

Environmental risk assessment of CCA leaching from treated vineyard posts

Vogeler I, Green S, Greven M, Robinson B, van den Dijssel C, Clothier B

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Report to Marlborough District Council

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Vogeler I, Green S, van den Dijssel C, Clothier B

HortResearch Palmerston North

Tennent Drive, Private Bag 11030

PALMERSTON NORTH, NZ

Tel: +64-6-356 8080

Fax: +64-6-354 6731

Greven M

HortResearch Blenheim

85 Budge Street, PO Box 845

BLLENHEIM, NZ

Tel: +64-3-577 0153

Fax: +64-3-577 2370

Robinson B

Institute of Terrestrial Ecology

ETHZ, Grabenstrasse 3

CH-8952 Schlieren

SWITZERLAND

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This report has been prepared by The Horticulture and Food Research Institute of New Zealand Ltd (HortResearch), which has its Head Office at 120 Mt Albert Rd, Mt Albert, AUCKLAND. This has been approved by:

Research Scientist

Date: 7 November 2005

Group Leader, Quality Systems

Date: 7 November 2005

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EXECUTIVE SUMMARY

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Report to Marlborough District Council

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- Marlborough District Council (MDC) requested that HortResearch carry out an assessment of fate of Copper-Chromium-Arsenic (CCA) from treated posts in vineyards. The study sought to:
 - Define the risk of CCA accumulation for the major soil groups west of State Highway 1 SH1, and to simulate CCA concentrations for 20, 100 and 500 years assuming 5% wastage.
 - Measure CCA leaching rates *in situ* for Rarangi soil and water table conditions.
- In our experiments at Rarangi, the initial results during the first six months of the experiment indicate that CCA is leaching out of the treated posts. Concentrations in the soils surrounding these posts already exceed, in some cases, the recommended guidelines for chromium (Cr) and arsenic (As) in agricultural soils in the National Environmental Protection Measures (NEPM, 1999) of 100 mg kg⁻¹.
- The CCA concentrations measured in the wood were quite variable, suggesting that more detailed sampling is needed.
- Modelling was performed on a per-post basis, and then spatially integrated to simulate a one-hectare field of 580 posts. Under the Rarangi shallow silt loam some 10% of the arsenic from the posts is predicted to leach below a depth of 1 m after a period of 30 years. At this depth, this equates to about 0.6 kg ha⁻¹ averaged spatially. The concentration of arsenic in the drainage water vertically entering the Rarangi Shallow Aquifer (RSA) would, after about 25 years, reach a spatially-based averaged As concentration of 0.01 mg L⁻¹, which is exactly the New Zealand Drinking Water Standard (NZDWS).
- Longer-term modelling, over 500 years, was also carried out, assuming a post lifetime of 20 years with replacement in the same hole. Soil differences are minimal for the long-term leaching predictions. The impact is largely determined by the amount of As lost from a post over its 20-year life, since the adsorptive capacity near the post becomes quenched, and so the As is eventually transported to depth. Across a range of soil types, the spatially averaged concentration of As in the leachate at 2 m would reach a steady-state value some 0.0125-0.0175 mg L⁻¹, which just exceeds the NZDWS. In soils with low adsorptive capacity, such as Rarangi, this steady level would be reached after about 100 years, but in soils with greater exchange capacity, such the Woodbourne soil, this would take about 300 years.

- The long-term simulations, with post-replacement, predicted that close to the post, and immediately under it, the concentration of As in the soil would after about 25 years meet, or exceed, the NEPM guideline values of 100 mg kg^{-1} . Differences are predicted between soils, and these reflect the soils' differing abilities to adsorb As. In the Woodbourne soil, the As concentration just under the post would eventually reach about six times the NEPM guideline value of 100 mg kg^{-1} , whereas for the Spring Creek soil this steady concentration would be two times the NEPM value, and at Rarangi the concentration in the soil underneath the post would be exactly the NEPM guideline value.
- These results of the long-term modelling were then used to determine the likely hydrogeological impact on the aquifer systems of the Wairau Valley. A simple mass-balance model of the aquifers was developed to predict the dilution by the laterally flowing water and thereby assess the probable long-term concentration of arsenic in the groundwater systems of the plains. From the steady-state spatially averaged value of As leaching to depth of some $0.0125\text{-}0.0175 \text{ mg L}^{-1}$, we could predict the distal concentration of As in subterranean water leaving the various aquifer systems. For the Wairau aquifer this would be 0.5 ppb, and for the Rarangi shallow aquifer 0.7 ppb; both more than an order of magnitude lower than the NZDWS. For the sluggish and distributed Southern Valley systems, the exiting concentration we predict to be 13 ppb, which is just above the NZDWS.
- In the long-term, the role of As leakage from the post over its lifetime of 20-25 years is critical. The movement of As is 40 times greater out the end-grain of the post's base, than it is through the wall of the post. The wall, nonetheless, has 20 times the surface area in the soil compared with the end-grain. Some means to limit this end-grain loss locally could be used to develop a sustainable solution. A preliminary calculation suggests that if the end-grain As-flux were zero, say by some form of capping, then the long-term, steady-state As concentration in the leachate would be halved. Further examination is merited.

For further information please contact:

Iris Vogeler or Brent Clothier
HortResearch Palmerston North
Private Bag 11 030, Palmerston North
Telephone: +64-6-350 8080
Email: ivogeler@hortresearch.co.nz
bclothier@hortresearch.co.nz

INTRODUCTION

In August 2002 the Marlborough District Council received a letter from the North Rarangi Water Supply Inc. noting the likely development of a vineyard, and voicing concern over the possible impact of Copper-Chromium-Arsenic (CCA) treated posts on the Rarangi Shallow Aquifer (RSA). This aquifer is relied on as a source of drinking water, and it is connected with receiving waters of the estuary and the sea.

Bourne (2003) expressed concern over the possibility of CCA timber treatment leaking from posts across the 10,000 ha of vineyards throughout the Marlborough region, New Zealand. Most vineyard posts are given an "H4" treatment that protects the wood against decay when in contact with soil. This results in a wood concentration of copper (Cu), chromium (Cr) and arsenic (As) of around 1730, 3040, 2710 mg kg⁻¹ respectively on a dry matter basis. Given a density of 579 posts per hectare, and an average post weight of 12 kg, each hectare of vineyard has a CCA loading of 12, 21 and 17 kg respectively. Anecdotal evidence indicates that the posts are replaced at a rate of 5% per year, indicating that if leaking from posts occurs, soil CCA contamination would be cumulative, given the general immobility of CCA in the soil. Copper is the most immobile component, followed by As and dichromate (Carey *et al.*, 1996a). However, dichromate [Cr(VI)] is generally reduced rapidly to Cr(III), which is less mobile and less toxic.

Recently, a general survey conducted by HortResearch (Robinson *et al.*, 2004) found elevated levels of copper, chromium and arsenic in soils surrounding vineyard posts in the Marlborough Region. Some 25% of the soils that were tested had levels of arsenic or chromium above the National Environmental Protection Measures (NEPM) of the Australian National Environmental Protection Council (ANEPCC) guidelines for agricultural soils (100 mg/kg). The study identified that the rate of CCA leaching is affected by the age of the post and the soil type. As expected, older posts tended to have higher CCA concentrations in the surrounding soil. Differences were identified between soil types, but because of the limited number of replicates, it was not possible to relate the degree of CCA leaching with any particular soil property or post age. Soil CCA concentrations decreased beyond a lateral distance of 50 mm and 100 mm beneath the post, but they were still significantly higher than the CCA concentrations in control soils taken from the inter-rows.

According to the US Environmental Protection Agency (EPA) "The amount and rate at which As leaches, however, varies considerably depending on numerous factors, such as local climate, acidity of rain and soil, age of the wood product, and how much CCA was applied." (US EPA, 2002). Soil conditions, especially pH, organic matter and clay contents, play an important role in leaching and movement of CCA (Carey *et al.*, 1996b; Hingston *et al.*, 2001).

The aim of this study was to determine the risk of CCA leaching from treated posts in Marlborough vineyards, with an especial focus on Rarangi and the RSA. Following on from the general survey, a lysimeter experiment was set up at Delegats' vineyard in the Rarangi district to determine the extent of any leaking of CCA from treated posts. In the Rarangi region, the risk of CCA leaching would seem to be enhanced as the soils are typically sandy gravels with low organic matter content, and the groundwater level periodically rises above the bottom of the posts. We have not considered the groundwater dynamics of the RSA, rather our predictions are for the vertical entry of leachate, spatially averaged across the vineyard, to groundwater at either 1 m or 2 m.

As well, soils from eight selected sites around Marlborough were sampled, and the adsorption isotherm for arsenic and the total carbon content from the soil was measured to parameterise HortResearch's Soil Plant Atmosphere System Model (SPASMO). This model was first used to calculate the likely environmental fate of CCA from treated posts in the Marlborough Region over the time-period of 32 years. Next, we carried out even longer-term modelling over 500 years considering the transport and fate of As and assuming a 5% post-replacement rate. So, on average, any given post would be replaced after 20 years.

INSTALLATION OF AN *IN SITU* CCA-LEACHING TRIAL

In 2004, Delegats set up a new vineyard in the Rarangi district. This gave us the opportunity to establish, at the same time, a leaching trial, under *in situ* conditions. The trial was initiated in November 2004. The location of the site is within a swale, so the soil at this site may have higher organic matter and clay contents than the neighbouring Taumutu soils (see orthophotographs below).



Aerial orthophotographs of the Rarangi region showing the site (red box) at Delegats where the experiments are being carried out.

METHODS AND MATERIALS

Thirty posts were driven into bare soil, away from any vines. Figure 1 shows the installation of the posts and lysimeters at Delegats. The pictures also show how shallow the groundwater is at the site. These posts are used to determine, by destructive sequential wood sampling, the rate and extent of CCA leaching. Another six posts were placed into lysimeters, three of them 80 cm deep, and the other three 120 cm deep. These depths mimic the very shallow and shallow water-table conditions of the RSA. Drainage from these lysimeters is collected regularly, and the concentrations of arsenic, copper and chromium in the drainage are measured. Figure 2 shows the trial setup and the lysimeters.



Figure 1. Installation of the posts and lysimeters at Delegats, Rarangi. The photos (top left) show the installation of the lysimeters, the nature of the shallow groundwater (top right), and the driving in of the other posts (bottom).

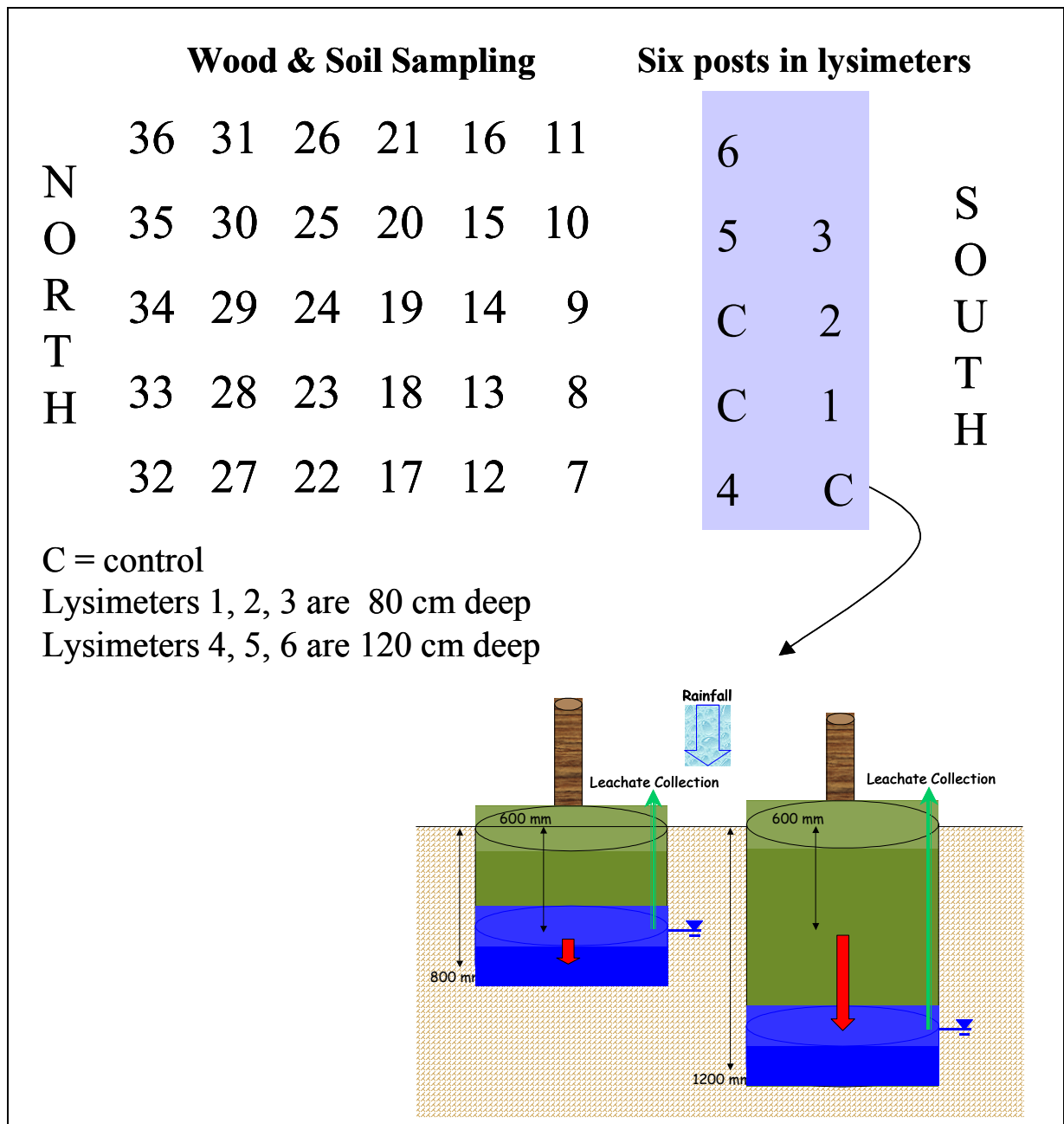


Figure 2. Experimental design at Delegats' vineyard. The setup of posts and lysimeters in the field at Rarangi. The two depths of lysimeters were chosen to mimic very shallow and shallow groundwater levels of the RSA.

To determine the rate and extent of CCA leaching from the posts, three posts were removed in April 2005, and the remaining posts will be removed in lots of three at time, over intervals of three months. To determine how much CCA is lost over time from the post, wood samples are taken from various positions of the posts (Figure 3). Approximately 20 g (dry weight) samples of wood are removed from these positions using a drill. To determine the extent of CCA movement in the soil, soil samples are taken around the posts. Figure 3 shows the sampling scheme for the soil surrounding the posts, and from the wood of the posts. The accumulated drainage from the lysimeters is collected every month, or after significant rainfall.

The samples are analysed at a commercial laboratory (Landcare Research, Palmerston North, New Zealand) for dry-weight determinations of Cu, Cr, and As using flame atomic-absorption for plants and soil, and Graphite Furnace Atomic Absorption for the drainage samples (GBC 908 instrument).

