Convention. A review is recommended following MfE's release of the final plan in 2006.

6 Appendices

6.1 Documents relating to prior evidence and consent assessment

1. Stuthridge TR, **1991**. The fate and impact of forest industry discharges to the Waikato River: bibliography of publications on the Upper Waikato River. Forest Research Institute.

2. NZFP Pulp & Paper Ltd., **1994**. Air discharge permit. Application and Assessment of Environmental Effects. Document prepared in support of application for air-related resource consents.

3. Mills GN, **1995**. The Upper Waikato River Study: an overview and summary. National Institute of Water and Atmospheric Research Ltd. (NIWA) consultancy report SCJ129/05. Prepared for Environment Waikato (Document 15958).

4. Carter Holt Harvey Ltd., **1996**. Water Related Resource Consents for the Kinleith Mill. Assessment of Environmental Effects document prepared in support of application for water related resource consents.

5. Carter Holt Harvey Pulp & Paper Ltd., **1996**. Additional information in relation to the air discharge permit application.

6. Woodward-Clyde (NZ) Ltd., **1997**. Audit of Assessment of Environmental Effects – discharges to air. Prepared for Environment Waikato.

7. Timperley M, **1998**. Audit of Assessment of Environmental Effects - Water Related Resource Consents for the Kinleith Mill. This is an independent review of the AEE carried out by an expert from the National Institute of Water and Atmospheric Research Ltd. (NIWA).

8. Waikato Regional Council, **1998**. Staff report and associated evidence for the Carter Holt Harvey (Pulp and Paper) Kinleith Mill Complex Hearing. This is a multi-authored document containing summary information and expert opinion evidence from a number of parties. Those of greatest relevance to this review are as follows.

   (a) David Stagg, Programme Manager, Waikato Regional Council. Applications for activities and processes associated with: the production of pulp and paper at the Kinleith Mill, and adjacent activities (Waikato Regional Council staff report to Chairman and Members of the Hearing Committee).

   (b) Evidence of William N Vant, Water Quality Scientist, Waikato Regional Council; relating to potential effects of nutrients in the discharge.

   (c) Evidence of John C Hadfield, Hydrogeologist, Waikato Regional Council; relating to groundwater aspects.

   (d) Evidence, supplementary evidence, and additional supplementary evidence of Michael Timperley, Senior Scientists with the National Institute of Water and Atmospheric Research Ltd. (NIWA); relating to proposed consent conditions.

9. Carter Holt Harvey Limited, **1998**. Evidence in relation to the water resource consent applications for the Kinleith complex. This is a substantial document originally intended for use at Environment Court, containing briefs of evidence from the following parties:

   (a) Kent Blumberg, Chief Executive of Carter Holt Harvey's Pulp & Paper Business Group. Most relevant area of expertise: Carter Holt Harvey's environmental policy.

   (b) James C Newfield, Manager – Technology, Carter Holt Harvey Pulp & Paper. Most relevant area of expertise: overview of water-related activities at the Kinleith mill.

   (c) Lorraine Marsh, Manager – Environmental Systems, Carter Holt Harvey Pulp & Paper. Relevant areas of expertise: nature and characteristics of the Kinleith waterwater treatment systems, environmental research and compliance monitoring.

   (d) Leslie R Galloway, Pulp & Paper industry engineering expert, HA Simons Ltd., Vancouver, Canada. Relevant areas of expertise: relative performance of the Kinleith Mill in terms of wastewater quality, effects on modernisation projects on environmental performance, options to improve performance and their feasibility.

   (e) Garry J MacDonald, Director of Environmental Engineering, Beca Carter Hollings & Ferner (BCHF) consulting engineers, Auckland. Most relevant area of expertise: treatment system options for reducing nutrient loadings.

   (f) J Christopher Rutherford, Research Scientist and Project Director with the National Institute of Water and Atmospheric Research Ltd. (NIWA). Relevant areas of expertise: mixing of water and contaminants in rivers and mathematical modelling of water quality, characteristics of the Kinleith wastewater plume in summer and winter.

   (g) Robert J Davies-Colley, Senior Scientist with the National Institute of Water and Atmospheric Research Ltd. (NIWA). Most relevant areas of expertise: optical water quality (visual clarity, light penetration, hue and brightness), and monitoring of these features for the Kinleith plume.

   (h) Trevor R Stuthridge, Research Scientist and Project Leader, Waste Management Opportunities, Forest Research. Most relevant areas of expertise: origin and characteristics of trace organic contaminants in Pulp & Paper wastewaters, Kinleith treatment system efficiency for these constituents, and environmental significance of trace organic contaminants in the Kinleith discharge.

   (i) Michael N Bates, Principal Scientist, Epidemiology Group, Institute of Environmental Science and Research Ltd. (ESR). Relevant area of expertise: toxicology, human exposure and risk assessment. (Evidence comprises an exposure and risk assessment of dioxin intakes from consuming fish caught in Lake Maraetai and downstream.)

