ARSENIC IN THE WAIKATO RIVER AN UPDATE

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SUMMARY Regional council monitoring data for the period 1995-1999, and new data for dissolved and acid-soluble **As** concentrations and for *As* bound to suspended particulate matter (SPM), have been used to clarify some unresolved aspects of **As** behaviour in the Waikato River system. A higher load of (total recoverable) *As* was consistently carried in the summer months of each year between 1995 and 1999. Dissolved **As** accounted for 73 -100% of all *As* carried in the water column. The degree of *As* adsorption on SPM was unaffected by temperature but influenced by the biological component of the SPM, specifically the presence of certain diatom species. The degree of **As** adsorption on SPM did not change significantly in the estuary, with **As** behaving conservatively in this zone.

1. INTRODUCTION

The Waikato River is New Zealand's longest and most utilised river, and includes within its catchment a large area of natural geothermal activity and several geothermal power stations. **It** has previously been estimated that the upper part of the river receives 224 t/yr of geothermal As (Aggett and Aspell, 1978). Mass flux calculations for the catchment (Timperley and Huser, 1996) confirmed the waste bore water from Wairakei Power Station as the largest single source of *As* in the river, but the contribution from this source has decreased from 156 t/yr to closer to 70 t/yr over the last 5 years (L. Bacon, pers. comm.).

Arsenic in untreated Waikato River water typically ranges from 0.02 to 0.06mg/kg (e.g. McLaren and Kim, 1995), exceeding the WHO (1993) recommended **As** guideline for drinking water of 0.01mg/kg. Significant progress has been, and is being, made in understanding the behaviour, toxicity and bioavailability of As in this river system (e.g. Aggett, 1988; McLaren and Kim, 1995; Timperley and Huser, 1996). The purpose of this paper is to report specifically on investigations into three aspects of **As** behaviour:

i) Seasonal variability in **As** concentrations, as reported for 1993/94 by McLaren and Kim (1995)

ii) Seasonal variability in the degree of **As** binding to suspended particulate material (SPM) in the water column.

iii) The behaviour of **As** in the estuary, as it has generally been assumed that all *As* transported by the Waikato River is carried out into the Tasman Sea (Aggett, 1988).

The paper draws on both Environment Waikato monitoring data for the period 1995-1999, and the authors' data collected for **As** in the water column, bed sediment and suspended particulate matter **(SPM)** over the 1998-2000period.

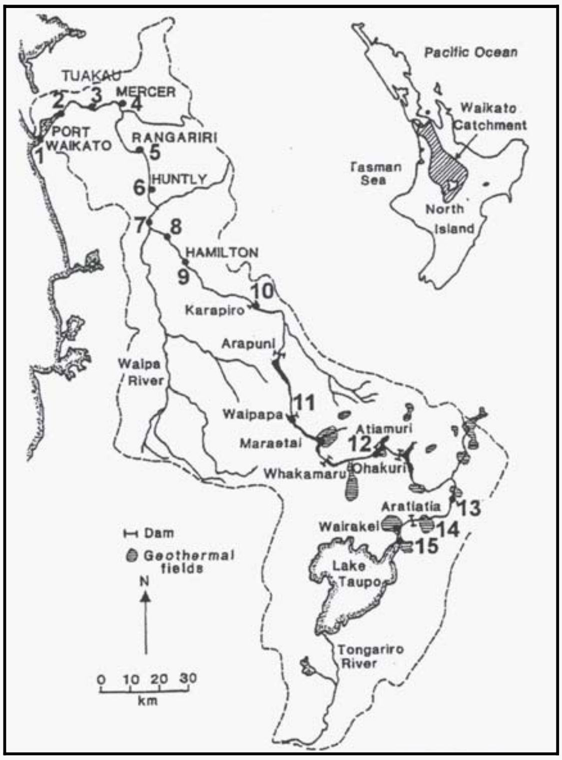

Figure 1. Waikato River 1998/1999 monitoring site localities (base map modified after Timperley and Huser, 1996)