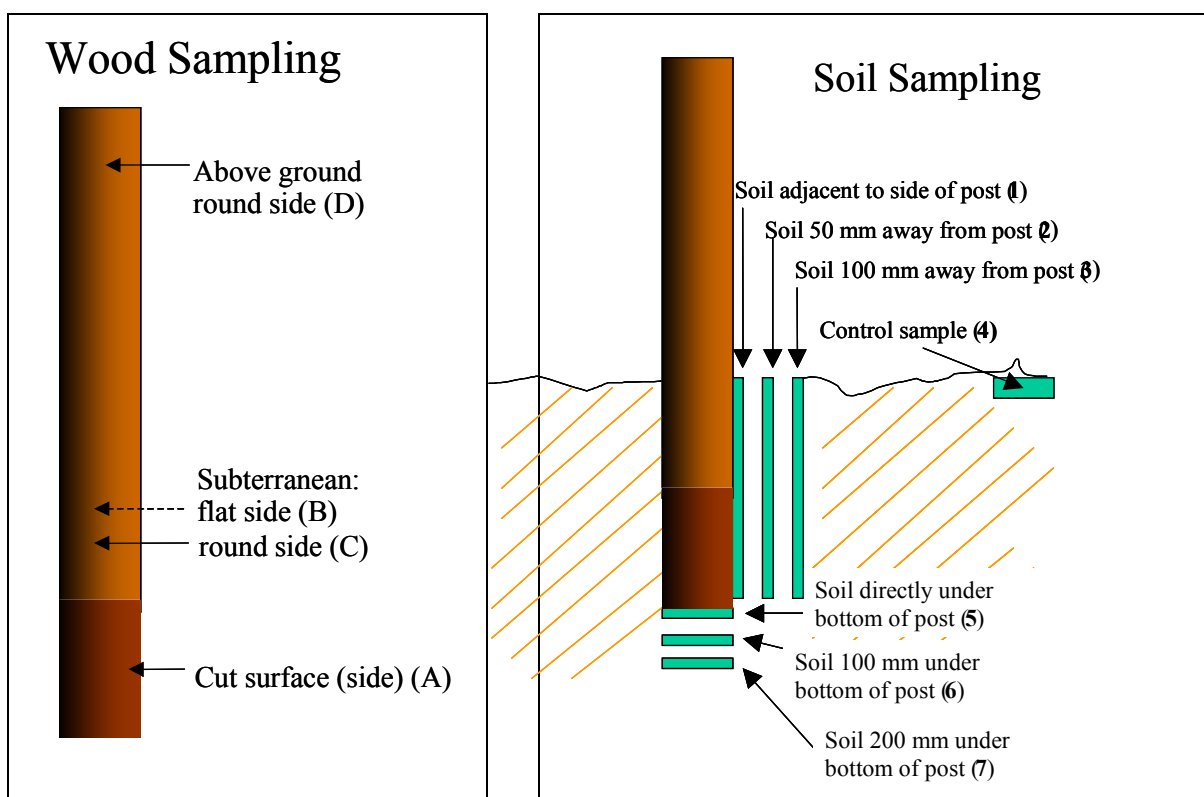


Figure 3. The sampling areas around each post.

CHARACTERISATION OF CCA ABSORPTION BY OTHER SOILS IN THE MARLBOROUGH REGION

Soil pH, organic matter and clay contents are of importance for the adsorption of CCA. Understanding the rate and extent of CCA adsorption by soil is essential in order to calculate the environmental fate of CCA. Thus, we measured the adsorption of CCA, and the total organic carbon content of various Marlborough soils from eight sites around the region (Figure 4). Soils were collected in three depth intervals up to about 30 cm depth. The adsorption isotherms for arsenic, which provide the distribution factor, K_D , were measured by batch studies by the Institute of Natural Resources, Massey University, Palmerston North. We assume the isotherm to be linear, and the K_d is the key parameter that describes the exchange or “stickiness” of the soil for arsenic. The values for K_D for the different sites and depth are given in Table 2. These results relate only to the 2 mm-sieved fraction of the soil, and not the bulk soil. Our subsequent modelling accounted for the stone fraction of the bulk soil.

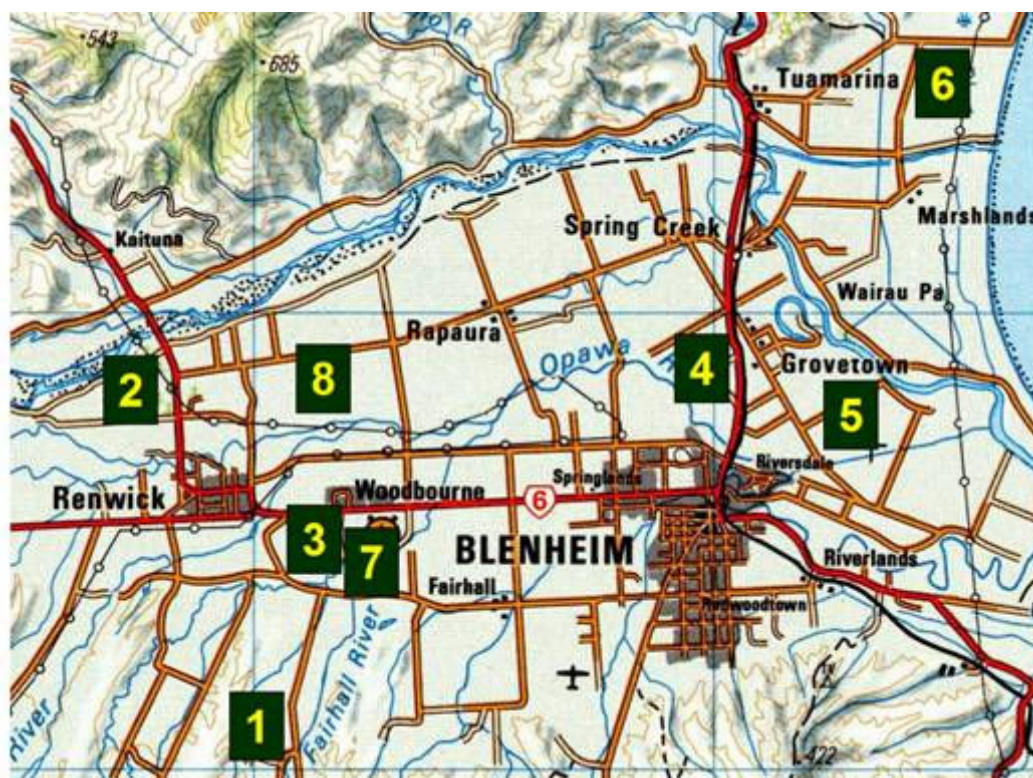


Figure 4. Sampling locations around the Marlborough Region. Table 1 contains a description of each site.

Table 1. Description of sample locations for measurement of adsorption isotherms and modelling As leaching. The physical and hydraulic properties of each soil were derived from data in the New Zealand Soils database. In the case of Rarangi, the soil's properties were measured during earlier work for the MDC (Green *et al.*, 2002).

No	Site	ID No	Series	Type	NZ revised soil class	Drainage class
1	Brancott	SB 10103	Brancott	deep silt loam	typic orthic melanic soil	moderately well
2	Kaituna	SB09289	Kaituna	silt loam	acidic orthic brown soil	well
3	Renwick	SB10132	Woodbourne	deep silt loam	pedal immature pallic soil	well
4	Rowley	SB10085	Spring Creek	clay loam	typic orthic gley soil	poor
5	Lower Wairau	SB10127	Grovetown	deep clay loam	typic orthic gley soil	poor
6	Nobilo		Rarangi	shallow silt loam	-	somewhat excessive
7	Fairhall	SB10101	Fairhall	shallow silt loam	weathered fluvial recent soil	somewhat excessive
8	Stoneleigh	SB10082	Rapaura	very shallow stony loam	typic fluvial recent soil	somewhat excessive

The total carbon content (TC) was measured with a Leco furnace (Laboratory Equipment Corporation, St Joseph, Michigan, USA) by Landcare, Palmerston North. The TC values are also given in Table 2. These K_D and TC values, adjusted by the appropriate stone fractions to represent the bulk soil, are used later in our SPASMO model to predict the risk of arsenic leaching at these various sites.

Table 2. Arsenic K_D values and carbon content for the 2 mm-sieved fraction of the soils.

Number	Sample code	Depth [cm]	K_D [L/kg]	Total C [%]
1	Brancott A	0-9	23.66	2.75
	Brancott B	9-17	44.52	1.94
	Brancott C	> 17	226.3	1.27
2	Kaituna A	0-10	57.52	1.73
	Kaituna B	10-20	53.69	1.26
	Kaituna C	> 20	62.84	0.22
3	Delegats A	0-10	28.13	3.95
	Delegats B	10-30	15.38	1.65
	Delegats C	> 30	22.73	0.15
3	Renwick A	0-10	81.11	1.96
	Renwick B	10-20	59.33	1.28
	Renwick C	> 20	128	0.54
4	Rowley A	0-10	10.16	0.88
	Rowley B	10-25	8.08	0.97
	Rowley C	> 25	24.93	0.31
5	Lower Wairau A	0-12	10.07	0.43
	Lower Wairau B	12-27	49.55	1.30
	Lower Wairau C	> 27	48.89	0.37
6	Nobilo A	0-10	38.29	3.82
	Nobilo A	0-10	67.94	4.34
	Nobilo B	10-30	21.3	1.89
	Nobilo C	>30	82.9	1.75
7	Fairhall A	0-10	50.05	2.92
	Fairhall B	10-30	32.52	1.83
	Fairhall C	> 30	45.04	0.52
	Fairhall Nth A	0-10	13.59	2.57
	Fairhall Nth B	10-20	61.44	1.79
	Fairhall Nth C	> 20	101.6	0.66
8	Stoneleigh North A	8	45.79	3.05
	Stoneleigh North B	20	25.07	2.41
	Stoneleigh North C	37	54.06	1.04
	Stoneleigh South A	0-10	36.02	1.93
	Stoneleigh South B	10-24	15.66	0.65
	Stoneleigh South C	> 24	42.3	0.32

RESULTS

The experiment was set up in late 2004, and thus only a few measurements have been collected so far. In November 2004, the initial CCA concentrations of the 36 posts installed in the Delegats' vineyard trial were measured at four locations within the post (Figure 5). In April 2005, three of these posts, 15, 18, and 29 were removed, and the CCA concentrations in the wood measured. The As concentrations in the soil were also determined around and under the posts, as outlined in the Methods and Materials section.

CCA WOOD CONCENTRATIONS

Figure 5 shows the measured concentrations in the wood at the different locations of the posts as they were put into the field. In Figure 6 we show the concentrations three months later for posts 15, 18 and 29. The concentrations exhibit strong variability between posts. This suggests that the current practice used to sample the wood might not be appropriate. It appears that more samples at better defined areas within the posts need to be taken. The large variability in CCA concentrations measured six months after installation makes it impossible currently to determine the release rate, just yet, of CCA from the posts. However, so far we have only one measurement, and it might be that the subsequent measurements will be less variable.

So, for the purpose of modelling we used the CCA release rates from a complementary experiment at the Marlborough Wine Research Centre (MWRC). There, we measured the release of CCA by immersing posts in water-filled lysimeters, and measuring the CCA concentrations in the water over time.

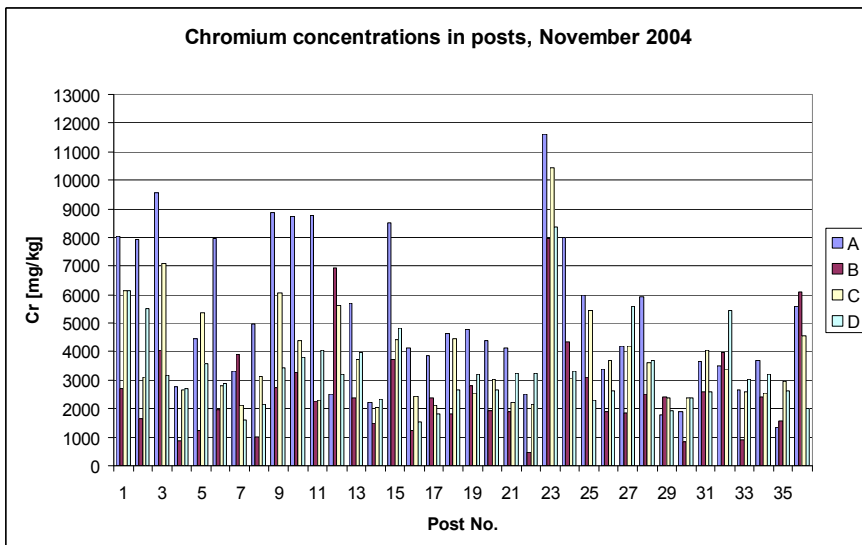
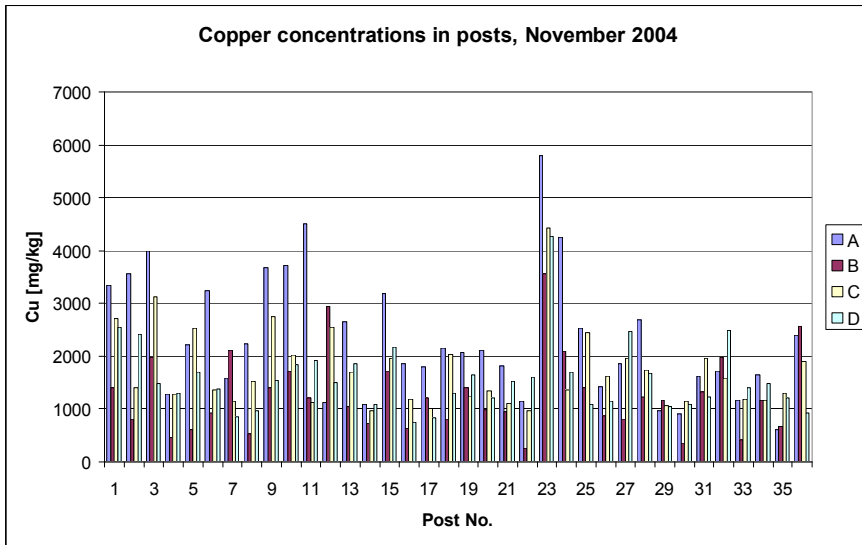
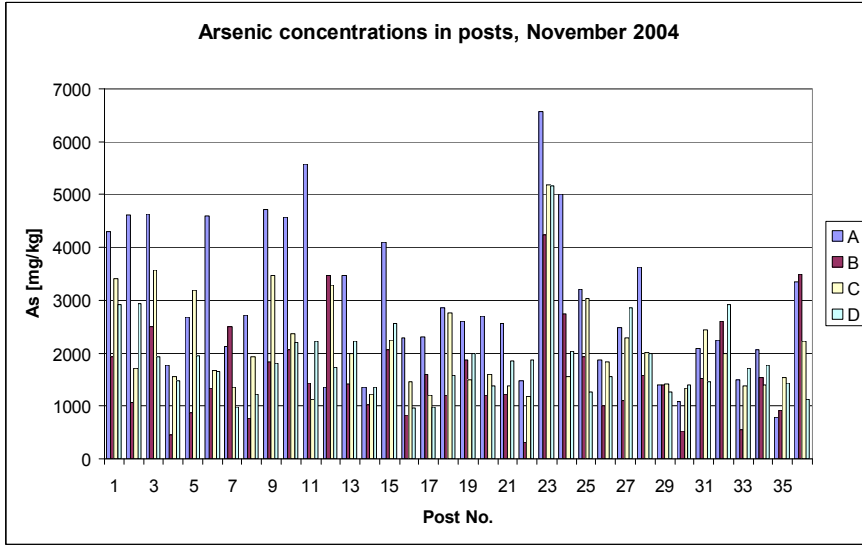


Figure 5. Initial CCA concentrations in the posts sampled in November 2004 at the various locations A, B, C and D which are shown in Figure 3.