   (j) Paul C Kennedy, Director Kingett Mitchell & Associates Ltd. Relevant area of expertise (for the wastewater discharge consent): results of monitoring undertaken to assess effects of the Kinleith discharge on water quality, sediment quality, fish quality, and uses of the river.

   (k) Jacques AT Boubee, Research Scientist with the National Institute of Water and Atmospheric Research Ltd. (NIWA). Most relevant area of expertise (for the wastewater discharge consent): effects of environmental disturbances on the health of freshwater ecosystems (flora, macro-invertebrates and fish).

   (l) Neil A Crampton, Senior Engineering Geologist, Pattle Delamore Partners Ltd. Area of expertise: geology and groundwater systems in the Kinleith – Tokoroa area. Impacts of the groundwater take and discharge to groundwater.

   (m) Jack Mockford, Chairman of the Kinleith Resource Consents Consultative Group.

   (n) Diane Wayne, long term Tokoroa community member.

10. Waikato Regional Council, **2003**. Resource Consent Certificate for Discharge to Water. Main consent number 961348 (file number: 60 40 10C, Environment Waikato document 653304). Activity authorised: To discharge water and contaminants into water from activities and processes associated with the production of pulp and paper at the consent holder's Kinleith Pulp and Paper mill, and from adjacent activites, near State Highway 1. Ancillary consents authorising discharges from scour valves, stormwater, *etc.*: consents 961350, 961351, 961352 and 961353.

11. Waikato Regional Council, **2003**. Resource Consent Certificate for Discharge to Air. Consent number 940664 (file number: 60 40 10X, Environment Waikato document 551728). Activity authorised: To discharge contaminants into the air from processes associated with the production of pulp and paper at the consent holder's Kinleith Pulp and Paper mill, near State Highway 1, at or about map reference NZMS 260 T16: 626-213. Supplementary consent relating to co-gen plant: consent number 940536.

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Research area: discharge to water – chemical characterisation

12. Wilkins AL, Langdon AG and Wang Y, **1998**. Cation, anion, conductivity, and absorbance characteristics of Tarawera River seepage water entering the Western Drain, Eastern Bay of Plenty, New Zealand. *Bulletin of Environmental Contamination and Toxicolog*y, Vol. 61, No. 3, pp 339-346.

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14. Kanber SA, Wilkins AL and Langdon AG, **2000**. Speciation of pulp mill derived resin acids in the Tarawera River, New Zealand. *Bulletin of Environmental Contamination and Toxicolog*y, Vol. 64, No. 5, pp 622-629.

Research area: discharge to water – environmental health

15. Sharples AD and Evans CW, **1998**. Impact of pulp and paper mill effluent on water quality and fauna in a New Zealand hydro-electric lake. *New Zealand Journal of Marine and Freshwater Research*, Vol. 32 No. 1, pp 31-53.

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Thomas JF (Eds.), 2004. *Proceedings of the 5th International Conference on Fate and Effects of Pulp and Paper Mill Effluents*, Seattle, Washington, June 1-4, 2003.

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22. Landman MJ, Ling N and van den Heuvel MR, **2004**. Pulp and Paper Effluent Hypoxia Interactions in Fish. In, Borton DL, Hall TJ, Fisher RP and Thomas JF (Eds.), 2004. *Proceedings of the 5th International Conference on Fate and Effects of Pulp and Paper Mill Effluents*, Seattle, Washington, June 1-4, 2003.

23. van den Heuvel MR, Ellis RJ, Smith MA, Finley M, Stuthridge TR, Bandelj E, Mccarthy I and Donald R, **2004**. Review of reproductive-endocrine effects of a New Zealand Pulp and Paper mill effluent. In, Borton DL, Hall TJ, Fisher RP and Thomas JF (Eds.), 2004. *Proceedings of the 5th International Conference on Fate and Effects of Pulp and Paper Mill Effluents*, Seattle, Washington, June 1-4, 2003.

24. Ellis RJ, van den Heuvel MR, Smith MA and Ling N, **2005**. Effects of maternal versus direct exposure to pulp and paper mill effluent on rainbow trout early life stages. *Journal of Toxicology and Environmental Health, Part A*, Vol. 68, No. 5, pp 369-387.

Research area: waste treatment efficiency or waste reduction[48]

25. Hunter R and Slade A, **1999**. Operation of an ASB wastewater treatment system treating kraft and newsprint wastewater without the addition of nutrients. *Proceedings - TAPPI International Environmental Conference*, Nashville, Apr. 18-21, 1999, 2693-701.