2. STUDY AREA AND METHODS

The locality of sampling sites is shown in Figure 1. To establish seasonal variability in **As** concentrations and the relationship to **flow** conditions, the results of water quality monthly monitoring undertaken at Lake Ohakuri (Site **12)** and Tuakau Bridge (Site **3)** by Environment Waikato have been used. This data was collected between 1995 – 1999 (Huser and Wilson, 1996,1997; Wilson et al., 1998; and unpublished data for 1998 and 1999), and methodology for sampling and analysis is outlined in the monitoring reports. All results in Environment

Waikato's reports are given as "total recoverable" As concentrations.

To determine whether there was seasonal variability in the degree of adsorption of **As** on SPM carried in the water column, dissolved As concentrations, acid-soluble As concentrations, and the As content of SPM were determined in late spring/summer (Nov. 1998) and winter (July 1999) surveys at the 13 freshwater sites (sites **3 –** 15) along the river (Figure 1). "Dissolved" **As** is defined as that portion of the As which passes through a 0.45µm membrane filter, and "acid-soluble" As as the As analysed in an unfiltered water sample acidified to pH 2. Monthly surveys of these parameters were also undertaken at Tuakau bridge (Site 3) between Nov. 1998 and Nov. 1999. Arsenic concentrations were measured using HGAAS, with a detection limit of 0.1µg/kg. SPM was collected on 0.45µm filter membranes, dried, weighed and digested in hot conc. HNO_3 prior to analysis for As by **ICP-mass** spectrometry. Field blanks were also analysed (below detection) and SPM digests corrected for blank filter membrane digests. The distribution co-efficient for **As** between the **SPM** and dissolved phase **has** been calculated as: $K_D = [As_{SPM}]/[As_{diss}]$.

The degree of As adsorption onto freeze-dried summer (January) and winter (July) SPM, as well as SPM collected during an algal bloom in April, was determined as a function of pH in a media of 0.01m $NaNO_3$. Laboratory batch experiments were undertaken under temperature controlled conditions, and pH was adjusted using HNO_3 and NaOH. Batches remained on an end-over-end mixer for 24hrs, before filtration through 0.45 µm and analysis for dissolved **As** by **HGAAS.**

To determine whether the degree of As adsorption onto SPM changes in the estuary, water and SPM samples were collected and analysed from the lower reaches of the river (downstream from site 3). Also, seawater from Piha Beach, just to the north of Port Waikato (1-2µg/kg As) was progressively added to unfiltered river water collected at Mercer (site 4). After 20min stirring, a 10ml aliquot was extracted and filtered through a 0.45µm membrane, and dissolved As measured.

3. SEASONAL VARIABILITY IN ARSENIC

3.1 Seasonal trends: 1995-1999

Over the last 5 years, Environment Waikato's monthly monitoring data has shown a clear and consistent seasonal trend for total recoverable As concentrations at Tuakau Bridge (Figure 2a). The As monitoring data shows broad maxima in the summer months, and minima in the winter months. Arsenic concentrations and water temperature at Tuakau showed a higher degree of correlation (R^2 = 0.5) than in the upper reaches at Lake Ohakuri where the **As** concentrations are higher (R^2 = 0.04). This suggests that sudden, short term fluctuations in As concentrations are more common in the upper reaches of the river.

3.2 Arsenic: Lithium

To eliminate fluctuations in As concentration relating to changes in river or bore water flow, As concentrations were normalised to the concentrations of Li. Lithium can be used as a conservative tracer, originating from the same source as **As**, as it is not readily removed from the water column and exists predominantly in dissolved form. The linear relationship between As and Li in the river water previously established by McLaren and Kim (1995), was confirmed using Tuakau and Lake Ohakuri monitoring data for 1995-1999 (R^2 = 0.84 for concentrations of up to 0.04 mgkg As and 0.14 mg/kg Li).