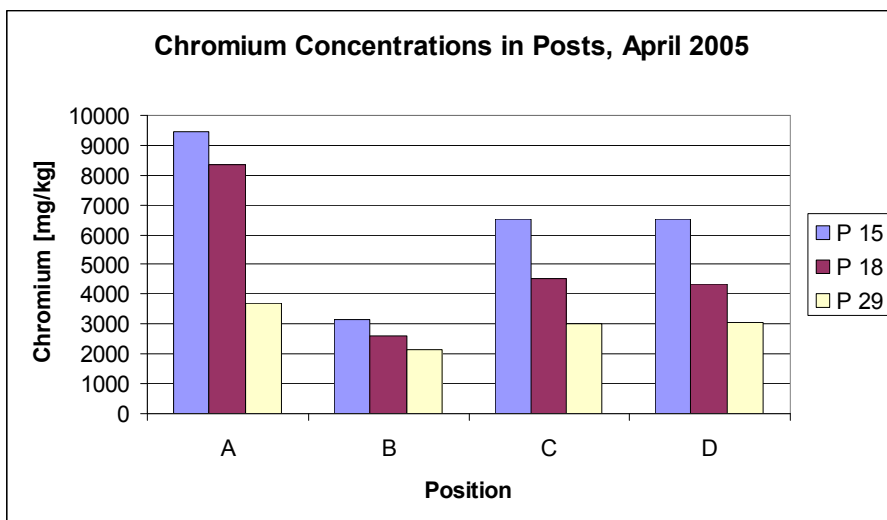
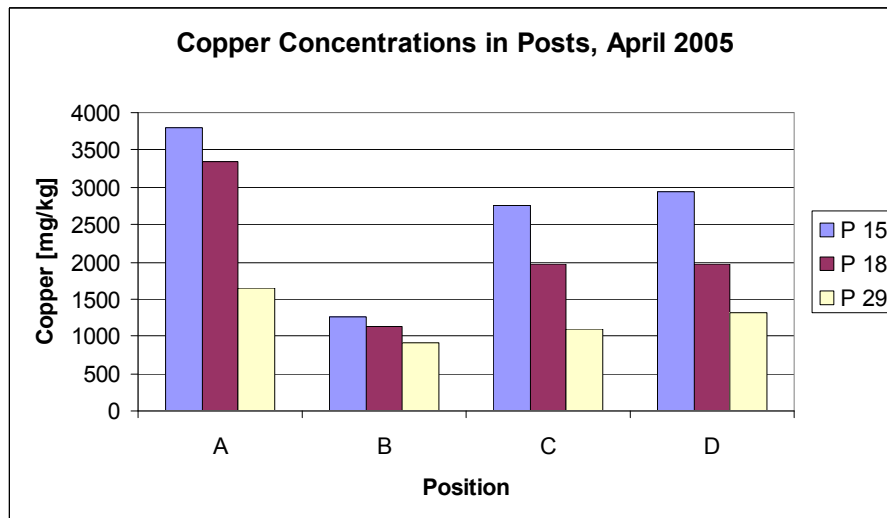
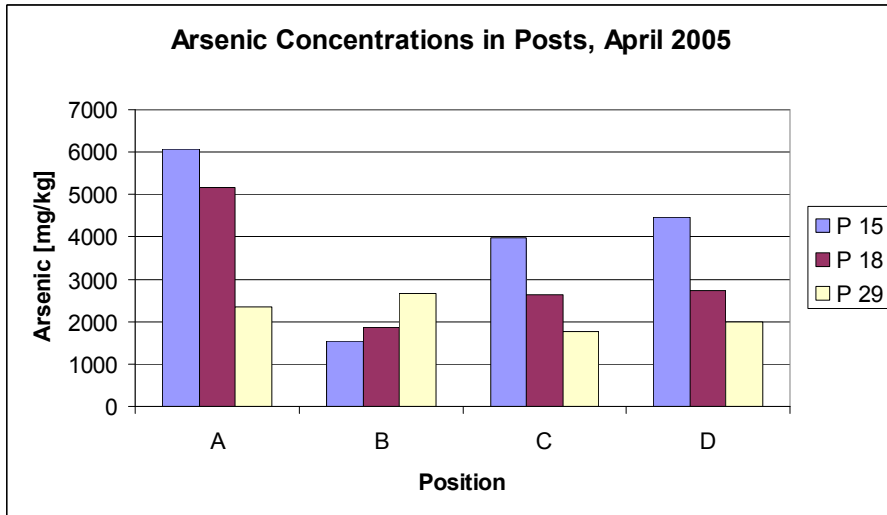


Figure 6. CCA concentrations in the posts removed on 8 April, 2005. P is the post number and the positions A, B, C and D are shown in Figure 3.

CCA SOIL CONCENTRATIONS

The CCA concentrations measured in the soil around the three posts removed in April 2005 are shown graphically in Figures 7 to 9. The highest concentrations of arsenic were found underneath the posts, with concentrations up to 200 mg kg⁻¹. The concentrations beside the posts were also elevated and compared with the average control As concentration of 8 mg kg⁻¹ taken 400 mm away from the posts.

We expected to find the highest concentrations underneath the posts, as end-grain penetration of CCA into wood is 40 times greater than lateral penetration (Morgan and Purslow, 1973). Thus, the leaching rate is also likely to be higher from the end grain, our position A. Archer and Preston (1994) demonstrated that leaching was 40 times greater out of the end of the post. The release of CCA from the bottom of the post also increases the likelihood of direct movement to groundwater. The CCA concentration measured at 200 mm below the posts showed that CCA has moved to at least that depth. Our next measurements in July/August 2005 were taken to a greater depth to see if CCA has moved further. These samples are currently being analysed by Landcare.

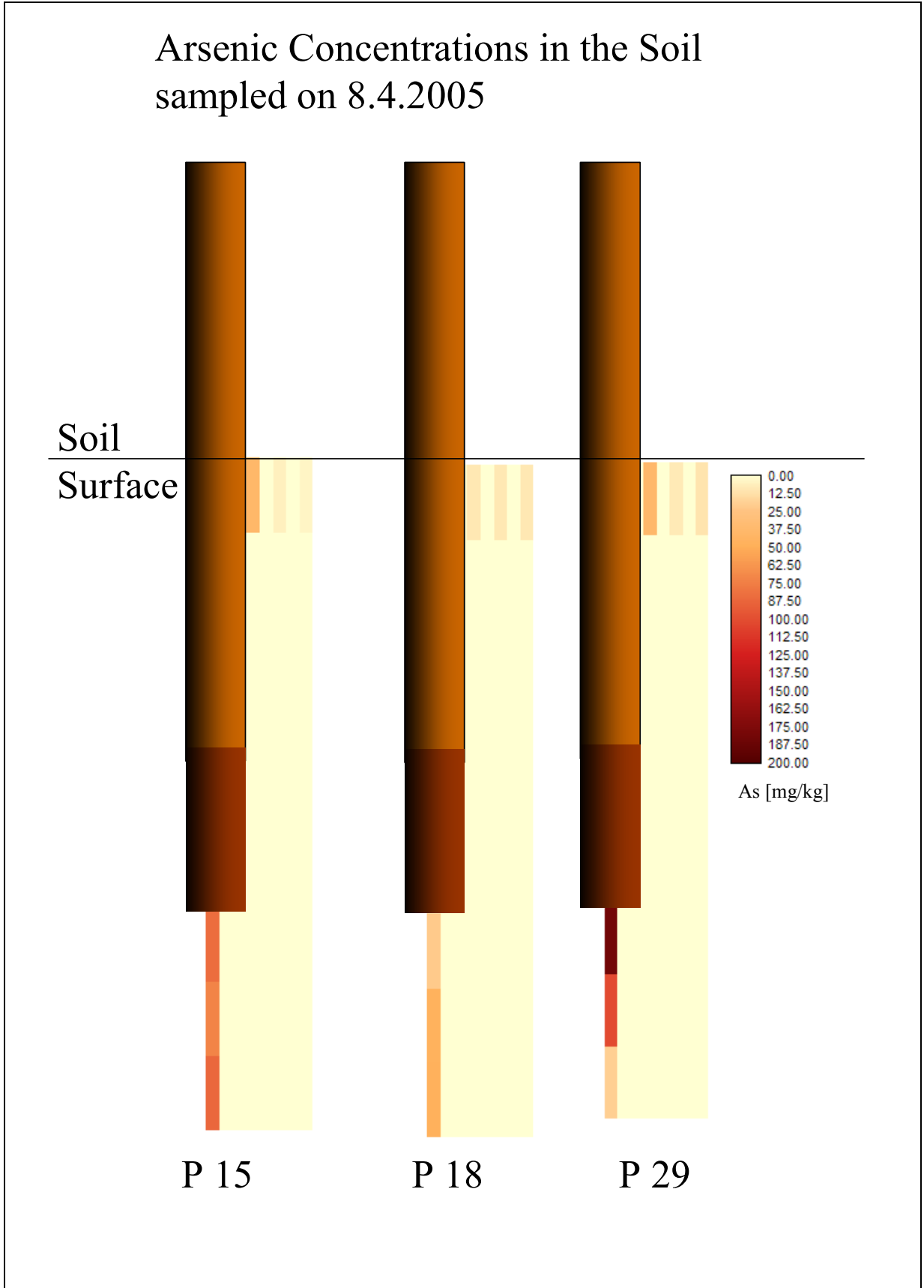


Figure 7. Arsenic concentrations measured in the bulk soil around and below the posts.

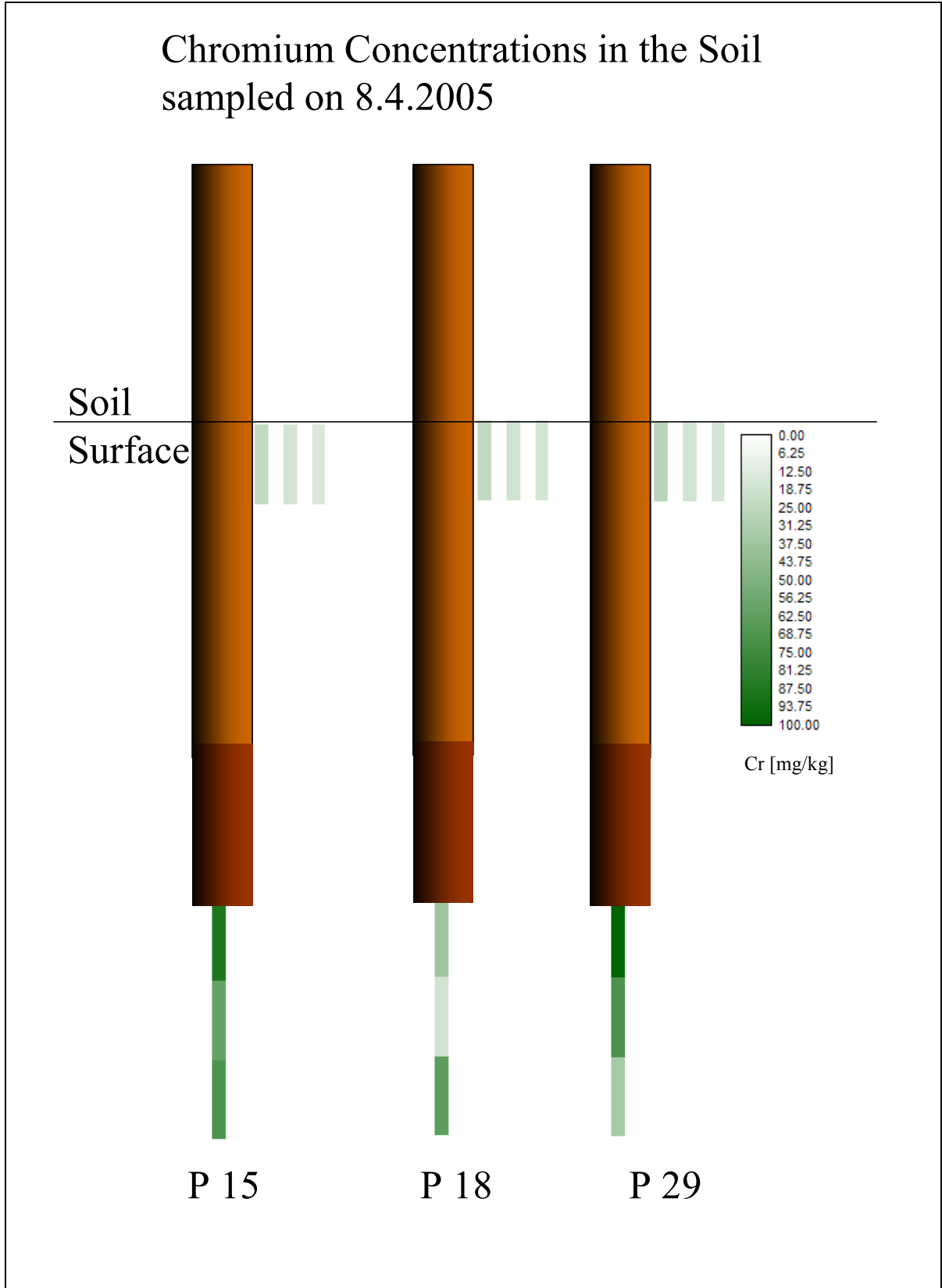


Figure 8. Chromium concentrations measured in the bulk soil around and below the posts.

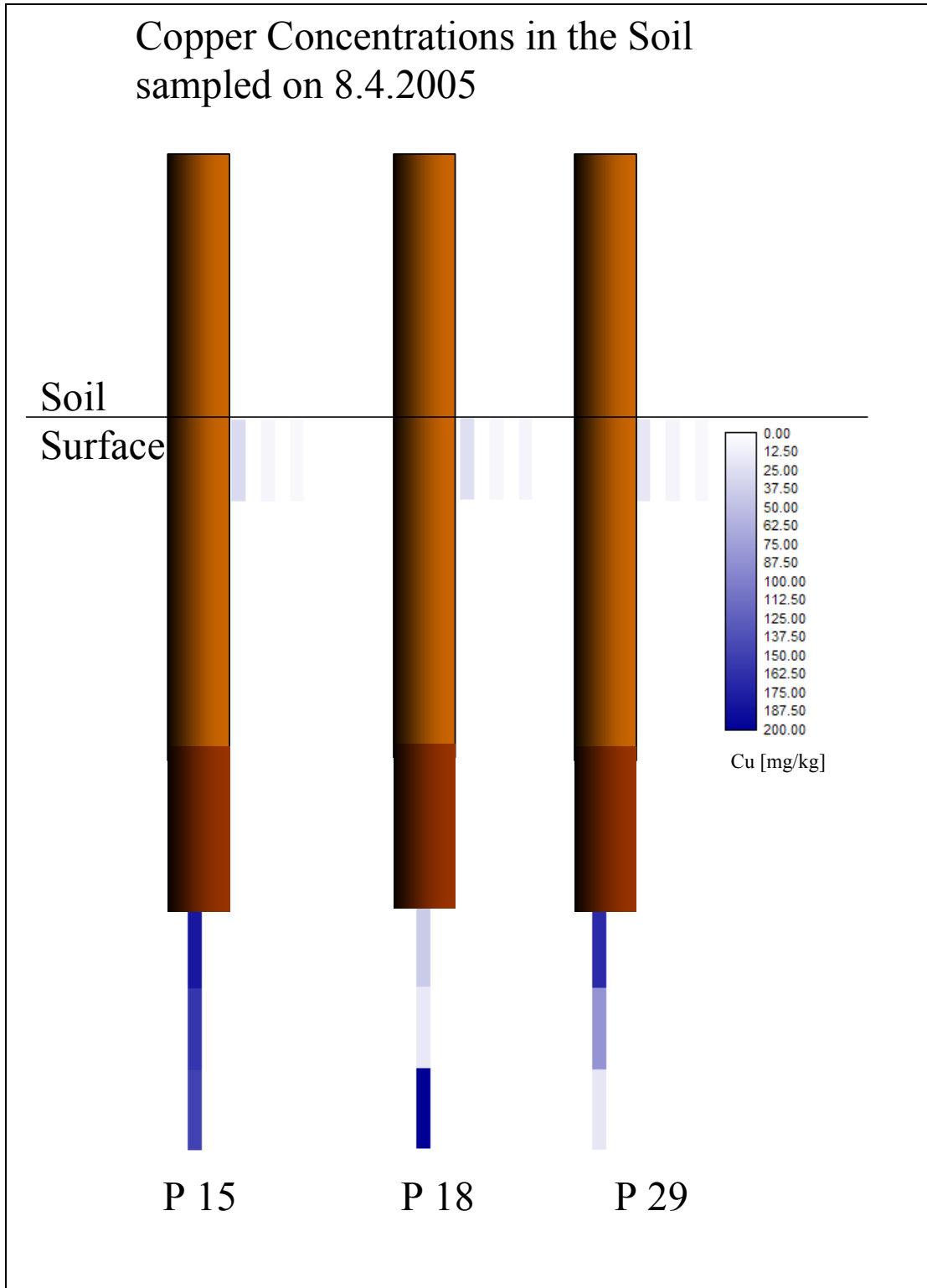


Figure 9. Copper concentrations measured in the soil around and below the posts.