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Research area: discharges to air

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Research area: land disposal of pulp mill biosolids (discharges to soil)

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Research area: process and chemical engineering

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6.5 Estimated Flows in Kopakorahi Stream and Wastewater Dilution Volumes

For future reference or assistance in interpreting previous evidence, some estimates can be made of possible dilution in Kopakorahi Stream based on stream gauging carried out by Environment Waikato.

1. Estimates for the natural flow volumes of upper Kopakorahi Stream above the Puniu Stream (Kinleith discharge point)[49] are:
   - Mean Annual Low Flow: 0.4 m^3/s (34500 m^3/d)
   - Mean Flow 1 m^3/s (**86400 m^3/d**)
   - Mean Annual flood 8 m^3/s (690000 m^3/d)

2. Average daily discharge volumes in the period leading up to granting of the resource consent are given in **Table 2**, and were estimated as having reduced from 182000 m^3/d in Feb 1991 to about 90000 m^3/d by 1998. The average wastewater discharge volume is currently about **85000 m^3/day**.[50]

3. In one-off gaugings, flows at the culvert where Kopakorahi Stream becomes the Kopakorahi arm of Lake Maraetai were measured as 258000 m^3/d on 11 December 1987, and 217000 m^3/d on 22 April 2004.[18] Currently, the average flow measured by CHH at this point is reported as **202000 m^3/d**.[19] This average flow represents the sum of Kopakorahi Stream ($\geq$86000 m^3/d), wastewater (about 85000 m^3/d) and other flows such as the Waituna Stream (by difference, estimated as about 30600 m^3/d).

On the basis of these figures, it can be seen that:

1. On average the wastewater is now diluted by a factor of **2.0** as it enters the Kopakorahi Stream, and has become diluted by a factor of **2.4** by the time it reaches the Kopakorahi arm of Lake Maraetai.

2. Under low stream flow conditions, and assuming the wastewater volume remained constant, the wastewater would be diluted by a factor of **1.4** as it enters the Kopakorahi Stream, and have been diluted by a factor of **1.6** by the time it reaches the Kopakorahi arm of Lake Maraetai.

3. Previous data for average resin acid concentrations were for the point the Kopakorahi stream enters the Kopakorahi arm of Lake Maraetai, and were at a higher relative wastewater flow, estimated as 124000 m^3/d. Under these conditions, total volume is estimated as 241000 m^3/d and the dilution factors as 1.7 (discharge point) and 1.9 (Kopakorahi arm entry point). The ratio of these two figures (1.12) can be used to estimate resin acid concentrations in Kopakorahi stream at the time earlier data was collected.

In previous evidence, Timperley [7, p 8] noted that the natural water flow of the Kopakorahi Stream was generally smaller than the wastewater volume, meaning that the water is fully mixed soon after the main discharge point to the stream.

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[49] Stewart D, **2004**. Environment Waikato. Personal Communication. Low flow estimates are based on correlation of gauging data with data from recorder sites; mean and flood flow estimates made by average of specific discharges.

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6.6 Compilation of Reported Concentrations of Trace Organic Compounds at the Point where Kopakorahi Stream Enters the Arm of Lake Maraetai (site K2).[a, b]

Compound class	Sampling date and concentrations reported (µg/L)									
	1994-1995[c]	Dec-01	Jun-02	Dec-02	Jun-03	Dec-03	Jun-04	Dec-04	Jun-05	Dec-05
Total resin acids	17.3	91.33	41.37	234.25	-	0.08	648.05	107.26	730.2	111.11
Dehydroabietic acid (DHA)	-	14.49	7.74	36.77	-	0.02	40.54	6.5	4.78	14.72
Resin acid neutrals	-	nd[d]	nd	nd	-	nd	nd	nd	nd	nd
Fatty acids	61.2	4.98	14.24	48.52	-	0.06	80.1	7.58	18.94	27.75
Phytosterols	-	10.09	16.37	nd	-	0.04	59.38	nd	nd	33.89
Monoterpenes	-	nd	nd	nd	-	nd	nd	nd	nd	nd
Phenolics	<2	0.33	nd	nd	-	nd	0.73	nd	nd	0.35
Total chloro-catechols	15	nd	nd	nd	-	-	-	-	-	-
Total chloro-guaiacols	84	nd	nd	nd	-	-	-	-	-	-
Total chloro-phenols	80	nd	nd	nd	-	-	-	-	-	-
Total chlorinated phenolics	-	3.12	0.22	0.04	-	-	-	-	-	-

Notes:
[a] All reported data for sites E1, E2 and K2, including data for all resin acids, is compiled in Environment Waikato document 1033009.
[b] Data is reported here to three significant figures.
[c] 1994-1995 values are from the AEE [4, p 93] and prior evidence [9h], and are the average values cited. Additional data given in these documents includes medians, minima and maxima.
[d] The notation 'nd' denotes that the compounds were not detected. The notation '-' denotes that test results are not available.