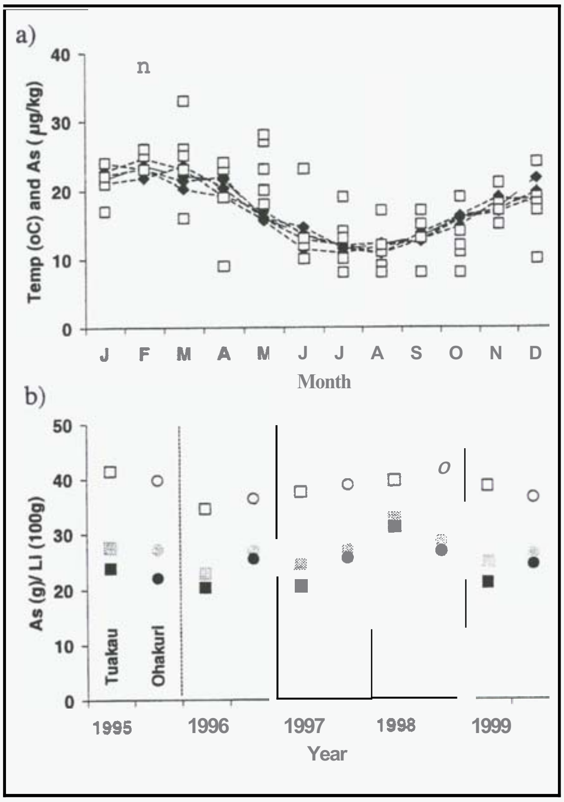

Figure 2. a) Monthly monitoring data for **As** (☐) and water temperature (+) at Tuakau Bridge for 5 years (1995 to 1999), b) Mean As/Li ratios at Tuakau (▨) and Lake Ohakuri (◍), for summer (January-March, open symbols), winter (June-August, black symbols) and the annual mean (grey symbols).

When normalised to Li concentrations, the seasonal trends in **As** concentrations remain evident (Figure 2b), with the mean of the summer months (January – March) significantly higher than the annual mean or mean of the winter months (June – August). Notably, neither the annual mean **As** concentrations nor As/Li ratios showed a consistent trend with time between 1995 and 1999.

McLaren and Kim (1995) suggested that the seasonal trend identified in 1993/94 was due to desorption of *As* from sediments during summer months, either as a direct effect of temperature on the adsorption process, or as an indirect effect of temperature influencing physiochemical or biological conditions. Evidence for a direct temperature affect on As adsorption is currently lacking (refer following section and Figure 5b). Potential indirect temperature effects include the influence of water temperature on As^V/As^{III} redox reactions. Although **As** enters the Waikato River from the Wairakei borefield in the form of As^V (Finlayson and Webster, 1989; Polya et al, 1998), high concentrations of $\mathbf{As^{III}}$ have often been measured in the river waters (Aggett, 1988; McLaren and Kim, 1995; Polya et al., 1998). As^{III} is less readily adsorbed onto the oxide surfaces in bed sediments and SPM than As^V (Swedlund and Webster, 1999). It is unlikely that a temperature increase of ~10°C could **significantly** increase the abiotic reduction of As^V. **However,** Freeman (1985) isolated a bacteria from the Waikato River ***(Anabaena oscillaroides)*** which was capable of reducing As^V to As^{III}, and noted that bacterial activity was higher in summer.

Release of **As** from the anoxic layers of a stratified lake during turnover, as noted for Lake Ohakuri (Aggett and Kreigman, 1988), could contribute to the summer **As** load. However, it is difficult to reconcile such short-term, erratic fluctuations in **As** concentration with the regular, broad summer maxima observed in Figure 2a.

4. ARSENIC BINDING TO SPM

Dissolved and acid-soluble **As** concentrations were measured at all sites in November 1998 and July 1999, and monthly at **Tuakau** Bridge.

Dissolved **As** predominates, constituting between **73%** and 100% of the **As** carried in the water column. Concentrations ranged between 0.010 and 0.025mg/kg dissolved *As,* for all sites except for below Lake Ohakuri (site 12) and at **Ohaaki** (site 13), when sampled in winter. In July, these sites in the centre of the geothermally active area registered 0.029 and 0.037mg/kg dissolved As respectively.