As with arsenic, the highest concentrations of copper and chromium also occurred below the posts, and the concentrations beside the posts were again only slightly higher than the controls, which had an average Cu concentration of 10 mg kg^{-1} , and an average Cr concentration of 18 mg kg^{-1} . Highest concentrations of Cu and Cr found in the soil were about 200 and 100 mg kg^{-1} , respectively.

Some of the measured soil concentrations of arsenic or chromium, below the posts, are above the NEPM guidelines for agricultural soils of 100 mg kg^{-1} . No Cu concentrations exceeded the NEPM guideline value for Cu of 1000 mg kg^{-1} . However, it is likely that soil health is affected at Cu levels above 100 mg kg^{-1} . Further investigations of the impact of CCA levels on soil health could be warranted.

CCA DRAINAGE CONCENTRATIONS

So far we have only been able to obtain a few drainage samples from the lysimeters, and the drainage results, both fluxes and concentrations, exhibit significant variation as the lysimeters 'settle-in'. Furthermore, most of the experimental period has been over the summer months, when drainage is generally negligible.

However, the first drainage samples, collected in January and April 2005, already show that levels of arsenic and chromium are in excess of the New Zealand Drinking Water Standard (NZDWS), which are 0.01 and 0.05 mg L^{-1} for arsenic and chromium respectively (Figure 10).

More drainage samples will be collected over the winter period, and then we can assess in greater detail the risk of CCA leaching from the posts to both shallow and deeper groundwater.

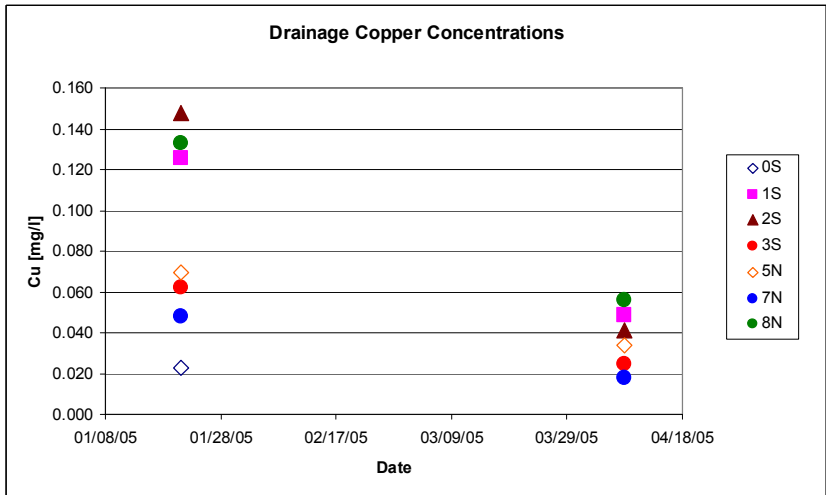
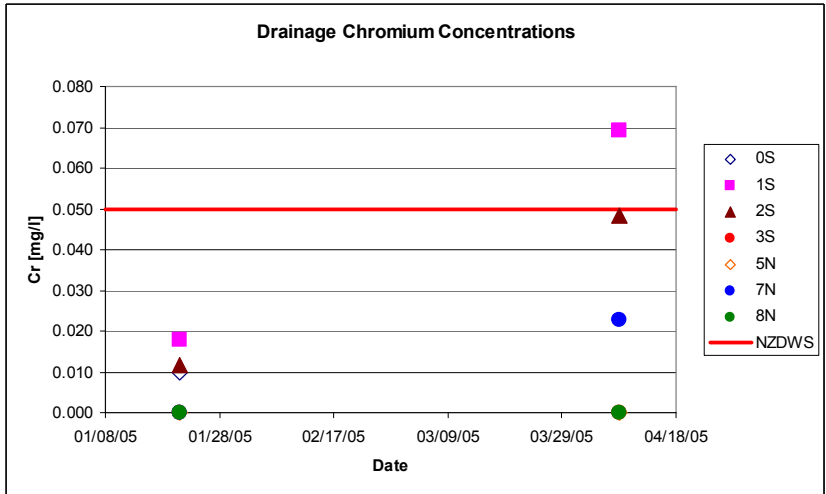
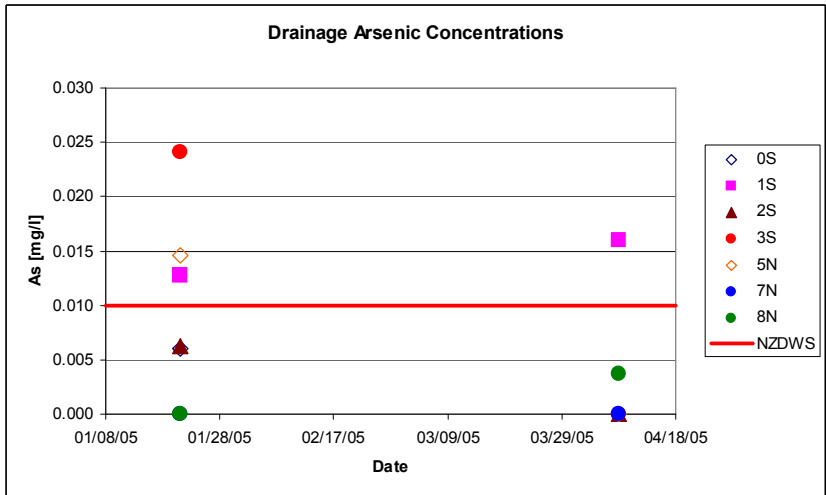


Figure 10. Arsenic, chromium and copper concentrations in the drainage samples from the lysimeters.

A MODEL TO PREDICT THE ENVIRONMENTAL FATE OF CCA

A mathematical model has been developed to describe the series of processes that control: (1) the rate of chemical release from the post to the soil water, (2) equilibrium partitioning of the chemical between adsorbed and an aqueous phases in the soil, and (3) the downward movement of dissolved chemical through the soil profile. A simple modelling approach is used to predict the temporal evolution of each process. Parameters for the modelling were taken from data collected during laboratory studies on a range of Marlborough soils, and from lysimeter studies using round and half-round vineyard posts submerged in water.

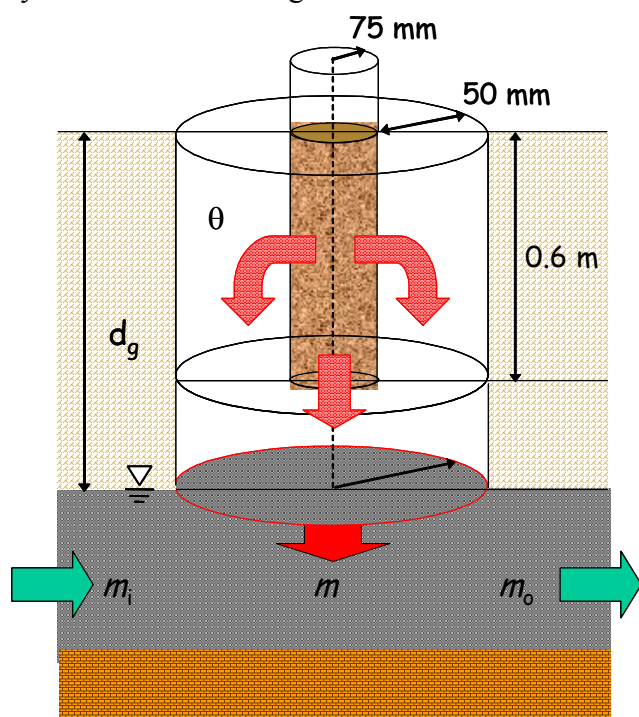


Figure 11. The CCA leaching processes described in the SPASMO model. Here d_g is the depth to groundwater, θ is the soil water content, m is the flux of As leaving the post, and m_i and m_o are the As concentrations in the groundwater upstream and downstream of the posts.

Model output is presented to track the fate of a chemical (arsenic) released from a treated timber post rammed into a bare vineyard soil. The calculations were run on a daily basis using local climate data spanning the years 1972-2004. Results are tabulated for a range of Marlborough soils to show the total amount of arsenic (per post, and per hectare) that leaches beyond a depth of 1, 2 and 3 m. A brief description of the model assumptions is presented below.

CHEMICAL RELEASE FROM THE POST

Fixation of CCA treated wood is a complex process in which the metals are strongly bound by a number of mechanisms such as ion exchange, and hydrogen bonding (Jin and Archer, 1991). How the chemical then leaves the wood, and how quickly these losses will occur are governed by complex processes. Chemical exchange in wood is a diffusive process with an effective diffusivity that depends on the chemical species, the wood porosity, and the overall

tortuosity of the wood pores. Data describing these processes are not normally available, and so they are best determined experimentally (Felton and de Groot, 1996). We recognise that water passage is facilitated through the longitudinal tracheids and vessels, yet it diffuses much more slowly in a lateral direction with ratios of 1:40 being quoted (Archer and Preston, 1994). Thus, water containing copper, chromium and/or arsenic in solution is more mobile along the longitudinal axis of a piece of wood than in a radial direction. So metal losses from end-grain are expected to be much greater than losses across the face grain.

The literature contains conflicting reports regarding release rates for CCA from treated posts, partly because of the different ratios of face to end-grain in the samples being studied (Brookes, 2005).

The first critical step in modelling the leaching risk to groundwater is to obtain the correct rate of chemical release from the posts. Here we use data being collected from other research that is being funded by the Marlborough Wine Research Centre Trust. Here half- and full-round posts (three replicates) have been placed in saturated (wet) and drained (dry) soil, as well as submerged in freshwater. Water samples are being collected at one-month intervals to assess leaching losses from the posts. Data from submerged posts are used here to examine the rate of chemical release out of the post. Figure 12 shows data for half-round posts, and Figure 13 shows data for full round posts.

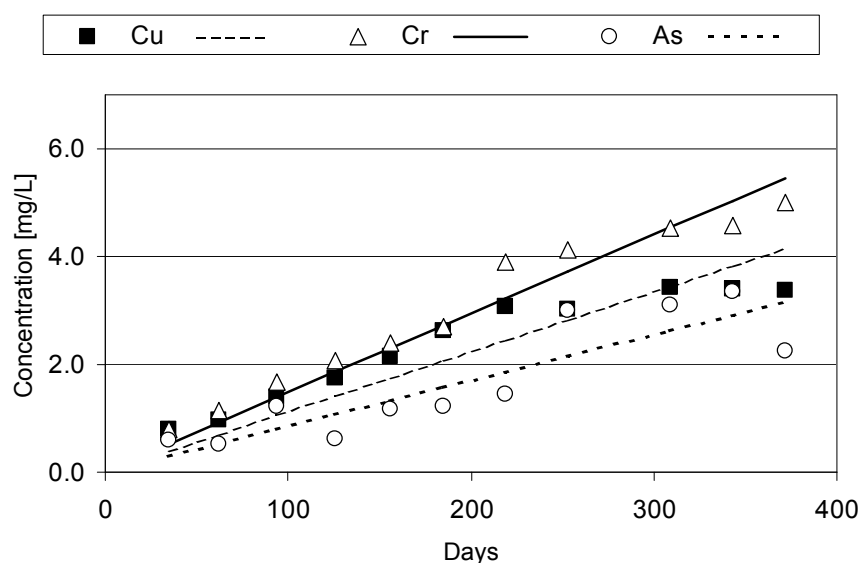


Figure 12. Release of copper, chromium and arsenic from half-round posts submerged in a 50 L container of fresh water (sample H#9). The fits of the first-order formulae are shown (Eq. 2).

Chemical leaching from treated posts submerged in ‘fresh water’, can be described using a zero-order rate equation of the form:

$$Q_i^w = \left[\frac{1}{S_A} \right] \frac{dM_i}{dt} = k_0^i \quad \text{Eq. [1]}$$

where Q_i^w ($\mu\text{g}/\text{cm}^2/\text{d}$) is the release rate of species i into freshwater, M_i [μg] is the total chemical content in the post, and k_0^i is a ‘constant’ determined from the rise in solution concentration over time (Figures 12 and 13). The parameterisation of k_0^i was achieved using a linear fit to the data, assuming a submerged area (S_A , m^2) that includes both face and end-grain

areas. Particular values of k_0^i for half and full-round posts are presented in Tables 3 and 4. The values are similar to those reported by Brookes (2002). He used a variety of sources to estimate that the short-term average loss rate from treated wood was: Cu=2.48, As=0.66 and Cr=0.09 $\mu\text{g}/\text{cm}^2/\text{d}$. Data collected from our lysimeter studies confirms that chemical release of CCA is ranked as Cr > Cu > As. Furthermore, chemical loss is faster for full-rounds than half-rounds, because of the larger surface area.

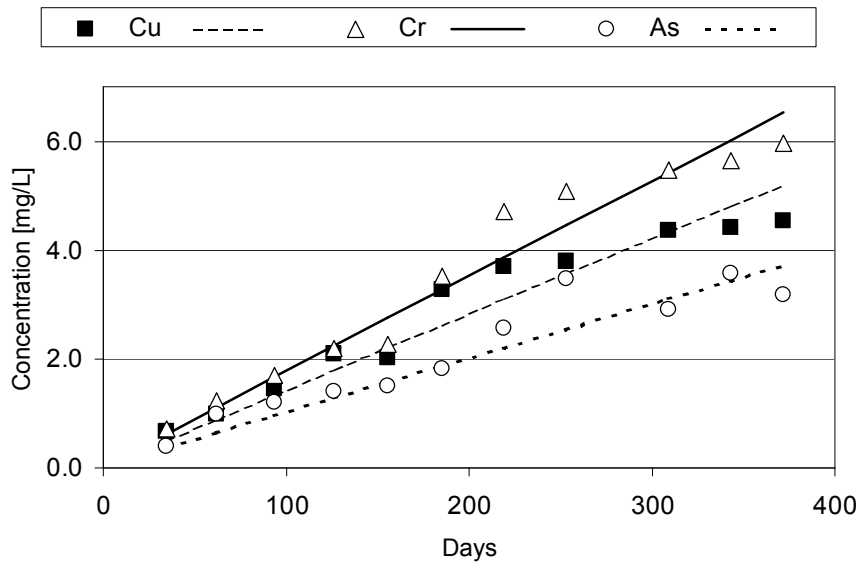


Figure 13. Release of copper, chromium and arsenic from full-round posts submerged in a 50 L container of freshwater (Sample R#7). The fits of the first-order formulae are shown (Eq. 2).

In the long-term (~20-30 years) a zero-order description will fail to adequately describe chemical release from the post. This is because Q_i will, in reality, eventually decline as M_T becomes exhausted. Some initial ‘tailing-off’ of loss from the posts can already be seen in the data in Figures 12 and 13.

So, in the longer-term, the release of CCA from treated wood is better modelled as a first-order process:

$$Q_i^w = \left[\frac{1}{S_A} \right] \frac{dM_i}{dt} = k_1^i M_i \quad \text{Eq. [2]}$$

where k_1^i [1/year] is a rate constant that represents the fraction of total chemical mass that is released each year. The other factors are the same as for Equation 1. Particular values of k_1^i for half and full-round posts are also presented in Tables 3 and 4. For the round posts, the annual release of chromium, copper and arsenic is calculated to be about 2%, 7% and 5% of the total mass, respectively. Leaching losses from the half-rounds are about half that value, presumably because of the reduced end-grain area. For all calculations presented later, the rate of chemical release into soil was modelled using Equation 2 with parameters values for k_1^i taken from Table 4. The fitted first-order equations are shown in Figures 12 and 13. This represents a worst-case scenario by predicting the maximum leaching from the posts. The modelled rate of non-linear loss of As from the posts is shown in Figure 19.

Table 3. Physical and chemical properties of round and half-round posts. The chemical load of arsenic (As), chromium (Cr) and copper (Cu) was measured in each post. The posts were then submerged to a depth of 0.4 m, with just one of the cut ends exposed to freshwater water. The round posts had a radius, R , a total mass, M , a surface area, S_A , and a volume, V . The half-rounds had a longitudinal face of width W .