SPM **As** concentrations mainly ranged from 61 – 271 mgkg As, but were again significantly higher below Lake Ohakuri and at Ohaaki. In July, for example, SPM at sites 12 and 13 contained **1550** and 1790mg/kg *As* respectively.

In monthly monitoring (Nov. 1998 to Nov. 1999) at Tuakau bridge, the same seasonal variation in **As** concentrations noted in the Environment Waikato monitoring data **was** evident, with a **maximum** of 0.029 mgkg dissolved **As** in February, and a minimum of 0.006 mg/kg in July.

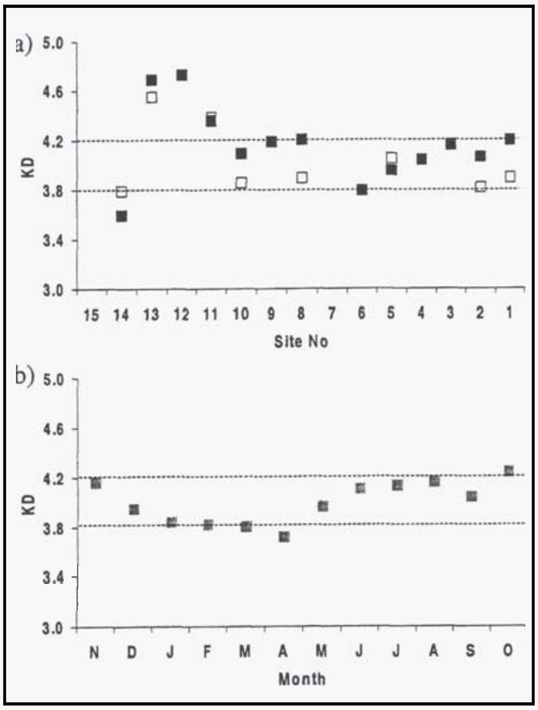

Figure 3. K_D in the Waikato River as a function of distance from Lake Taupo (a) and for monthly monitoring at **Tuakau** bridge (b).

SPM **As** content at Tuakau did not show a clear seasonal trend, but instead had distinct minima in the March/April and July/August periods. SPM **As** concentrations ranged from 61 mg/kg **As** (July) to 239 mg/kg As (May).

4.1 K_D in the Waikato River

A distribution coefficient, K_D, is used to relate SPM ***As*** content to dissolved As concentrations in the water column. K_D values calculated for each sample site along the Waikato River (Figure 3a) were similar for the Nov. and July sampling periods, falling within the range of K_D = **3.8** – 4.2 for most sites. However, K_D values at sites 12 and 13 were significantly higher, indicating a higher degree **of As-SPM** association in this stretch of the river. $\mathbf{K_D}$ variation in monthly samples collected at Tuakau bridge (Figure 3b) did not appear to be strictly related to temperature, but instead showed a broad minimum over the period **January** – April.

4.2 The nature of the SPM

The characteristics of the SPM which affect its ability to adsorb ***As*** include mineralogy, particularly that of oxide phases, organic content, and particle size and surface area. Specific characteristics likely to be influencing K_D in key SPM samples are summarised in Table 1. Neither MnO_2 nor surface area appeared to correlate with SPM **As** content. However, the As-rich SPM in the upper river (site 11 and above) had a higher SiO_2 content than at Tuakau, and a higher TOC. **SEM** confirmed that the sample **was** composed almost entirely of diatoms, predominantly

Fragilaria capucina. The higher As content of this SPM may be due to adsorption or uptake by these silica-based microalgae. Downstream of Lake Waipapa, the SPM had less SiO_2 and TOC, and correspondingly lower K_D values.