Rounds	Circ. [m]	Radius [m]	Vol [m ³]	Post mass [kg]	S_A [m ²]	As [mg/kg]	Cr [mg/kg]	Cu [mg/kg]
r7	0.330	0.053	0.003466	1.64	0.14	3800	5930	2810
r8	0.342	0.054	0.003723	1.78	0.15	3480	5350	2150
r9	0.390	0.062	0.004841	2.20	0.17	3640	6060	2690
Half rounds	Width [m]	Radius [m]	Vol [m ³]	Post mass [kg]	S_A [m ²]	As [mg/kg]	Cr [mg/kg]	Cu [mg/kg]
h7	0.162	0.081	0.004122	1.93	0.18	3510	5910	2810
h8	0.185	0.087	0.005066	2.37	0.20	3470	5790	2820
h9	0.155	0.087	0.004265	2.00	0.18	2430	3780	1990

Table 4. Chemical release properties of round and half-round posts submerged in freshwater. Here, k_0 and k_1 are the zero-th and first-order rate constants defined by Equations 1 and 2.

Full rounds release rate [ug/cm ² /d]	Mean	Std	Full rounds Rate constant (1/yr)	Mean	Std
k_0 -As	0.33	0.06	k_1 -As	0.019	0.003
k_0 -Cr	0.76	0.19	k_1 -Cr	0.068	0.011
k_0 -Cu	0.42	0.12	k_1 -Cu	0.055	0.013
Half-rounds release rate [ug/cm ² /d]	Mean	Std	Half-round Rate constant (1/yr)	Mean	Std
k_0 -As	0.20	0.05	k_1 -As	0.024	0.005
k_0 -Cr	0.39	0.07	k_1 -Cr	0.026	0.004
k_0 -Cu	0.27	0.06	k_1 -Cu	0.044	0.010

CHEMICAL DISTRIBUTION IN THE SOIL

Once the chemical enters the soil, it will be partitioned in either the vapour, liquid or solid (adsorbed) phase. Chemical mobility and its propensity to leach will depend on how the given quantity of chemical is partitioned across the three phases. Any chemical that is adsorbed onto the soil particles will not leach. For modelling purposes, we assume a linear equilibrium partitioning between the three chemical phases. The adsorbed-liquid partitioning is expressed through an isotherm:

$$C_S = K_D C_L, \quad [\text{Eq. 3}]$$

where C_S is the adsorbed concentration [mg/kg-soil], C_L is the solution concentration [mg/L soil solution], and K_D [L/kg] is the distribution coefficient found from the adsorption isotherm. We assume here for simplicity that the isotherm is linear, whereas it has been shown that as concentration rises the adsorption curve flattens (Islam *et al.* 2003). At our

somewhat low values of As in the soil solution, a linear isotherm is reasonable. Particular values of K_D for a range of Marlborough soils are shown in Figure 14. Here the results relate to the 2-mm sieved fraction. In the simulations, the K_D for the entire soil was found by ‘diluting’ this 2-mm sieved fraction by the appropriate stone fraction. So the effective K_D value for the Rarangi soil would be much lower than that shown in Figure 14, because of the small percentage of the soil’s volume in the 2-mm sieved fraction.

In general, there will be greater propensity to leach if a chemical has a low K_D value. Goldberg *et al.* (2005) found arsenate adsorption to be directly related to cation exchange capacity, both inorganic and organic C content, plus iron oxide content and surface area.

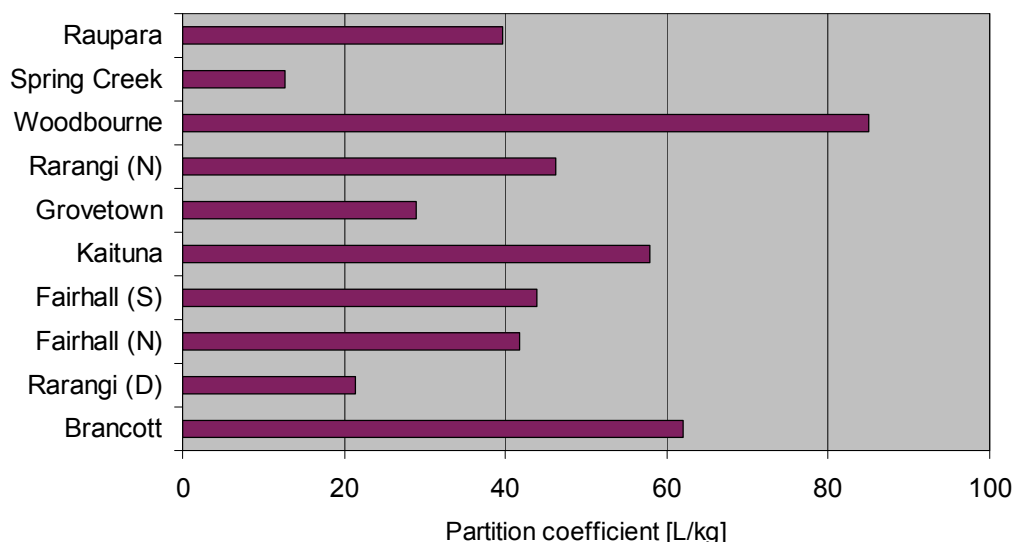


Figure 14. Batch isotherms for the 2-mm-sieved fraction of the soils were used to determine a partition coefficient, K_D [L/kg], to describe the arsenic partitioning in a range of Marlborough soils. Here K_D is calculated from the ratio of the total amount sorbed, C_S (mg/kg), divided by the total amount in solution, C_L (mg/L). For the purpose of modelling, a geometric mean was calculated for each soil series based on three soil samples taken from the top 30 mm of soil.

Measurements of K_D often show wide variability amongst soils. For pesticide chemicals, this variability is typically reduced to an extent by defining an organic-carbon distribution coefficient (Wauchope *et al.*, 1992):

$$K_{OC} = K_D / f_{OC}, \quad [\text{Eq. 4}]$$

where f_{OC} is the fraction of organic C in the soil. Our SPASMO model uses a K_{OC} value to define the chemical adsorption and partitioning. Thus, for each soil series, measured values of K_D have been divided by the corresponding fraction of organic carbon in the top 300 mm of soil (see Table 2). With this approach, soils with a low organic C content will tend to exhibit more chemical leaching, all other factors being equal. This general approach is broadly supported by the findings of Goldberg *et al.* (2005) and Islam *et al.* (2003) who noted the link between As adsorption and organic C content. Other land management factors could, nonetheless, have an impact on arsenic leaching; Álvarez-Benedi *et al.* (2005) and Smith *et al.* (2002) found that phosphates, through competition for exchange sites, decreased the adsorption of As, whereas nitrate had the opposite effect. We have not considered this.

The liquid-vapour partition for a chemical is generally represented through Henry’s Law:

$$C_G = K_H C_L, \quad [\text{Eq. 5}]$$

where C_G is the concentration of CCA in the vapour phase [g/m^3 soil air] and K_H is Henry's law constant, which is dimensionless. For simplicity we have ignored the vapour phase of CCA compounds, as well as any volatilisation losses that are associated with them.

WATER AND CHEMICAL MOVEMENT THROUGH THE SOIL

We consider the case of a single, treated, full-round post rammed into a bare vineyard soil. The post is considered buried to a depth d_g ($=0.6$ m), and it has the chemical and physical properties that are defined in Table 2. Chemical release is modelled as a buried source with 1/3 of the chemical being released through the side face, and the remaining 2/3 being released through the post end. This fraction is consistent with the end-grain diffusivity being 40 times greater than the face-grain. Total chemical release from the post into soil Q_i^s is calculated by modifying the loss into water, Q_i^w , that is described by Equation 2. We assume all leaching into the soil occurs from the subterranean part of the post only, and that the loss rate from the post into the soil-water solution is that from water alone, multiplied by the volume fraction of water in the soil at saturation, θ_s , so

$$Q_i^s = \theta_s Q_i^w \quad [\text{Eq. 6}]$$

This assumption provides a worse-case scenario, for the soil will often be at water contents less than saturation; $\theta \leq \theta_s$. However, this saturated assumption is probably more realistic at Rarangi, where the shallow aquifer can rise to inundate the lower parts of the post, especially the end-grain (see Figure 1. Top right). We also limit the sideways chemical movement to within 50 mm of the post (Figure 11).

Water and chemical movement through the soil is modelled using SPASMO (Green *et al.*, 2003). This model considers a 1-dimensional soil profile of 5 m depth that is divided into 0.10 m intervals, or slabs. The calculations were run on a daily time step, and the water balance is considered to be that of a bare soil. A standard crop-factor approach is used to relate the soil evaporation to the prevailing weather (Allen *et al.*, 1999). Water movement through the soil profile is calculated using a water-capacity approach (Hutson and Wagenet, 1993) that considers the soil to have both mobile and immobile pathways for water and chemical transport. The mobile domain represents the soil's macropores (e.g. old root channels, worm holes and cracks), with the immobile domain being the soil's matrix.

After rainfall or irrigation, any dissolved chemical is allowed to percolate rapidly through the soil in the mobile domain only. Subsequently, on days when there is no significant rainfall, there is a slow approach to equilibrium between the mobile and immobile phases, driven by a difference in water content between the two domains. Chemical partitioning is described using a linear isotherm, with the particular K_D values taken from Figure 4.

Model calculations were first run on a daily time step using a 32-year sequence of weather data (1972-2004) recorded from the Marlborough Research Centre. These data was obtained from the NIWA climate database using the on-line search engine 'METSEEK' developed by HortResearch (M. Laurenson, Orchard 2000TM). The soil physical and hydraulic properties were deduced from data contained in the NZ Soils Database (Landcare Research), or our earlier measurements at Rarangi.

MODELLING THE LEACHING OF AS FROM TREATED TIMBER POSTS OVER 30-YEARS

Model calculations of the arsenic concentration in soil close to the post are shown in Figure 15. Similar results for soil immediately under the post are shown in Figure 16. Because

arsenic is strongly bound to the soil, a steady release of chemical from the post leads to a gradual accumulation in the soil. Put simply, the soil has a characteristic attraction for the As, so that the arsenic leaching from the post becomes bound to the soil. The ability of the soil to bind As is parameterised by K_D .

On the heavier and more-adsorptive soils, the concentration in the soil beside the post is predicted to exceed 100 mg/kg (Figure 15), and soil under the post could exceed 520 mg/kg (Figure 16) after some 30 years. On the lighter Rarangi soil, where the stone fraction is ~70%, the corresponding arsenic concentration both beside and underneath the post is predicted to reach about 100 mg/kg (Figures 15 and 16). Higher and more-rapidly rising levels of arsenic in the heavier soils directly under the post are partly to the result of enhanced release of arsenic from the end-grain wood. The Rarangi soil does not adsorb as much arsenic, despite what seems quite a high exchange coefficient in Figure 14. However, the K_D in Figure 14 is just for the 2-mm sieved fraction only, and for the bulk soil the effective K_D is that value 'diluted' by the 70% volume stone fraction of the Rarangi soil. For this reason, the Rarangi soil is thus more likely to leach, rather than accumulate As, as we will determine later.

The NEPM guideline level for arsenic in agricultural soils has been set at 100 mg/kg (Australian National Environment Protection Council, 1999). Our calculations suggest this value could be reached on the heavier soils after just 10-20 years (Figures 15 and 16). However, it is worth noting that the actual contamination zone represents just 0.05% of the vineyard surface area, given that there are 600 posts per ha and that we consider the bulk of the adsorption is contained within 50 mm of the post's surface.

We are encouraged by the fact that the predicted SPASMO soil concentrations are broadly similar to the data reported by Robinson *et al.* (2004), who sampled soil around many vineyard posts of varying ages (Figures 15 and 16). This comparison is across a broad range of soils and location, and the measured variation is naturally large. Nonetheless, the similarity of these general survey results with our simulation modelling is heartening. So the model output seems to have been generally verified, as the data are of a similar magnitude, and show a similar accumulation over time. We would not expect an exact match between those measurements and our modelling, because of simplifications in the model, and natural variability of the measurements in the real world. Furthermore, the model results depend on the assumed transport volume surrounding the post (Figure 11). If the adsorption zone were extended to 100 mm from the post, then the predicted (average) soil concentration would drop by about one half. However, such a lateral extension of the diffusive transport of As would be unlikely, as the flow of water, and hence convective transport of As, is primarily in the vertical.

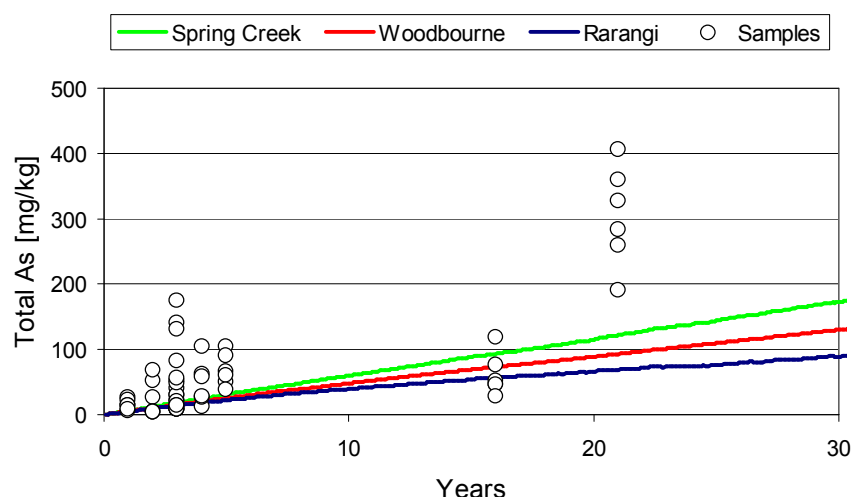


Figure 15. The effect of soil type on soil arsenic concentration very close to the post was modelled using SPASMO (lines). The symbols represent individual samples collected within 5 cm of posts of various ages on a range of Marlborough soils (Robinson *et al.*, 2004). The different lines are a reflection of the ability of the soil to exchange and ‘hold’ arsenic.

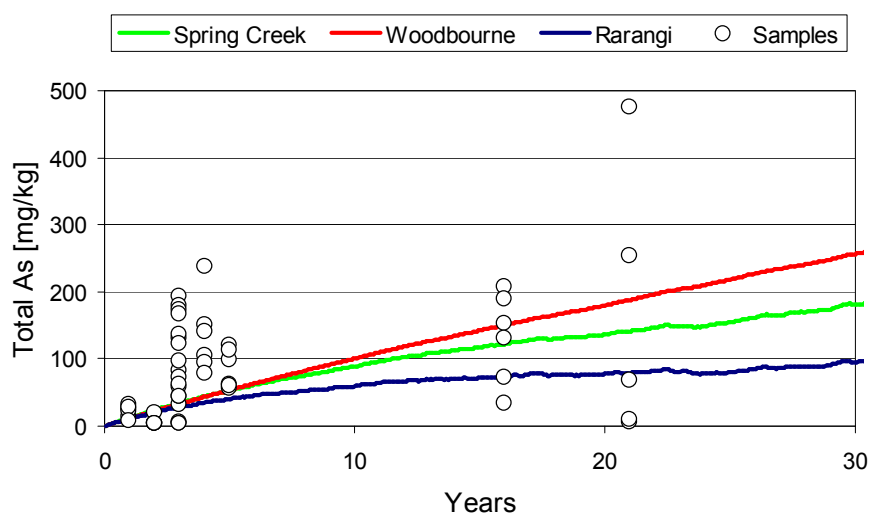


Figure 16. The effect of soil type on soil arsenic concentration immediately under the post was modelled using SPASMO (lines). The symbols represent individual samples collected within 5 cm of posts of various ages on a range of Marlborough soils (Robinson *et al.*, 2004). The different lines are a reflection of the ability of the soil to exchange and ‘hold’ arsenic.

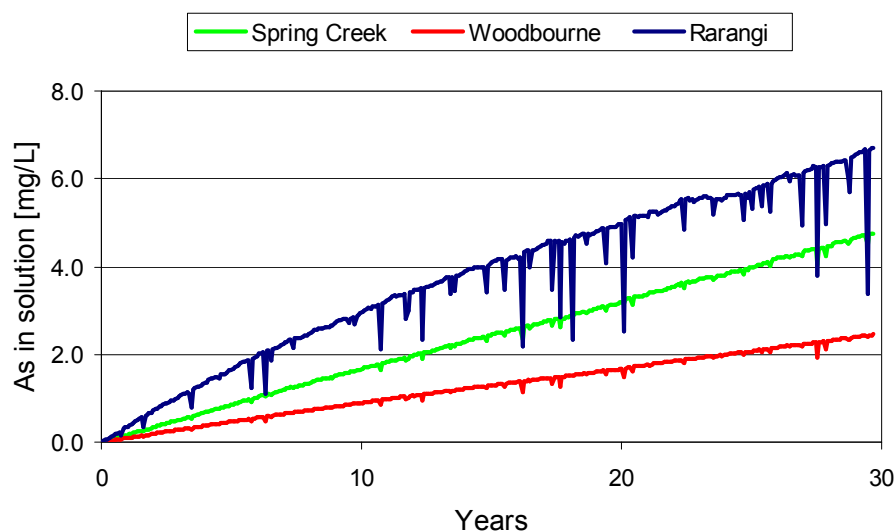


Figure 17. The effect of soil type on dissolved arsenic in the soil solution very close to the post was modelled using SPASMO (lines). The different lines are a reflection of the ability of the soil to adsorb arsenic. The ‘spikiness’ of the Rarangi values result from the plotting of just monthly values (cf. daily results), and the fact that the Rarangi soil has a very low water content that can change rapidly.

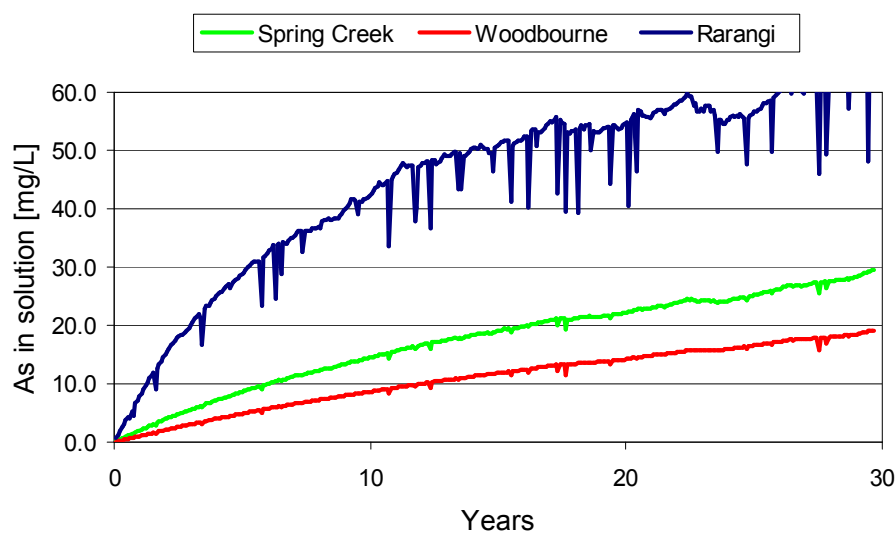


Figure 18. The effect of soil type on dissolved arsenic in the soil solution immediately under the post was modelled using SPASMO (lines). The different lines are a reflection of the ability of the different soils to adsorb arsenic. The Woodbourne soil is the most adsorptive, and the Rarangi the least (see Figure 14).

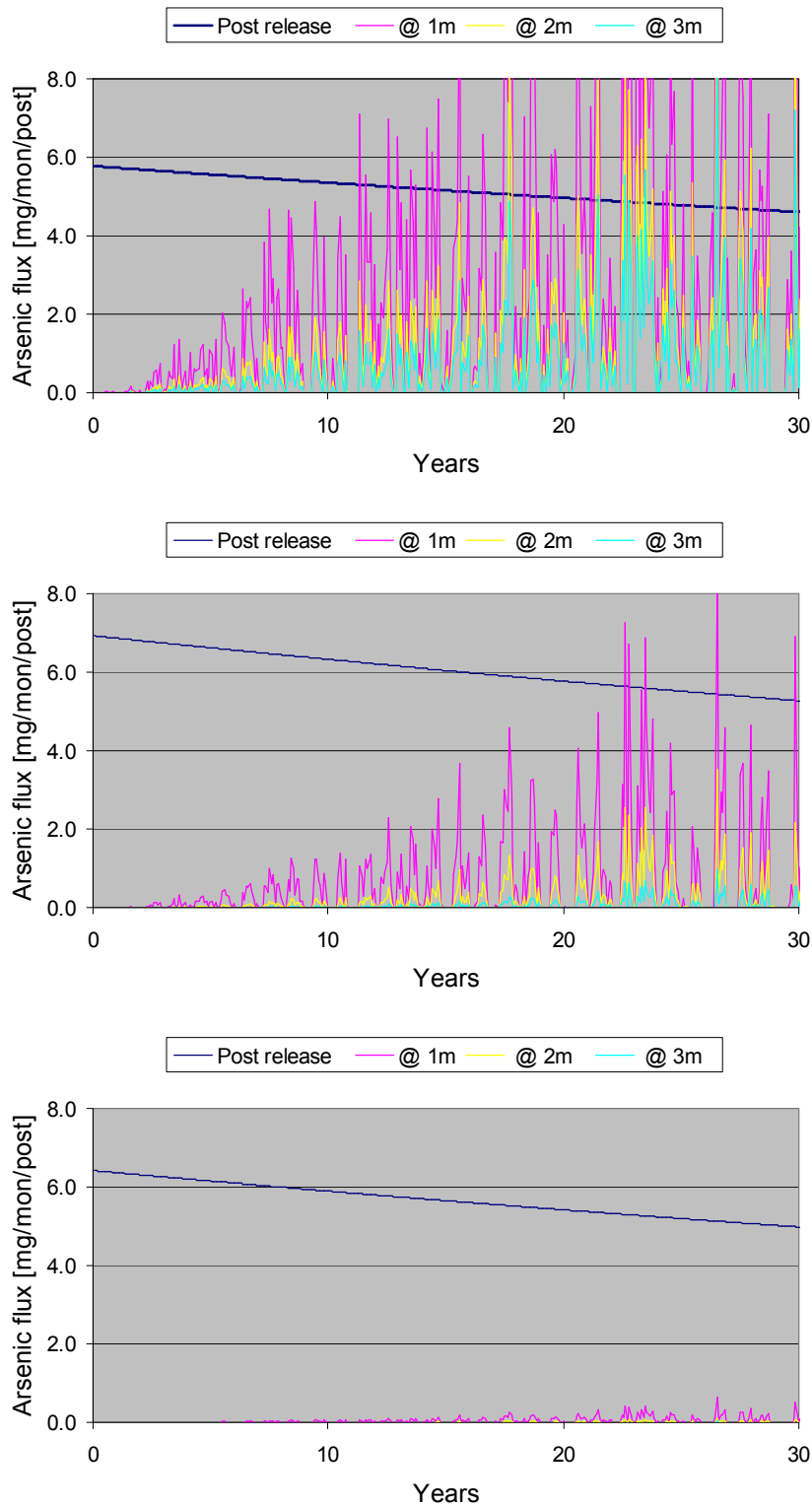


Figure 19. Calculations of the amount of arsenic released from a treated timber post (see m , Eq. 7), and the amount that leaches below a given depth. The top panel is at Rarangi, then next is the Spring Creek soil, and the bottom panel is a Woodbourne soil. The Woodbourne soil has a greater capacity to adsorb arsenic and there is nearly a 10 to 20 times attenuation in leaching losses between depths of 1 and 3 m, over the 30 years.

The concentration of arsenic in the soil's water draining through the soil profile is presented in Figure 17 for the soil solution close to the post, in Figure 18 for the soil solution directly under the post, and in Figure 19 in the soil solution at the depths of 1, 2 and 3 m. Here, for simplicity, rather than plot the nearly 12,000 data points in Figures 17 and 18, we have produced the graphs using only the value on the 1st of each month. This renders the graphs somewhat 'spiky', especially for Rarangi where there are rapid changes in the soil's water content. There is a wide variation between the adsorptive soils of Spring Creek and especially Woodbourne, and the light soil at Rarangi. In the case of Rarangi, the K_{OC} of the bulk soil is relatively low (Table 2), so a greater fraction is partitioned to the solution phase. Meanwhile, the soil is also very stony (~70% v/v), so the same amount of chemical is released into a much smaller volume of soil water. Conversely, the relatively low solution-concentration in a Woodbourne silt loam soil is a result of the combination of a much higher K_{OC} value and a greater water holding capacity.

Table 5. The effect of soil type on the fate of arsenic leaching from a treated timber post after 30 years. The results are presented in terms of the mass balance for a single post (mg/post) and for the entire vineyard area (kg/ha). The initial mass of arsenic was taken to be 9.9 g per post and the post density was assumed to be 600 posts/ha. The values reported at 1 m, 2 m, and 3 m represent the accumulated leaching at those depths.

Soil series	Factor	loss	@ 1m	@ 2m	@ 3m
Rarangi	Mass [mg/post]	2097	1010	475	295
	% lost	21.2	10.2	4.8	3.0
	leached [kg/ha]	1.26	0.61	0.29	0.18
Fairhall	Mass [mg/post]	408	55	22	12
	% lost	4.1	0.6	0.2	0.1
	leached [kg/ha]	0.24	0.03	0.01	0.01
Rapaura	Mass [mg/post]	2094	462	188	92
	% lost	21.1	4.7	1.9	0.9
	leached [kg/ha]	1.26	0.28	0.11	0.06
Brancott	Mass [mg/post]	2301.4	264.4	81.2	24.8
	% lost	23.2	2.7	0.8	0.3
	leached [kg/ha]	1.38	0.16	0.05	0.01
Spring Creek	Mass [mg/post]	2457	281	90	22
	% lost	24.8	2.8	0.9	0.2
	leached [kg/ha]	1.47	0.17	0.05	0.01
Kaituna	Mass [mg/post]	2455	60	15	6
	% lost	24.8	0.6	0.2	0.1
	leached [kg/ha]	1.47	0.04	0.01	0.00
Woodbourne	Mass [mg/post]	2299	18	2	1
	% lost	23.2	0.2	0.0	0.0
	leached [kg/ha]	1.38	0.01	0.00	0.00
Grovetown	Mass [mg/post]	2611	274	22	1
	% lost	26.4	2.8	0.2	0.0
	leached [kg/ha]	1.57	0.16	0.01	0.00

In the case of the Woodbourne soil, a smaller fraction of the released chemical is partitioned to the solution phase, and that smaller amount goes into a much bigger pore volume of water. The New Zealand Drinking Water Standard (NZDWS) for arsenic is set at 0.01 mg/L (MoH, 2000). Model predictions in close vicinity of the post, especially under the post, indicate that the As concentration in the soil-solution that is leaching are orders of magnitude greater than

this drinking water standard (Figures 17 and 18). But as noted earlier, the actual contamination zone represents just 0.05% of the vineyard surface area.

When assessing the actual risk of contamination to the groundwater, we need to take account of drainage losses that also occur from the remaining 99.95% of the vineyard area through soil that typically has a low background level for arsenic (~5 mg/kg). For simplicity, we have assumed that no arsenic originates from that part of the vineyard. Thus, predicted drainage losses per hectare of vineyard area are diluted by the appropriate area-weighting factor, as the diagram in Figure 20 illustrates. Mass balances for the fate of arsenic are presented in Table 5. After a period of about 30 years, we calculate that some 20-25% of the original mass of arsenic will be lost from the buried part of the post. This equates to a total of 2.5 g As per post, or the equivalent of some 1.5 kg-As/ha, being released into the surrounding soil volume over the period of 30 years. At a depth of 1 m at Rarangi, after about 30 years, the concentration of arsenic averaged over a vineyard rises to become the New Zealand Drinking Water Standard of 0.01 mg/L (Figure 21).

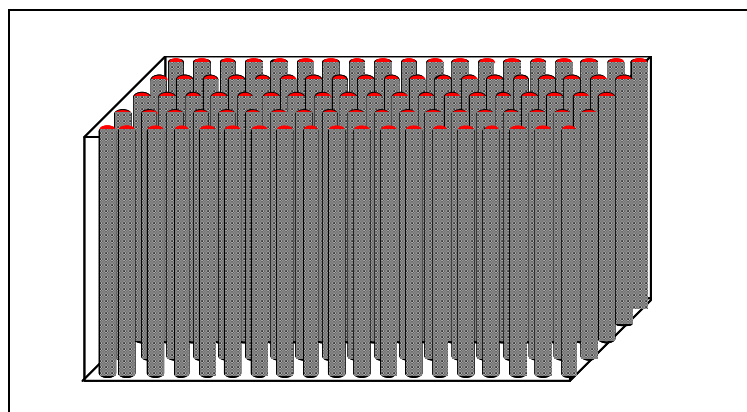


Figure 20. Schematic diagram of the modelling approach used to calculate the spatially averaged concentrations of As at the depths of 1 and 2 m. The red columns represent the ‘plumes’ of arsenic around the posts.

At a depth of 2 m, after 30 years, the spatially averaged soil solution concentration of As is at about three-quarters the NZDWS. It seems that these concentrations have stabilised after about 25 years.

Our 30-year simulations of leaching losses indicate:

- On the heavier and more adsorptive soils of Kaituna, Woodbourne and Fairhall, less than 0.6% of the post arsenic ends up leaching below a depth of 1 m, and less than 0.1% will travel beyond a depth of 3 m.
- On the medium soils of Brancott, Grovetown, Rapaura and Spring Creek less than 5% of the post arsenic ends up leaching below a depth of 1 m, and less than 0.1% will travel beyond a depth of 3 m

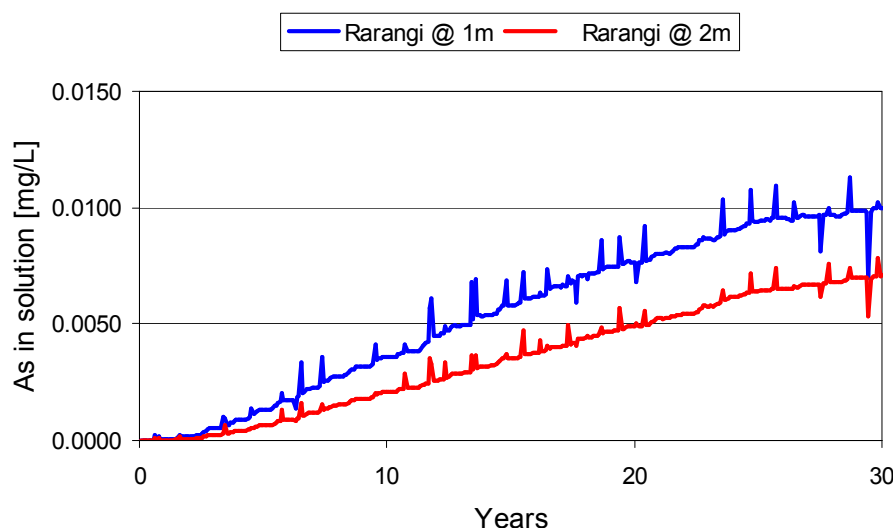


Figure 21. The SPASMO predictions of the spatially averaged arsenic concentrations in the soil solution at 1 and 2 m depth under Rarangi soil.

- On the light soils of Rarangi some 10% of the post arsenic ends up leaching below a depth of 1 m, and up to 3% will travel beyond a depth of 3 m.

LONG-TERM PREDICTIONS OF AS LEACHING, WITH POST REPLACEMENT

To predict the long-term fate of As in the leachate and soil, we carried out SPASMO modelling over 500 years. To do this we have used repeatedly the same 32-year weather record. We considered first the transport and fate from a single post sitting in the soil for the entire 500-year period. Then we modelled the system dynamics with 5% post replacement. This means that, on average, any given post is replaced after 20 years, and a new one installed in the same hole. Thus the leaching process begins anew some 25 times during the 500-year simulation.

Figure 22 shows the long-term trend in dissolved arsenic in soil close to, and alongside a CCA-treated timber post. In the case of a single permanent post, the arsenic solution concentration reaches a peak of about 4 mg/L after about 100 years. Thereafter the solution concentration declines because less arsenic is released from the ageing post. We model this situation by assuming a new post is placed back into the same hole in the soil every 20 years. In this case, it takes about 300 years for the dissolved concentration to reach a peak of about 8 mg/L, and this is about twice the peak solution-concentration for soil around a single, permanent timber post.