The period of lowest K_D at Tuakau bridge (January – April) corresponded to a time when the SPM had a relatively low Fe-oxide and high TOC content. It also corresponded to the period of highest chlorophyll-a measurements in the water column (a mean of 0.035μg/kg, compared with the June-Nov. mean of 0.008μg/kg), and an abundance of diatoms as observed by SEM (Figure 4). Algal blooms of Asterionella spp. (January) and *Melosira* spp. (April and May) were particularly evident. In and after July, however, the SPM was predominantly comprised of inorganic particulate material?with few diatoms in evidence.

Table 1. Chemical characterisation of Waikato River SPM, with Fe analysis by AAS (recalculated as wt% Fe_2O_3), wt% SiO_2 by XRF, and wt% TOC by CHN analyser. SSA (specific surface area: m^2/g) was measured by p-nitrophenol adsorption (Theng et al., 1995).

Site	Fe_2O_3	TOC	Si02	MnO_2	SSA
11'	6.46	9.7	86.9	0.71	
8'	4.60	8.1	65.9	0.44	29
5^1	8.09	5.5	60.3	0.25	
3'	6.86	7.0	62.6	0.34	49
2'	6.08	2.2	59.0	0.29	
3^2	6.23	8.4		0.42	36
3^3	3.80	7.3		0.44	54
3^4	8.97	4.3		0.17	
3^5	9.78	5.0		0.22	72

'November, 'January, [3]April, [4]July, [5]September.

4.3 Experimental adsorption of arsenic

The degree of As adsorption onto three SPM samples from Tuakau Bridge was experimentally determined. Freeze-dried SPM from January (summer conditions, *Astrionella* bloom), April (autumn conditions, *Melosira* bloom) and July (winter conditions, mainly inorganic SPM), was resuspended at a concentration of 100mg/kg, approximately 10 times that of the Waikato River.

The As concentrations were also ~ 10 times higher than in the river (0.1 to 1.0mg/kg), to maintain a similar As:SPM to the river water. Arsenic adsorption as a function of pH, onto SPM collected in January, April and July is shown in Figure 5a. For all surfaces, maximum adsorption occurred at low pH (pH 3-4) as is expected for anion adsorption onto oxide surfaces (Dzombak and Morel, 1990). Arsenic adsorption onto SPM collected in July was the highest (24% at pH 6.7), followed by July SPM (13%), and then April SPM collected during the *Melosira* algal bloom (5.4%).

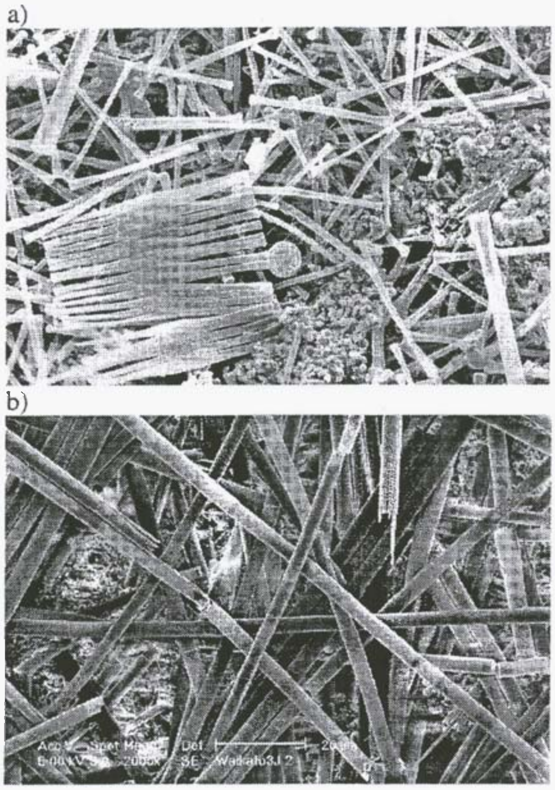

Figure 4. SEM images of SPM collected on a 0.45μm membrane in: a) January, when the predominant diatoms are *Asterionella formosa* (spindles ~100μm long) and *Fragilaria capucina* (frayed flat tapes ~150μm wide), and b) April when the predominant diatom is *Melosira granulata* (strands of ~5μm wide). The finer grained matrix is inorganic SPM and diatom fragments.

Adsorption edges were also measured over a temperature range of 5-35°C on July SPM (Figure 5b). Even over a 30°C temperature interval, As adsorption did not appear to be significantly affected.

Notably adsorption at higher As concentrations (0.5 and 1.0mg/kg; not shown) indicated that a maximum adsorption density of 1,500-1,800 mgAs/kg SPM occurs under favourable pH conditions. This maximum adsorption density is very similar to that measured in SPM below Lake Ohakuri and at Ohaaki (sites 12 and 13).

Therefore, both *in situ* data for the Waikato River and experimental results suggest that As adsorption onto SPM was not directly influenced by water temperature. This was evident in the similar K_D values for the winter and summer surveys, and in the adsorption edges at 5 – 35°C. Arsenic adsorption was, however, affected by the presence of microalgae; enhanced in the presence of abundant Si-rich diatoms downstream of geothermal inputs, but inhibited by the growth of *Astrionella* and *Melosira* spp. in the lower river in summer and autumn.

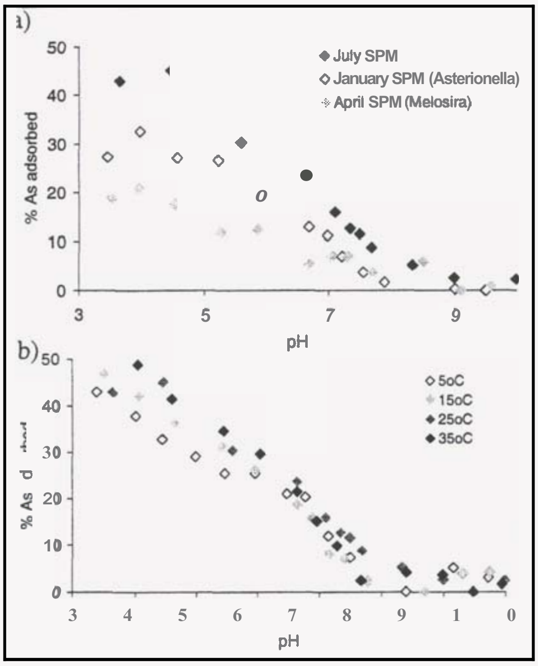

Figure 5. Arsenic adsorption onto SPM as a function of pH at 25°C (a) and at a range of temperatures (b). Dissolved As concentration = 0.1mg/kg and SPM concentration = 100mg/kg.

5. ARSENIC IN THE ESTUARY

Major chemical, physical and biological changes occur within a freshwater/seawater mixing zone of an estuary. One of the most important of these, from a metal transport perspective, is the flocculation and settlement of fine colloidal SPM under conditions of increasing salinity. Metals with a strong affinity for SPM tend to accumulate in estuarine sediments as a result of this process. Previous studies of As behaviour in overseas estuaries mainly support conservative behaviour, i.e. little or no change in the dissolved As load during estuarine mixing (e.g. Andreae et al., 1983). However, increased adsorption of arsenic onto hydrous iron oxide or organic particulate matter in the low salinity estuarine zone has also been proposed (Van der Shoot et al., 1985).

5.1 Dissolved As and K_D

Dissolved As concentrations were measured in water samples collected along a transect between Mercer bridge and the Port Waikato jetty. The results are plotted as a function of conductivity in Figure 6a. Dissolved As values were close to those expected for conservative mixing of As-bearing river water and seawater, indicating that As was not being adsorbed or otherwise removed from solution in the estuary. A further 11 water samples were collected at and between sites 1 and 2, under a range of tidal conditions, and analysed for dissolved and SPM As. Estuarine K_D values remained within the range of values (3.8 – 4.2) observed at and above site 3 (Figure 6b).