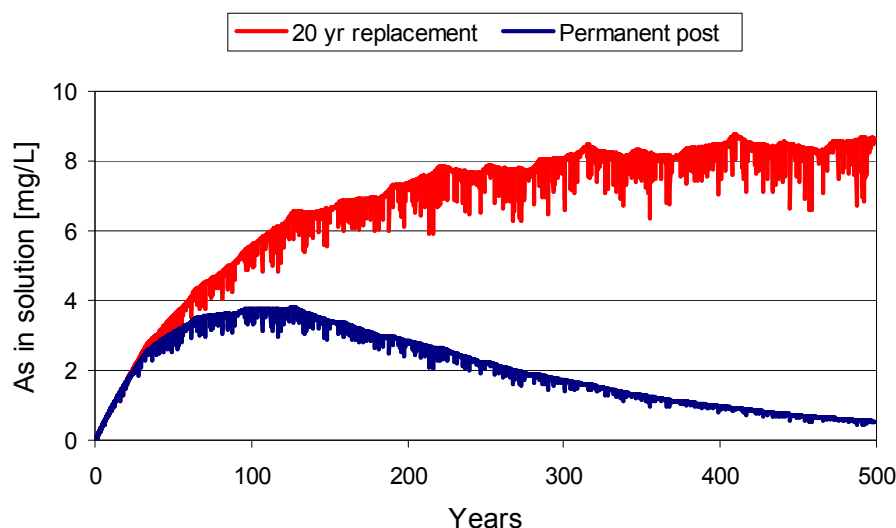


Figure 22. The long-term trend in dissolved arsenic in Woodbourne soil close to the post was modelled using SPASMO. The lower line represents the case of a single, permanent post and the upper line represents the case of post replacement once every 20 years.

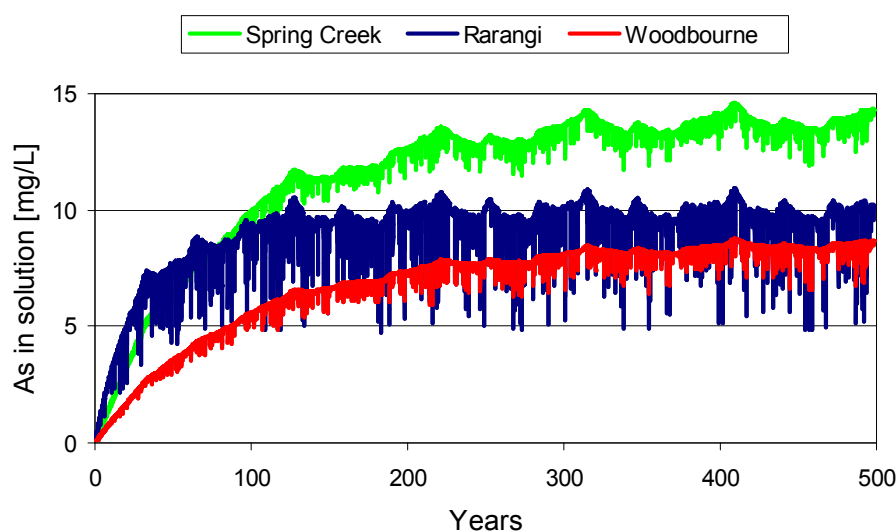


Figure 23. The long-term effect of soil type on dissolved arsenic in soil close to the post was modelled using SPASMO (lines). The different lines are a reflection of the ability of the soil to exchange and adsorb arsenic.

The effect of soil type on the long-term trend in dissolved arsenic in the soil close to a CCA-treated timber post is shown in Figure 23. These results assume a new post is placed back into the soil once every 20 years. In the case of a Rarangi soils it takes about 100 years for the dissolved concentration to reach a peak of about 10 mg/L, and this is intermediate to the final solution concentrations found in the other soils.

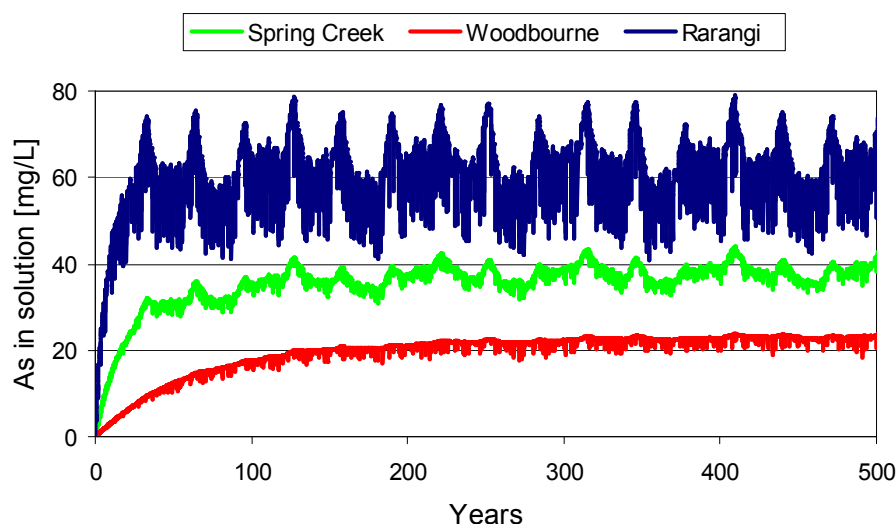


Figure 24. The effect of soil type on dissolved arsenic in soil immediately under the post was modelled using SPASMO. The different lines are a reflection of the ability of the soil to adsorb arsenic, and the profile pattern of that capacity.

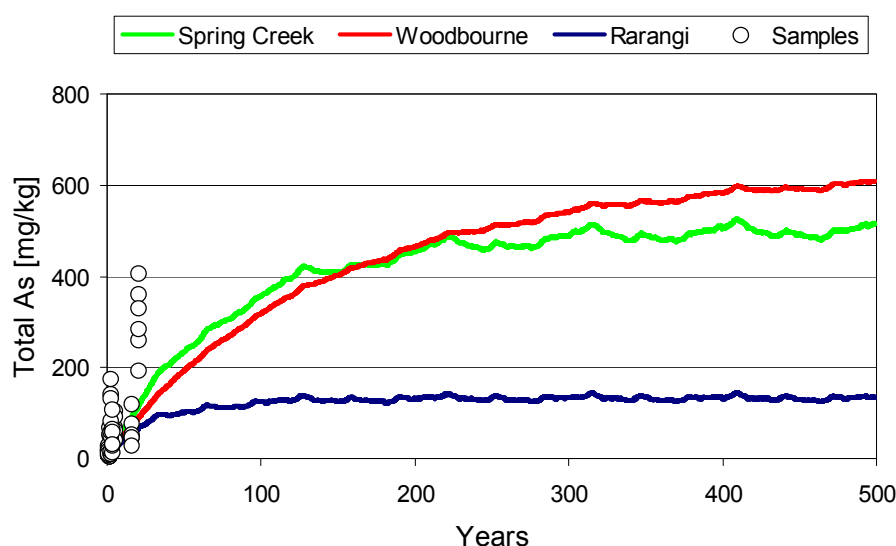


Figure 25. The effect of soil type on soil arsenic concentration close to the post was modelled using SPASMO (lines). The symbols represent samples collected within 5 cm of posts of various ages (years) on a range of Marlborough soils (Robinson *et al.*, 2004). The different lines are a reflection of the ability of the soil to adsorb arsenic.

Because the loss of As is 40 times greater through the end-grain, the concentrations immediately under the post (Figure 24) are greater than those immediately alongside the post (Figure 23). The variability in the record for Rarangi reflects the soil-water dynamics of this permeable soil, with its low water-holding capacity, and weak adsorption of As. The changing order between the three soils (Figure 24 cf. Figure 23) is a result of the different profile patterns in the soil's adsorptive capacity for As.

SPASMO can also predict the long-term trend of adsorbed concentration of As near the posts for the range of soils considered (Figure 25). The different abilities of the soil to exchange and adsorb As and retain it alongside and close to the post are shown in Figure 25. The

Rarangi soil, because of its large stone fraction, has a low bulk K_D , and so the concentration retained alongside the post is lower than that for either Spring Creek or Woodbourne soils. Nonetheless, after about 30 years, we predict that the local concentration of As near the post for the Rarangi soil would plateau at about 150 mg kg^{-1} , and this exceeds the NEPM guideline value of 100 mg kg^{-1} . At Spring Creek the steady value would reach nearly 500 mg kg^{-1} , and at Woodbourne, because of the greater adsorptive capacity of this soil, the final steady concentration in the soil reaches about $600 \text{ mg-As kg}^{-1}$, after about 400 years. Figure 26 shows the predictions of the soil-adsorbed As immediately under the post.

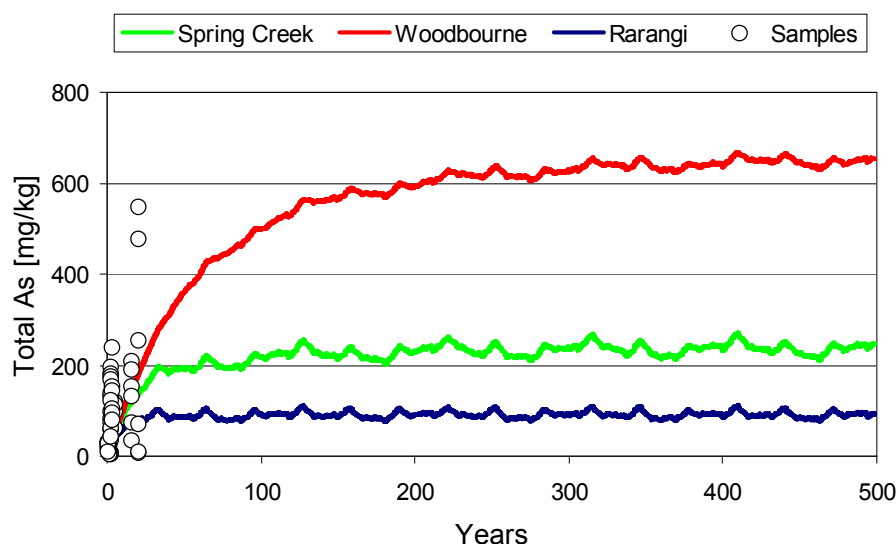


Figure 26. The effect of soil type on soil arsenic concentration immediately under the post was modelled using SPASMO (lines). The symbols represent samples collected within 5 cm of posts of various ages (years) on a range of Marlborough soils (Robinson *et al.*, 2004). The different lines are a reflection of the ability of the soil to adsorb arsenic.

Figure 25 shows the sampled values from the earlier general survey, for all soil types (Robinson *et al.*, 2004). The same trends are found in the predicted soil concentrations immediately under the post (Figure 26). The field data include all soil types from our survey across Marlborough, and therefore they exhibit natural variation.

Next, we predicted, using SPASMO, the long-term spatially-averaged concentrations of As in the leachate at depths of 1 m and 2 m (Figure 27). These concentrations would mimic the spatially averaged As concentration of the leachate entering the groundwater, should the water table be at these depths. For the three different soils, there is much less variation between the final steady-state values of the As concentration, nor is there much difference in the long-term values between the 2 different depths. At Rarangi, the final concentration plateaus at about 0.0135 mg L^{-1} after some 100 years. At Spring Creek the final steady value is about 0.017 after 200 years, whereas the final value at Woodbourne is about 0.012 mg L^{-1} after about 300 years. These are all just above the NZDWS of 0.01 mg L^{-1} .

This concurrence across the different soil types after 500 years is because by then all of the soils' adsorptive capacity has been quenched, and the concentration in the descending plume of As is controlled by the strength of the As source, which is sustained by the continual replacement of posts. So in these very long-term simulations, the greatest control on the final leachate concentration is the amount of As that can leach from the post during its 20-year life in the soil. The adsorptive capacity of the surrounding soil is quenched after 100-300 years.

Thus the concentration in the leachate reflects the strength of the As source, that is the rate of As leaching from a post over its lifetime of 20 years. The fact that the leaching loss from the end-grain is 40 times that through the post walls, suggests a remedy, as we will discuss later.

The main difference between the three soils in Figure 27 is the dynamics of the various sites, not the final values of the spatially-averaged concentrations. At Rarangi, the permeable and low water-holding capacity nature of the soil means that the rising trend in As is spiky, and the low adsorptive capacity for As results in steady-state being reached after just about 100 years. In contrast, the greater K_D for As at Woodbourne means that equilibrium is not achieved until about 300 years. Because these values for the spatially-averaged leachate concentration exceed the NZDWS, unless the groundwater dynamics are such that sufficient lateral subterranean flows can dilute and flush the As leachate arriving from above, then there are prospects for groundwater degradation through an eventual build-up of As.

Next, therefore, we carried simple hydrogeological modelling of the Marlborough aquifer systems to assess whether the descending As plume might be diluted by lateral flow in the aquifer.

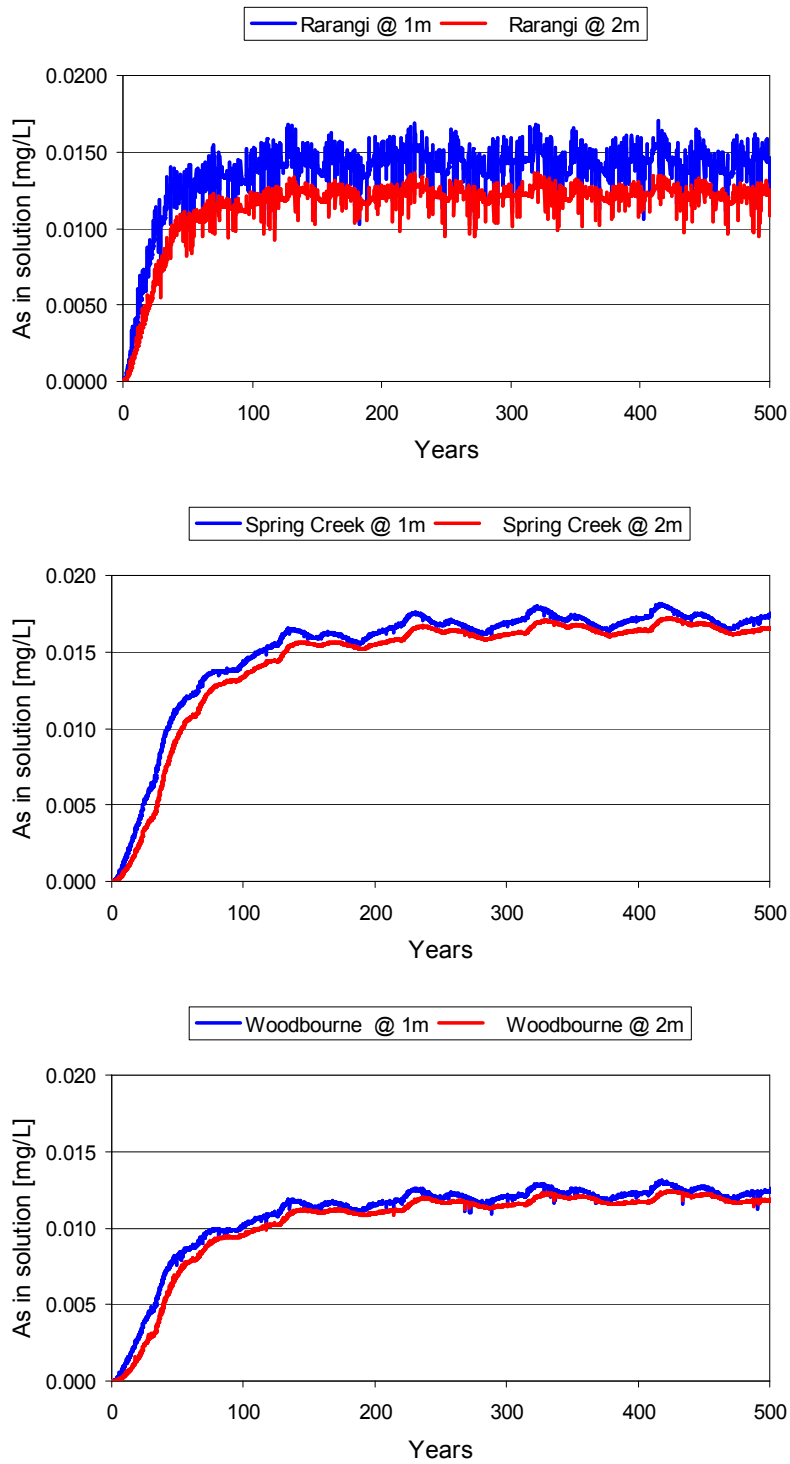


Figure 27. The SPASMO predictions of the spatially averaged arsenic concentration in the soil solution at 1 and 2 m depths under Rarangi, Spring Creek and Woodbourne soils. The NZDWS is 0.01 mg/L. The life-time of a post is taken as 20 years.