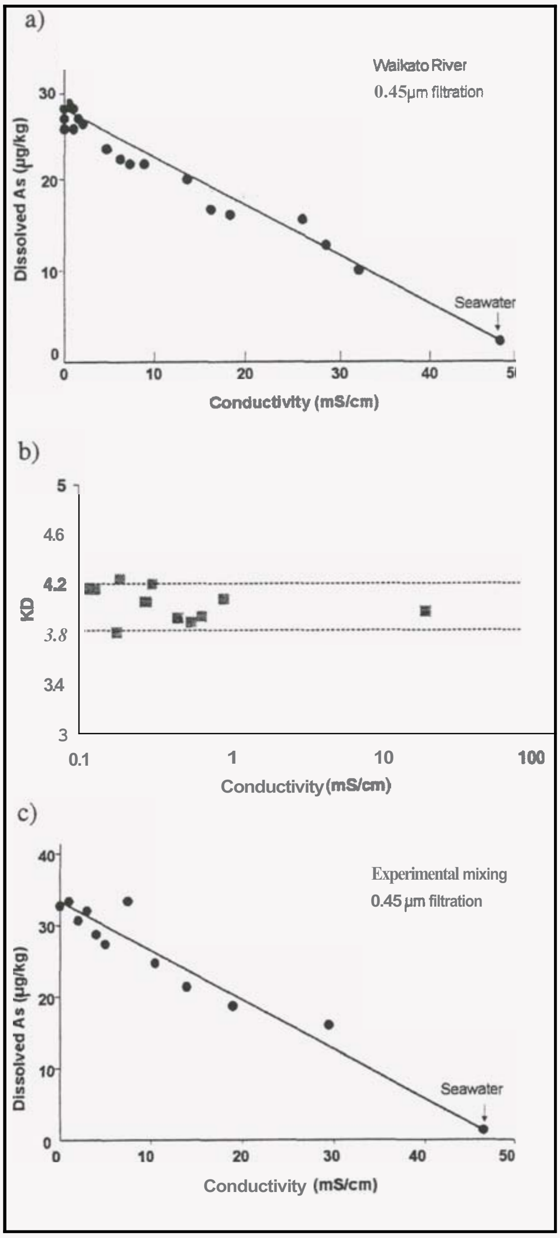

Figure 6. a) Dissolved As concentrations in the Waikato River between Mercer and Port Waikato, b) K_D in the lower Waikato River, and c) experimental simulation of estuarine conditions by mixing unfiltered river water and seawater.

5.2 Simulated estuarine mixing

Unfiltered river water containing 0.033mg/kg As was collected at Mercer Bridge, and mixed with various quantities of unfiltered seawater as described previously. Dissolved As was then measured following filtration through 0.45µm membrane (Figure 6c). Conservative behaviour was once again evident. Recognizing the fact that 0.45µm is an arbitrary demarcation, and that the As described as "dissolved" may include As bound to fine colloidal SPM of <0.45µm size, the experimental mixing described above was repeated using 0.2µm and then 0.1µm membranes. Filtration through 0.2µm yielded similar results to those shown in Figure 6c. However, filtration through 0.1μm indicated a degree of dissolved **As** removal from solution. This suggests that a small proportion of the "dissolved" **As** is, in fact, bound to fine colloids (0.1-0.2μm) which may aggregate under more saline conditions.

6. CONCLUSIONS

i) Even allowing for variations in river and bore water flows, the Waikato River has carried a consistently higher **As** load in summer than in winter, for the past *5* years.

ii) Arsenic was predominantly carried in dissolved form (i.e. <0.45μm).

iii) The seasonal variation in **As** load did not appear to be a result of temperature directly affecting As adsorption processes.

iv) Arsenic adsorption onto SPM appeared to be sensitive to the presence of specific microalgae. Adsorption was inhibited in the presence of ***Astrionella*** and ***Melosira*** spp., but may have been enhanced in the presence of other Si-based microalgae present in the geothermally active area of the catchment.

v) Arsenic behaved conservatively in the Waikato River estuary and is unlikely to have been significantly removed from the water column before entering the Tasman Sea.

7. ACKNOWLEDGEMENTS

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