HYDROGEOLOGICAL MODELLING

The results of the long-term modelling are now used to determine the likely impact on the aquifer systems of the Wairau Valley. A simple mass-balance model is developed to predict the likely long-term concentration of arsenic in the groundwater systems of the plains.

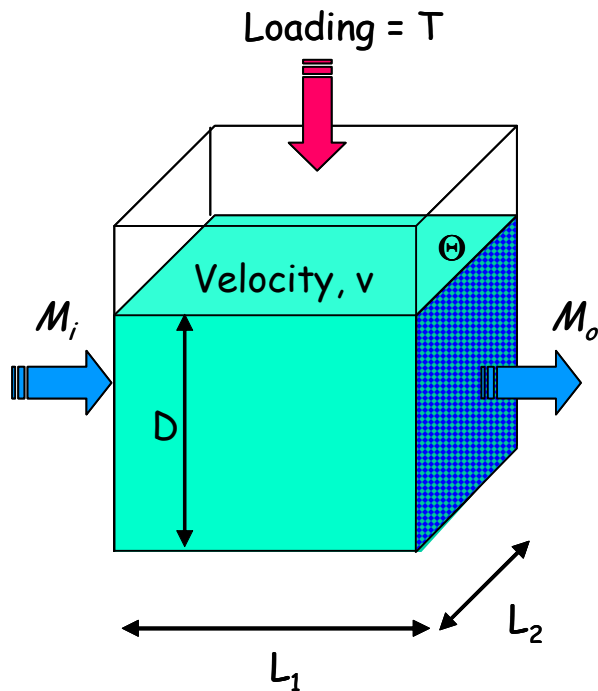


Figure 28. A simple rectangular-slab aquifer receiving a long-term arsenic loading at flux T (mg-As yr⁻¹) on the soil surface.

A simple rectangular-slab model of an aquifer is presented in Figure 28. The aquifer of thickness D [m], whose phreatic surface is some distance below the soil surface, is considered to have water travelling at pore-water velocity v [m day⁻¹] along its length L_1 (km). The aquifer is of width L_2 (km) and has porosity Θ . The flux of arsenic loading is T (mg-As yr⁻¹), which can be found from:

$$T = m \rho L_1 L_2 \quad [\text{Eq. 7}]$$

where m is the average flux density of As loss from the post over its 20-year life [mg-As post⁻¹ yr⁻¹] (see Figure 19), and ρ is the effective density of posts in the plan area above the aquifer [posts ha⁻¹]. We take m as θm_w where θ is the water content of the soil, and m_w is the average loss rate from the post into water over its 20-year life.

In Figure 28, M_i and M_o are the mass fluxes of arsenic into and out of the aquifer slab, being:

$$M_i = v \Theta c_i D L_2 \quad ; \quad M_o = v \Theta c_o D L_2 \quad \text{[Eq. 8]}$$

where c_i and c_o [$\mu\text{g-As L}^{-1}$] are the concentrations of arsenic in the groundwater entering and exiting the system. Since $M_i + T = M_o$, the concentration of As in the groundwater leaving the slab system, if none is entering, will be:

$$c_o = \frac{1}{3650} \frac{m \rho L_1}{v D \Theta} \quad [\mu\text{g-As L}^{-1}] \quad \text{[Eq. 9]}$$

For an prismoidal aquifer (Figure 29) there is loading only on the triangular surface and the mass-balance calculations for c_o would give an exit concentration of half that of Equation 9.

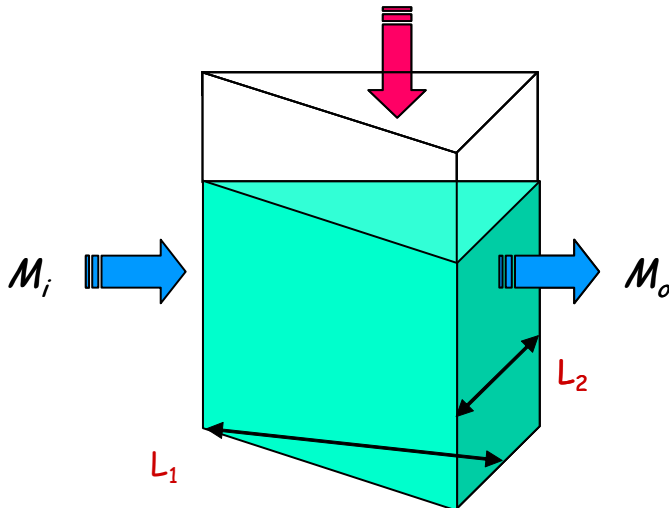


Figure 29. Mass flows into and through a prism-shaped aquifer.

Calculations were carried out using Equation 9, to predict the As concentration of water leaving the triangular Wairau aquifer system, and the rectangular Brancott and Rarangi shallow aquifer systems (Figure 30). Whereas the density of posts within a vineyard is 580 ha^{-1} , we take a spatially-averaged value across the whole surface land-area to be three-quarters of this: $\rho=435 \text{ posts ha}^{-1}$.

Wairau Aquifer. From Figure 19, we take the steady mass flux of As through the surface, m , to be $72 \text{ mg-As post}^{-1} \text{ y}^{-1}$. For the geometric characteristics of the prism we take $L_1=15 \text{ km}$ and consider the depth of flowing water in the aquifer to be $D=20\text{m}$. We assume the porosity of the gravels to be $\Theta=0.4$. From these parameters, we predict the As concentration in the water exiting to surface streams beyond Hammerichs' Road to be $c_o=0.5 \text{ ppb}$. This is 5% of the drinking water standard (NZDWS) of 10 ppb for As, as a result of the dilution by the large volume of rapidly-moving subterranean water.

Rarangi Shallow Aquifer. Near the coast, the Rarangi shallow aquifer (RSA) is about 3 km wide, with a depth of flow of about 8 m through gravels of porosity 0.4. Because of the lower porosity of the surface soil ($\theta_s \approx 0.3$) above the RSA, the mass flux of arsenic is lower, even if we consider the soil to be continually saturated (Figure 19). Here, $m = 60 \text{ mg-As post}^{-1} \text{ y}^{-1}$. So even if the RSA rose to bathe the entire subterranean portion of the posts, the low porosity of this stony soil limits post-water contact. Use of Equation 9, predicts that water leaving the RSA will have an As concentration of just 0.7 ppb, less than 10% the NZDWS.

We even considered an extreme worst-case scenario where all posts have become loose with no soil contact, and the RSA is continually at the soil's surface. Here we predict m to be $150 \text{ mg-As post}^{-1} \text{ y}^{-1}$, and the value of c_0 would rise to 1.75 ppb, which is still less than 20% the NZDWS.

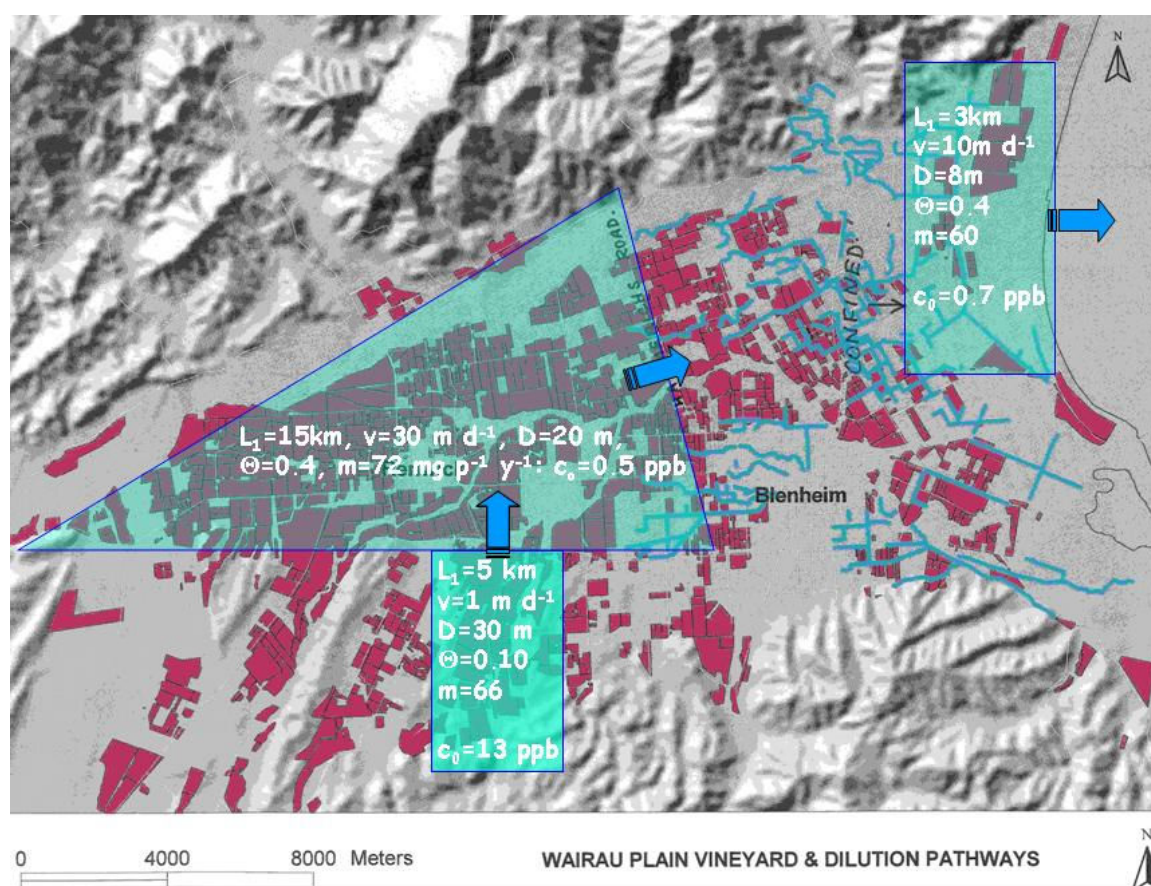


Figure 30. Vineyards and dilution pathways of three Wairau Valley aquifer systems, and the predicted concentration of As in the water leaving the systems.

Southern Valley Aquifers As an example of the Southern Valley Aquifer systems (SVA) we consider the Brancott Valley. Here the length of the aquifer is about 5 km, and the distributed aquifer is over a depth of 30 m. The pore-water velocities here are sluggish, and the distributed nature of the aquifers comprising the system means that flow is through just some 10% of the gravels: $\Theta \approx 0.10$. The mass flux of As at the surface here is $m = 66 \text{ mg-As post}^{-1} \text{ y}^{-1}$ (Figure 19), so that the exit concentration of As is predicted to be 13 ppb, which is just over the drinking water standard.

LONG-TERM MANAGEMENT OPTIONS

If required, an obvious alternative to the treated-post issue would be to use posts other than those treated with CCA.

However, our results suggest a remedy, if needed, even for CCA-treated posts. The critical points are:

- The mass flux of arsenic leaving the posts over its 20-year life is critical, whereas there is little long-term difference between various soil types.
- The mass flux-density of arsenic leaving the posts is 40 times greater through the end-grain, than through the walls of the post.
- The surface area of the end-grain is one twentieth of the total surface area of the cylindrical wall of the post in the soil.

If some capping, or As-adsorptive material were used to seal the basal end-grain, the mass flux of As leaving the post, into the soil, over 20 years would be reduced. If this were significant, the final steady-state value for the As concentration in the leachate would be reduced.

We carried out a very simple calculation to predict the changed level of the As concentration in the leachate, if the flow through the end-grain were taken to be zero. Whereas the end-grain releases 40 times more As than through the wall, the ratio of the wall's surface area to the end grain is 20. So despite the lesser flux through the wall, there is a much larger area through which As can be leached. So the net result would suggest that treating the end-grain would halve the concentration of As in the leachate at steady-state.

For moderate to heavy textured soils where there is good post-soil water contact, say with $\theta \approx 0.35-0.45$. We have predicted that the averaged concentration of As in the leachate is at about the NZ Drinking Water Standard of 10 ppb (Figure 27). If the end-grain were sealed, the resulting halving of the As flux from the post would bring the finally steady As-concentration down to something around 0.05 mg L^{-1} , which is about 50% of the NZDWS of 0.01 mg L^{-1} . Further investigation would seem merited.

CONCLUSION

In the first year of our experiment at Delegats we have observed CCA leaching out of treated posts. Soils surrounding these posts already exceed, in some cases, the recommended guidelines for chromium and arsenic in agricultural soils as set out in the NEPM of the Australian National Environment Protection Council's "Guidelines on the Investigation Levels for Soil and Groundwater" (1999).

A simple mechanistic model, SPASMO, has been set up to calculate the leaching risk for arsenic coming from treated timber posts. The model has been run on a daily time-step using local soil and climate data over a 30-year period. We also carried out long-term simulations

over 500 years, and assumed a post life-time of 20 years. So every 20 years, a new H4-treated post would be reinstalled into the same hole.

In our modelling we utilized batch isotherm data carried out to determine the chemical partitioning for arsenic in a range of Marlborough soils. We also took a conservative approach to the modelling by assuming the maximum losses from the post, and accounting for the contact of the post with the soil-water solution. The chemical release is based on data collected from other work, funded by the Marlborough Wine Research Centre Trust, with their kind permission. Here half- and full-round posts (three replicates) have been submerged in freshwater. Our modelled predictions over the short-term of As levels in the soil were a general match with measurements made during an earlier regional survey in 2004.

Our long-term modelling over 500 years highlighted the prime role played by post-replacement in determining the As concentration in the spatially averaged plume of leachate moving below a vineyard. The key determinant of this concentration in the leachate is the amount of arsenic that leaches from the post during its 20-year lifetime. After about 100-300 years, the adsorptive capacity of the surface soil is quenched, and the As leaching from the post is then transported to depths beyond about 2 m. For a range of soils, we predict that the final steady concentration of As in the leachate at 1-2 m would be 0.0125-0.0175 mg L⁻¹, which is just above, or up to nearly two times the NZDWS of 0.010 mg-As L⁻¹ (MoH, 2000).

To account for the potential dilution of this vertically moving As in the receiving groundwater by lateral flow in the aquifer, we developed a simple hydrogeological model of the Marlborough aquifer systems. This indicated that for the major Wairau aquifer system, the water at the distal end near Hammerichs' Road where the aquifer supplies surface water, the concentration of As would be just 0.5 ppb: just 5% of the NZDWS. For the Rarangi Shallow Aquifer we predict an exit concentration of As of 0.7 ppb, again more than an order of magnitude lower than the NZDWS. For the distributed Southern Valley aquifer systems, the groundwater flow is sluggish, and we predict an exit concentration at 13 ppb, which is just above the NZDWS.

The CCA issue could be reduced perhaps by using alternative posts, such as steel, recycled material, or untreated woods such as *Eucalyptus* or beech.

Alternatively, CCA-treated posts could have the end-grain part of the post protected, for example, to reduce the rate of CCA leaching. Such a modification would, we consider halve the concentration of As in the leachate. However, more work needs to be done to quantify this possibility. Because in the long-term it is the amount of As leaving the post over 20 years that is the major controlling factor, and since the end-grain is 40 times more likely to leach As, remedies that focus on the region near the base of the post would seem to offer the best prospects.

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